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*Zinātnisko rakstu krājumā iekļauti VIII starptautiskās zinātniski praktiskās konferences "Vide. Tehnoloģija. Resursi" raksti.*
*Rakstu tematika saistīta ar vides kvalitāti, tās kontroli un nodrošināšanu, piesārņojuma novēršanas tehnoloģijām, tīrāku ražošanu, ilgtspējīgo lauksaimniecību, dabas resursiem, degradēto teritoriju atjaunošanu, vides izglītību un ilgtspējīgo attīstību. Tiek pētītas atjaunojamās enerģētikas problēmas. Rakstu krājumā pārstāvēti referāti, kas ir saistīti ar datorzinātnes, matemātikas, mehānikas un mehatronikas pielietošanu vides zinātnes un citu nozaru problēmu risināšanā.*
*Proceedings include papers presented at the 8th International Conference "Environment. Technology. Resources."*
*The themes of the papers are – the environmental quality, control and providing, pollution prevention technologies, cleaner production, sustainable agriculture, natural resources, remediation of degraded territories, environmental education and sustainable development. The problems of renewable energy are analysed. A separate section of the conference includes papers on applications of computer science, mathematics, mechanics and mechatronics for solution of environmental and other problems.*



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# I

# ENVIRONMENTAL PROTECTION AND MONITORING

# TECTONIC PROCESSES MODELING FOR HIGH-LEVEL RADIOACTIVE WASTE DISPOSAL

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**Abstract.** *The possibility of using deep geological formations to dispose of high-level radioactive waste (HLW) is a subject raising heated debate among scientists. In Russia, the idea of constructing HLW repository in the Niznekansky granitoid massif (NKM) in Krasnoyarsk area is widely discussed. To solve this problem we are elaborating a technology associated with time – space stability prediction of the geological environment, which is subject to geodynamic processes evolutionary effects. It is based on the prediction of isolation properties stability in a structural tectonic block of the Earth's crust for a given time. The danger is in the possibility that the selected structural block may be broken by new tectonic faults or movements on a passive fault may be activated and thus underground water may penetrate to HLW containers.*

**Keywords:** *tectonic, radioactive waste, evolution of Earth's crust, stress, faults, GPS.*

## Introduction

Scientists have heated discussions on the possibility of using deep geological formations to dispose of high-level radioactive waste (HLRW). In Russia the possibility of construction a HLRW repository in the NKM in the area of city Krasnoyarsk is being widely debated [1]. The major problem is the required prognosis of the geological environment isolation characteristics persistence for a long interval of time such as $10^4$ – $10^5$ years. In such a period of time, geodynamic processes are able to make radical changes in engineering geology and hydrogeology features (variation of groundwater level, water-bearing horizon head, new infiltration channels formation and others) and result in the destruction of HLRW repository with disastrous impacts on the environment. Solving this problem, we are developing a technology to predict the stability in time and space of the geological environment, which is subject to evolutionary effects of geodynamic processes [2-3]. It is based on the use of a combination of methods having the final goal to make a prognosis of structural tectonics blocks destruction of the Earth's crust.

Any area of the Earth's crust in which a repository could be planned to be located is a system of blocks limited with surfaces of tectonic dislocations of various hierarchy levels. The technique of selecting sites suitable for HLRW repositories construction is based on the search in stable geological areas for structural tectonic blocks having the least density of faults in maximum volume. At the same time, evidently, there are no areas free of dislocations in the crust and the separated blocks are relatively less dislocated; local stress fields, which are non-stationary with time, surround them. The blocks get destroyed, and new channels of ground water infiltration are formed.

## Materials and methods

The elaboration of prognosis technology (fig. 1) is based on the following prerequisites:

1. The evolution of the Earth's crust is determined by the intensity of tectonic process development in the region. The process velocity depends on the level of effective tectonic stresses and physical and mechanical characteristics of rocks.

2. Tectonic stresses field retaining the inherited tendencies of the region tectonic evolution varies in time and space.
3. Modern stress – strain state in combination with the inherited tendency of time – space variation of tectonic stress local fields is a basis of the destruction processes development in structural tectonic blocks.
4. Inherited directions depending on the effective tectonic stress tensor determine the direction of new tectonic faults formation and the old faults activation.
5. Local areas of increased stress concentration are the most likely places to initiate destruction of the geological environment and the structural block.

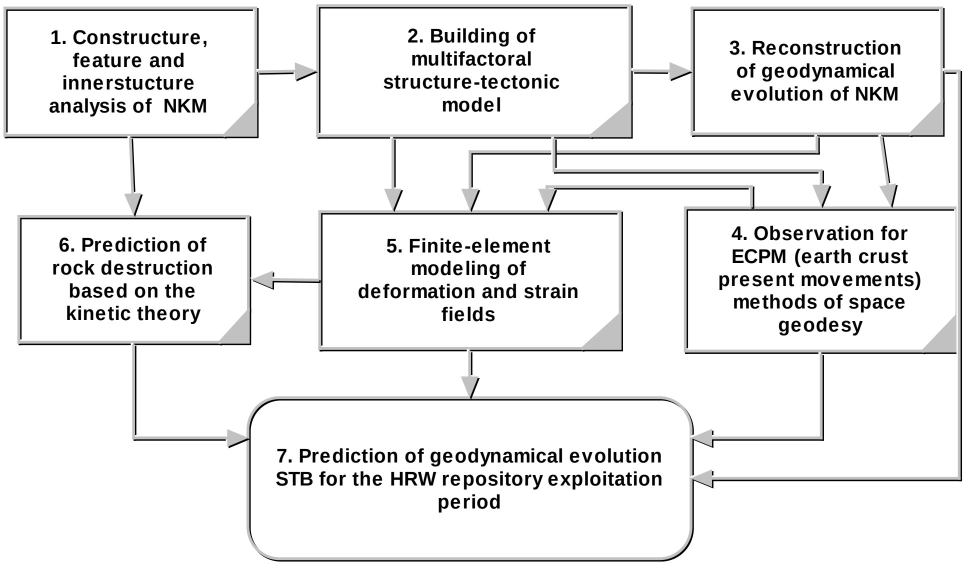


*Fig.1.* **The basic stages of technology**

From practical viewpoint, it is reasonable to predict crustal blocks evolution of NKM in Russia where work is being carried out to select a site of underground laboratory construction. The urgency of work in that region is caused by the fact that now a decision is to be made on the underground laboratory construction (this stage is obligatory in compliance with the concept of HLRW repositories construction). Thus the prediction of geological environment evolution will allow us to avoid unjustified financial loss and to decrease the risk of radionuclide pollution of the environment if the selected sites do not meet safety standards.

**Results**

*Multifactoral structure-tectonic model of NKM.* NKM is a single, independently formed and synorogenic bathylite (fig. 2).

*Top edge morphology.* Massive top edge morphology analysis is important because the surface of top edge is its depth geodynamical activity «mirror». NKM occupies a floor space of 2000 sq. km. Its length amount to 60 km. in the north-west direction and its width amount to 23-35 km. Top edge densely desiccated with present erosion processes. Vary of absolute elevation is amount 250 m with a maximum elevation more than 500 m.

Relief flattering action, which was added by present elevation average thickness diminution from of loose deposits in amount of 50 m, was applied for the revealing of general regularity for NKM top edge structure. Scheme on fig. 3 is a result of this transformation. Its analysis shows that east roof half is raised and has enough simple rolling relief with smooth isolines and minimum number of areas with harsh grade of isolines massif roof.

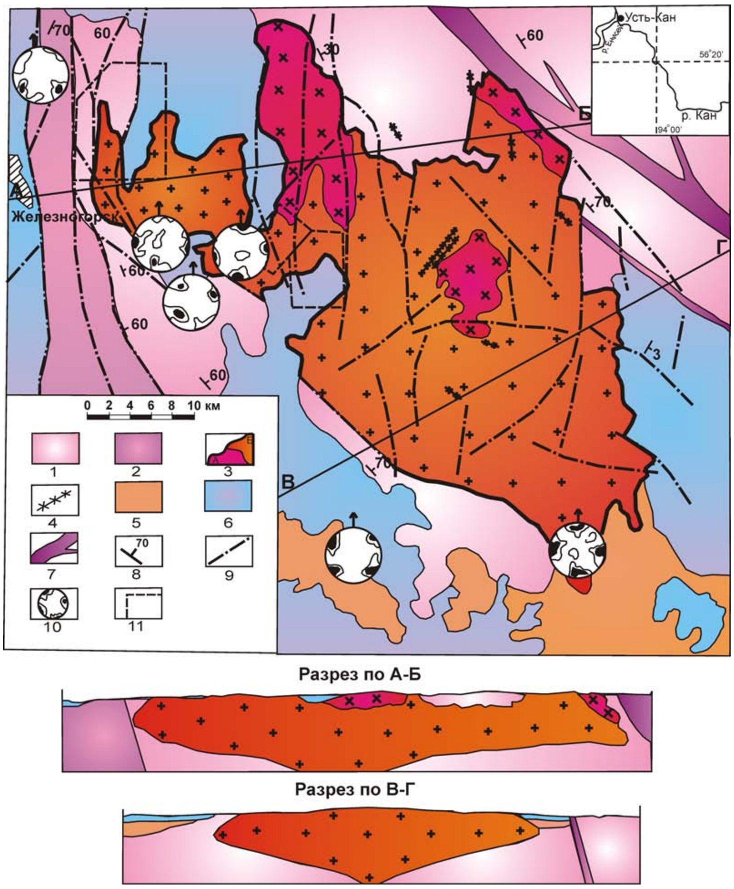


*Fig.2.* **NKM area geological structure scheme**

1- geiss (AR); 2- amphibolite, quartzite and marble (AR-PR); 3- contour of NKM granitiods: a-diorite of 1-st stage; b- granite of 2-nd stage; 4- dikes; 5- terrigenous-volcanic deposits ($PZ_2$); 6-terrigenous deposits (J); 7- mylonite areas; 8- main faults; 9- grike orientation diagram; 10- rock position elements; 11- areas of detailed research (from south-east to north-west: “Kamenniy”, “Itatskiy”, “Eniseiskiy”)

*The Tectonic features of Relief*. Relief is a second element of NKM structure-tectonic model, cause it describes its present tectonic activity. Relief density dissection scheme is the integral characteristic of activity. This scheme built in $C_{IR}$ isolines (fig. 4). This coefficient was estimated by clusters with 4x4 km. sliding window, like a dependence of difference between minimum and maximum absolute elevation to unit area. $C_{IR}$ reflects type of vertical ECPM and present endogen area activity. Level of $C_{IR}$ rises when rate elevation becomes density.

Right side of NKM, situated to the east from Maliy Itat river, defines by more density elevation ($C_{IR} \approx 200\div400$). Area with maximum values of $C_{IR}$ situated on the territory with maximum roof elevation. In this area Kan river changes its course direction from meridional to latitudional and valley becomes deeply incised into massif. Just at that place occurs maximum thickness of granites. Another part, situated to the west from M. Itat river, defines by low $C_{IR}$ amount ($\approx 150\div100$) and that gives an tectonic stability evidence of this area.

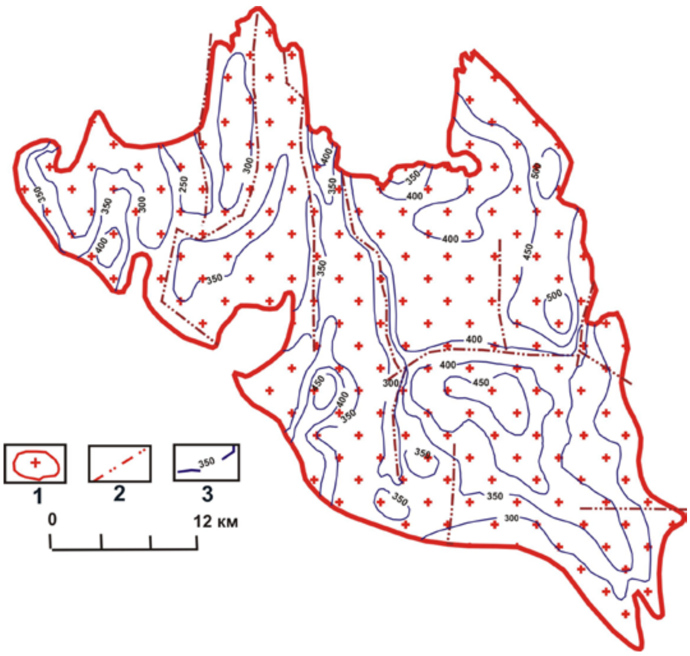

*Fig.3.* **Scheme of NKM top edge morphology**

1- NKM contour; 2- main faults; 3- contour lines of NKM top edge

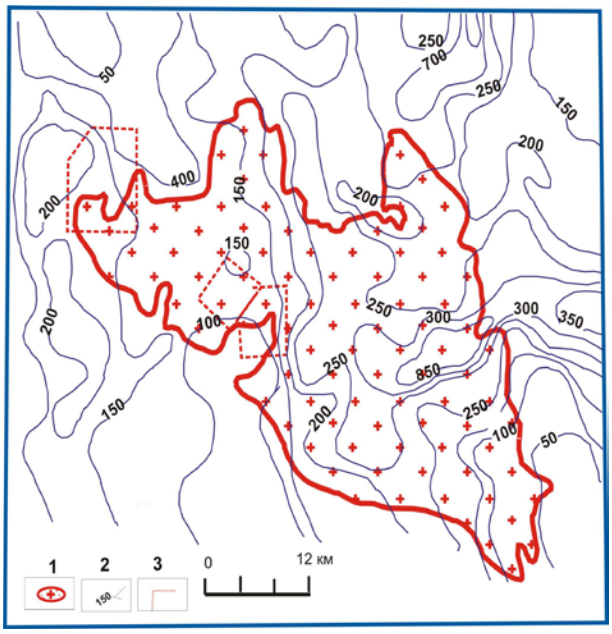

*Fig.4.* **Relief desiccate density map**

1- granites, 2- isolines of $C_{IR}$; 3- “Kamenniy”, “Itatskiy”, “Eniseiskiy” areas contours

“Eniseiskiy” block situated in rather unsafe area, which one contacts in the west to the maximum $C_{IR}$ level area. Blocks “Kamenniy”, “Itatskiy” situated within the stable part of NKM. This part of NKM slowly rises on the present stage of region tectonic evolution.

*Analysis of block morphostructures and cleavage.* Morphostructural relief analysis of 1:200 000 scale enabled creating detailed block composition of the area. This included revealing relief faults and blocks of varied height (fig. 5) into ten block levels with 50 m hypsometric gaps and 580 to 230 m height range. They are mainly isometric 2 to 8 km in diameter with often intra-block faults that could not be referred to as inter-block due to different height of their sides. The Eastern part of NKM features higher hypsometric level with blocks absolute height of 530 to 380 m. The Western part has lower blocks ranging 430 to 280 m.

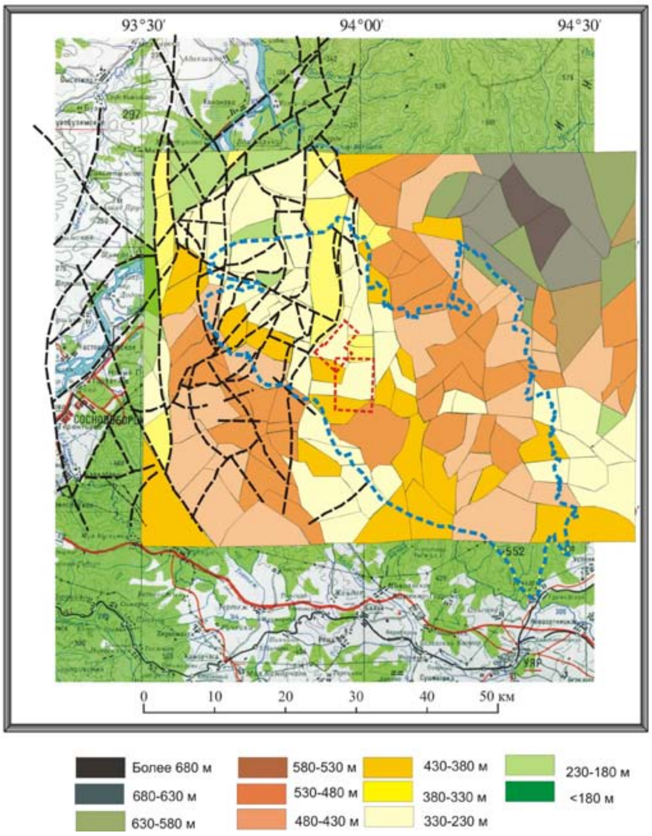


*Fig.5.* **Structural and tectonic blocks of NKM**

*Finding structural non-uniformities and sign of tectonic activity.* The described NKM model can be substantially improved and adjusted based on the survey of geophysical field, which enable identifying and tracing deep-earth geodynamic zones. In these terms, the data of airborne magnetic survey shall be processed through Euler inverse filtering with *RODIN* and *KRISTALL* artificial intelligence algorithms. See details in [4].

Fig. 6 displays interpretation of anomaly magnetic field for n=3,0 and pattern 15 (center of mass for anomaly-forming objects). Application of cluster analysis enabled identifying isometric structure blocks dominating the NKM structure with average size of 6 to 9 km. Linear zones of different height found could be large tectonic faults.

*Simulating stress-deformed state.* The aforementioned results of structural-tectonic and cluster analysis were used as the basis for SDS simulation through isoparametric rectangular finite elements of the finite elements method. Reconstructing the tectonic conditions of the area directed and measured the main stress activities (NE – SW).

Distributing the stress fields identified the following specificities:

1. Linear zones that can be geodynamic zones of faults through elongated zones of increased $\sigma_1$ and $\tau_{xy}$ values, with dominating orientation 45° to the main stress direction.
2. The fault system of the central part of the area generally contributes to unloading a rock mass with average stress field of 10 to 25 megapascal.

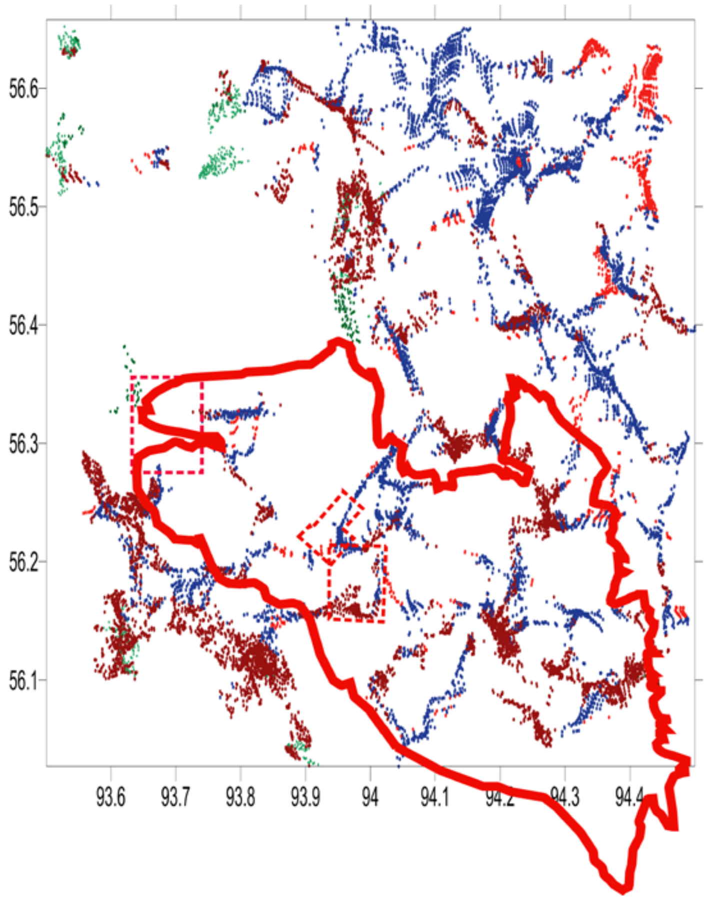


*Fig. 6.* **Interpretation of anomaly magnetic field**

*Monitoring the modern earth crust movements with GPS.* Monitoring of the modern earth crust movements is a crucial step when forecasting how safe the isolation features of geologic formations will be. No geodynamic mode can be researched without definition of the rate the main tectonic deformations within the area of 100-200 km radius have. Analyzing the entire database, including space-geological images, geological and geophysical data, different tectonic maps and real topography of the area enabled identification of GPS/GLONASS points and optimizing the geodynamic network (fig. 8).

The main problem was selecting the place meeting the following criteria for survey:

1. No forest and radio wave deflector within 15 m from each mark.
2. Exposure of bedding rocks or a building with secure basement.
3. Transportation availability of the survey site.

Meeting all the requirements above was not feasible for the NKM area, because almost no exposures found. This is why uneven configuration of the network is intended to optimization and density increasing. Survey is planned to be carried out twice a year in a 5-6 year term.

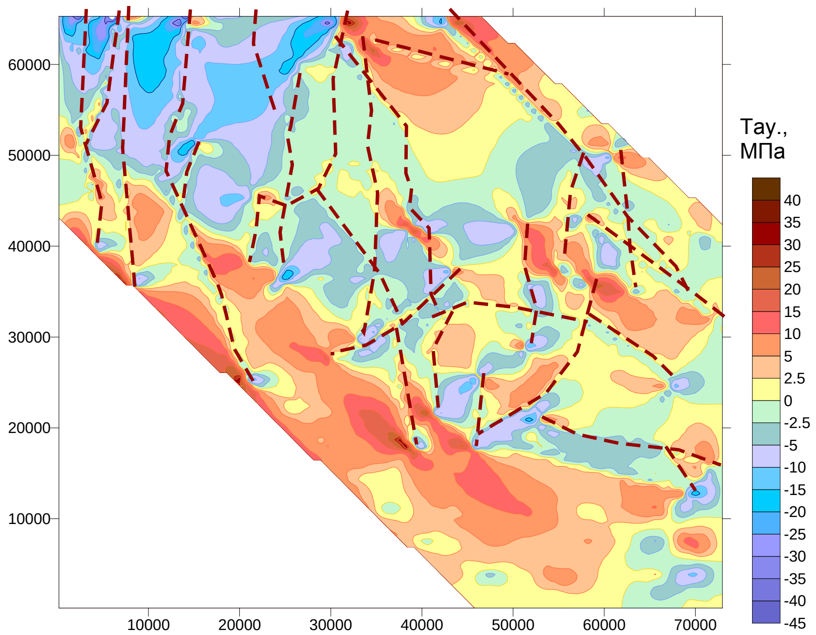


*Fig. 7.* **SDS simulation, $\tau_{xy}$ component**

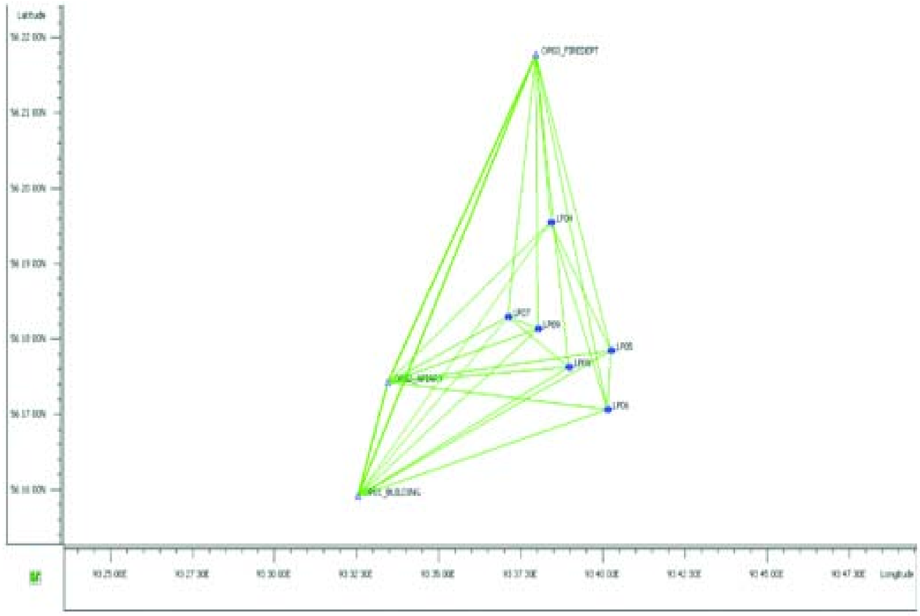

*Fig. 8.* **GPS point location in**

**References**


1. Anderson E. B., Alekseev E. P., Datsenko V. M. et al. The results of combined geological and geophysical and specialized research in the area of Kamenny and abutting areas (Nizhnekansky massif). Report on research work of GUP NPO V. Khlopin Radium Institute. S-Petersburg, 2001 (in Russian).
2. Morozov V. N., Tatarinov V. N. The methods of selecting crustal areas of the Earth to dispose of ecologically hazardous waste. Geoecology. M. 1996. No. 6. Pp. 109 – 120 (in Russian).
3. Morozov V. N., Tatarinov V. N. Tectonic processes development with time in the areas of HLW disposal from expert assessment to prognosis. Int. Nuclear Energy science and Technology, Vol. 2 . No, 1/2. 2006. Pp. 65-74.
4. Mikhailov V., A. Galdeano, M. Diament, A. Gvishiani and etc. Application of artificial intelligence for Euler solutions clustering. Geophysics. 2003, vol. 68, no. 1, p.168-180 (in Russian).

# GEODYNAMIC ZONING FOR UNDERGROUND ISOLATION OF RADIOCTIVE WASTE

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**Abstract.** *The problem of area selection for underground isolation of radioactive waste is important for all countries using nuclear power. The paper presents the results of modeling the stress-deformed state of Nizhnekanskiy granitoid massif and shows the possibility of using such simulations for the geodynamic zoning of areas. The calculation is given to the most probable directions of groundwater filtration, which is one of the main threats for the nuclear waste repository.*

**Keywords:** *high-level radioactive wastes, stress-deformed state, filtration of groundwater, Niznekansky granitoid massif.*

## Introduction

The development of nuclear power in Russia is impossible without resolution of the problem of high-level radioactive waste (HLRW) disposal in deep geological formation. The selection of sites for the environmentally safe underground isolation of high-level radioactive solidified waste remains to be the major problem for the states that use nuclear energy, such as Russia.

Methodologically, the choice of the site for HLRW disposal is based on the finding in the relatively stable areas of the least disturbed structurally tectonic blocks (STB), which have maximum size [1] [2].

The expert assessments of the current "quality" of the site where the HLRW repository will be built, do not answer the fundamental question: how will the tectonics affect the rock mass safety during 100 thousand years and more, until there will be an environmental hazard of radionuclide.

The greatest threat is the formation of new faults or intensification of the existing tectonic faults and infiltration of surface water and groundwater to containers with high-level radioactive waste (HLRW), followed by the removal of the radionuclide in the human environment.

The basic principle of ensuring safe disposal of nuclear waste is to prevent the formation of zones of dangerous stress concentrations at the design phase of nuclear fuel (SNF) repository on the basis of geodynamic zoning. The forecast of the evolution of the stress-deformed state (SDS) of the geological environment from a position of insulating properties of rock masses as a major barrier against the spread of radionuclide is required.

The purpose of this paper is to analyze the possible development of the tectonic process in Niznekansky granitoid massif on the basis of structural-tectonic model and calculation of the stress-deformed state of the local area. The most probable direction of groundwater filtration under the influence of tectonic stress is simulated.

## Materials and methods

Niznekansky granitoid massif (NKM) is located a few kilometers to the north-east of Krasnoyarsk. Three sites for HLRW disposal: "Kamenniy", "Itatskiy" and "Eniseiskiy" were selected according to the geological and geophysical, structural, and geomorphologic studies in the western part of the massif, and partly in the surrounding rocks [3].

The analysis of geological data displays [3] that the stress-deformed state (SDS) of the massif is determined mainly by compressive forces oriented towards the south-west — north-eastern direction.

We used an elastic model of generalized plane stress for simulate the stress-deformed state. We used finite element method (FEM) as a method of calculation. Empowering the finite element with different mechanical properties enables to generate a heterogeneous finite element model, which reflects the real properties of rock massif. Fig. 1 displays a structural model of NKM to simulate the distribution of stress fields by FEM. We took the following values of the tectonic stress: sub latitudinal $N_x$ = 30 MPa and sub meridian $N_y$ = 10 MPa. These values are close to the stresses in the undisturbed rocks measured in the underground workings [4] at depths of up to 400 m. Detailed program of the stress calculation is presented in [5].

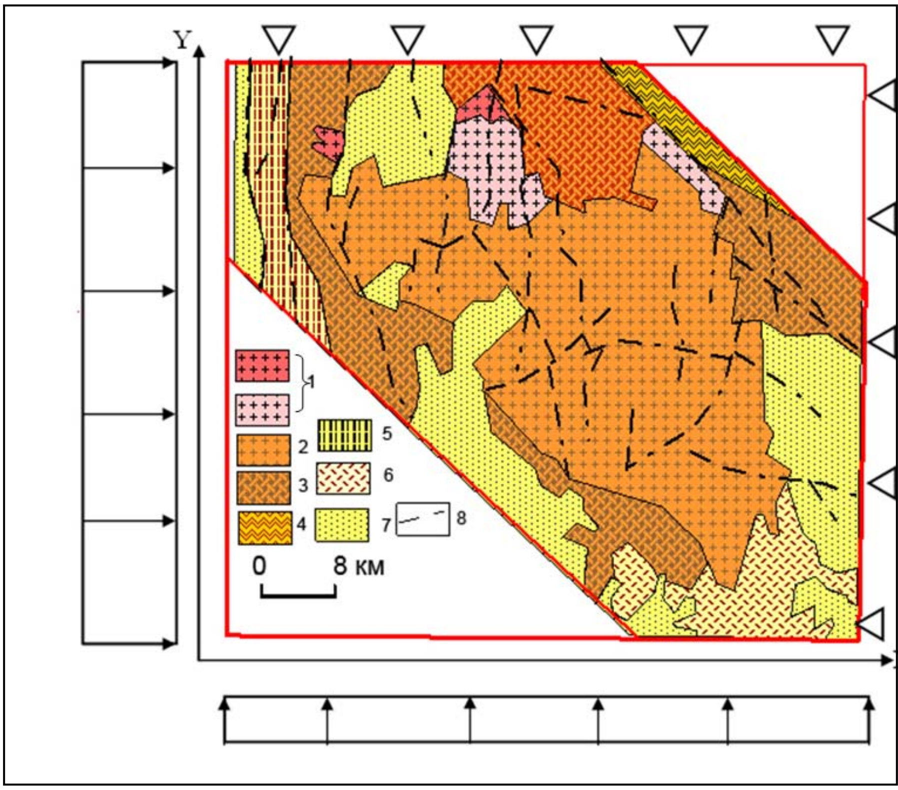


*Fig. 1.* **Structural model for simulate the distribution of stress fields by FEM**
1, 2- contour of NKM granitiods differ in their elastic-strength properties, 3- gneiss complex (AR); 4- mylonite areas, 5- amphibolite, quartzite and marble (AR-PR); 6- terrigenous-volcanic deposits ($PZ_2$); 7- terrigenous deposits (J); 8- main faults

## Results and discussion

We used stress intensity $\sigma_i$ as a generalized criterion of the level of SDS of the local areas NKM. Figure 2 displays contour map distribution of stress in the NKM. Figure 3 displays 3-D model of the distribution of stress intensity.

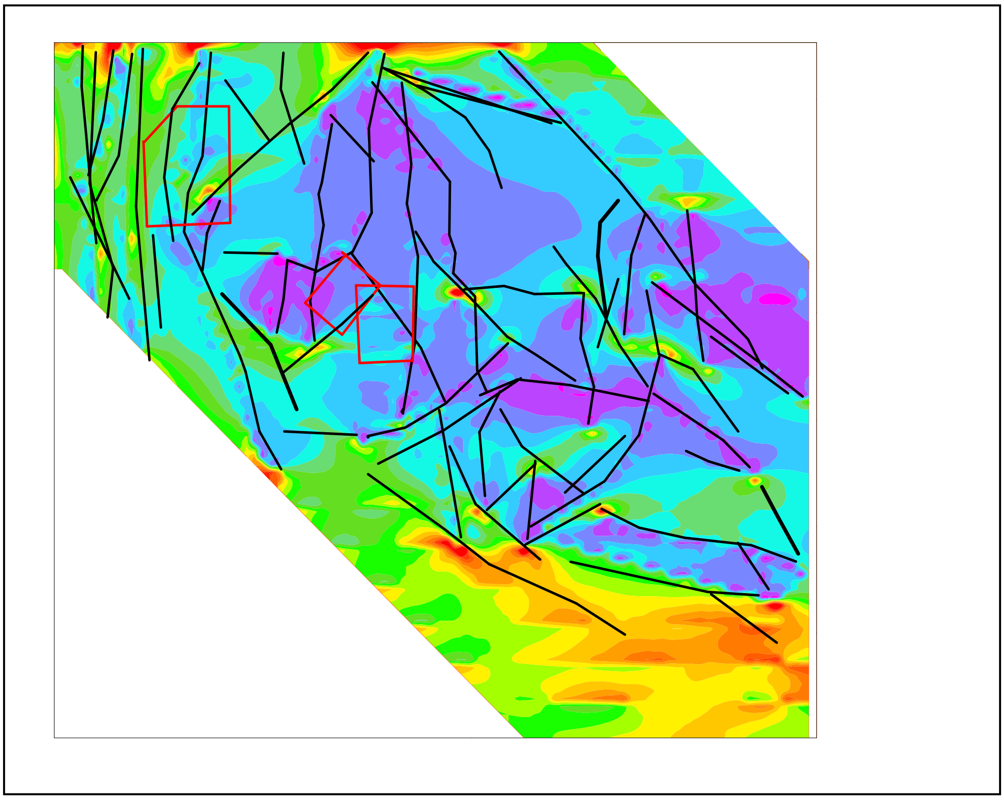

*Fig. 2.* **Distribution of stress intensity in the NKM according to calculations by finite element method. Lines indicate faults**

The rectangles marked areas of detailed studies: 1- “Eniseiskiy”, 2- Itatskiy, 3- “Kamenniy”

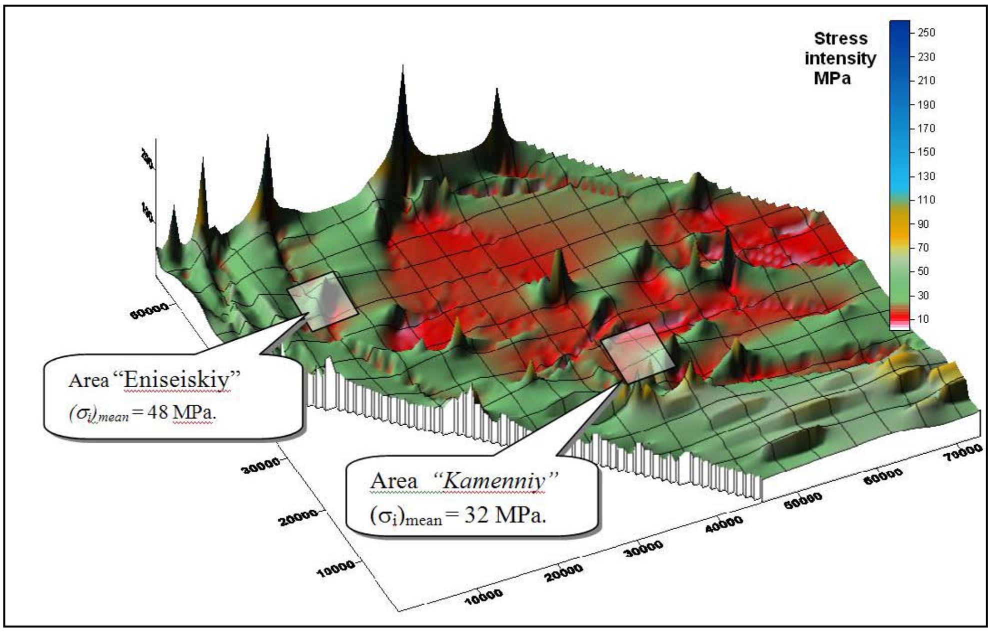



*Fig. 3.* **3D model of the distribution of stress intensity in the NKM**

The high level of differentiation distribution of the stress intensity $\sigma_i$ within the model of NKM gives rise to the selection of potentially dangerous areas (not suitable for isolation of HLRW). 3-D model is the basis for virtually geodynamic zoning in the purpose to select the areas geoenvironmentally safe for underground isolation of HLRW in geological formation.

We can confidently assert that the zones of stresses intensity concentration are possible sources of large-scale destruction of the geological environment in the working tectonic stress fields.
One of the major threats for the reliability of HLRW repository is the penetration of ground water to the containers, followed by removal of radionuclide in the human environment.
Filtration through an environment is described by Darcy's law:

$$V_x = -\frac{k}{\mu}\frac{dP}{dx}, \tag{1}$$

where $V$ – value of the filtration rate through a porous environment; $k$ – permeability of the medium; $\mu$ – dynamic viscosity of fluid; $P$ – pressure.
Coefficient $k$ is constant for a given liquid, if the porous environment is incompressible and isotropic.
For an isotropic environment the equation can be written:

$$V = -\frac{k_0}{\mu}\nabla\left(P\right) \tag{2}$$

where $V$ – velocity vector of the filtration. Applying the divergence operation we receive:

$$-\frac{k_0}{\mu}\nabla^2(P) = 0. \tag{3}$$

Thus, filtration through the isotropic environment can be reduced to solving the Laplace equation with appropriate boundary conditions. If the distribution $P$ is known, then the filtration rate can be obtained from Darcy's law in the form (2).
In many cases, the porous environment is anisotropic and the permeability depends on the direction of flow. In this case, the equation can be written as:

$$\frac{\partial^2 P}{\partial x^2} + \frac{\partial^2 P}{\partial y^2} + \frac{\partial^2 P}{\partial z^2} = 0. \tag{4}$$

Thus, we have the Laplace equation again. Consequently, the true physical meaning can be represented as a fictitious isotropic in the transformed coordinates.
In accordance with Darcy's law, we proceed from the assumption that the filtration rate in the gradient field of the tectonic stress is proportional to the gradient of the effective stress:

$$\overrightarrow{V_f} = \begin{bmatrix} \overrightarrow{V_x} \\ \overrightarrow{V_y} \end{bmatrix} = \begin{bmatrix} kE\nabla^2 U \\ kE\nabla^2 V \end{bmatrix} \tag{5}$$

Assuming that filtration coefficient is a constant.
The filtration rate is expressed in terms of stress components, in a plane-stressed state:

$$\overrightarrow{V_f} = \overrightarrow{V_x} + \overrightarrow{V_y} = kE\left(\sigma_{xx} + \sigma_{yy}\right) \tag{6}$$

Using these equations, it is possible to calculate and predict the development of hydrogeological conditions in the area of hypothetical construction of nuclear waste repository at the change of SDS rock mass as a result of the predicted tectonic destruction of the rock mass.
Note, that the filtration velocity vector is orthogonal to the direction of the effective forces that cause compression along the respective axes in this coordinate system.
The level of the stress state of the rock massif in its local zones is defined by the value of stress intensity. Transfer to the stress intensity allows you to build a model of liquid filtration independent from that particular system of coordinates. Based on the assumption that the filtration rate is determined by this integral assessment of the level of working stress in the volume element of rock mass, we get:

$$\overrightarrow{V_f} = grad\left(\sigma_i\right) \tag{7}$$

This simplifies the calculations of the first approximation, since the problem of estimating the stress state and filtration are solved separately. In this case, the filtration rate makes it possible to count water inflows in the weakened zones of tectonic fractures as a basis for further calculations of the migration rate and the predicted migration of radionuclide in the mass transfer process.

Figure 4 displays the calculation of the gradients vectors $\vec{G} = \left\langle grad\,\frac{\sigma_i}{2} \right\rangle$ of the working tectonic stress for NKM.

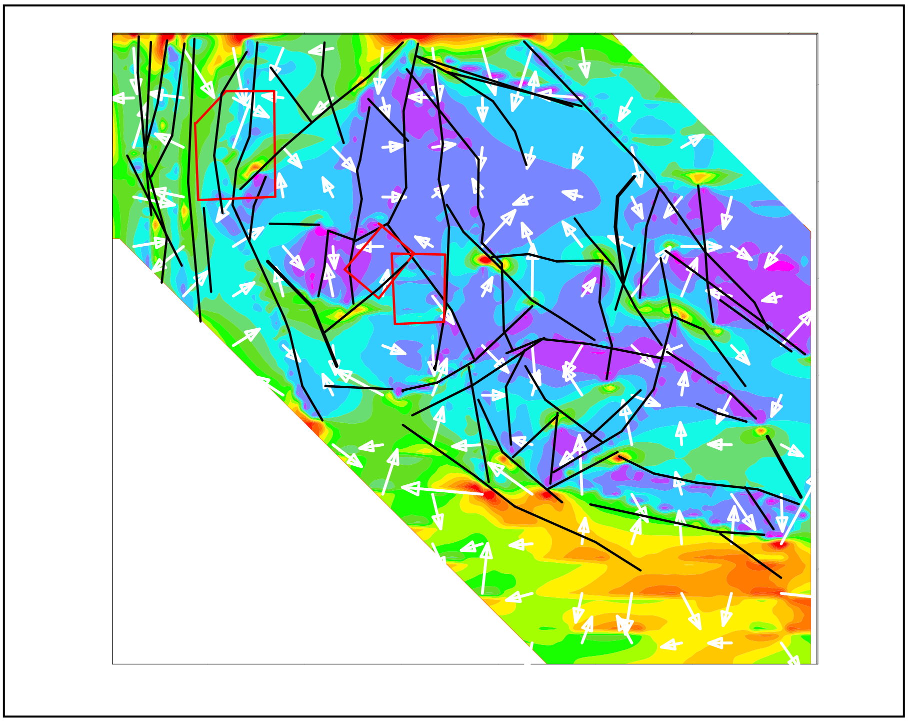

*Fig. 4.* **Vectors of filtration rate in NKM**

At the present time, area «Eniseiskiy» is the most promising in terms of creating a repository for HLRW. On this basis, we simulated the stress-deformed state of rock massif within the area «Eniseiskiy». The boundary conditions for this simulation were taken from the model for NKM.

Figure 5 displays the calculated vectors of filtration rate for «Eniseiskiy» area. Vector indicates the most probable direction of groundwater filtration under the influence of tectonic stress.

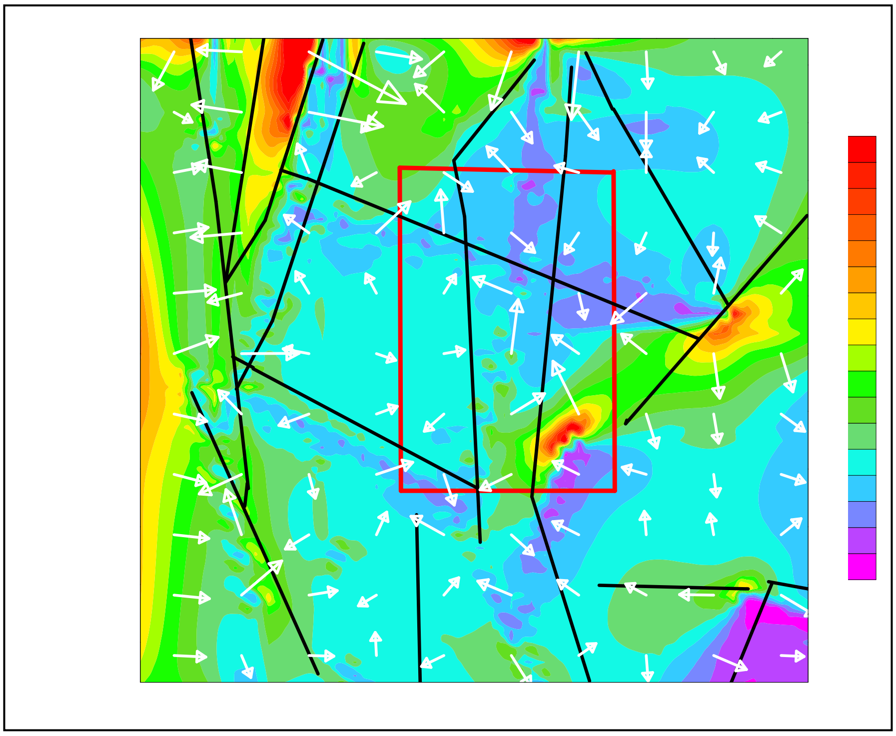

*Fig. 5.* **Vectors of filtration rate in area «Eniseiskiy»**

Fig. 6 displays the concentration of shear stresses for area «Eniseiskiy». The areas with maximum level of shear stress concentration are potentially dangerous from the position of the formation of tectonic movements, i.e. formation of tectonic faults containing the shear component. The risk of faults is more likely in areas of high concentration of shear stress.

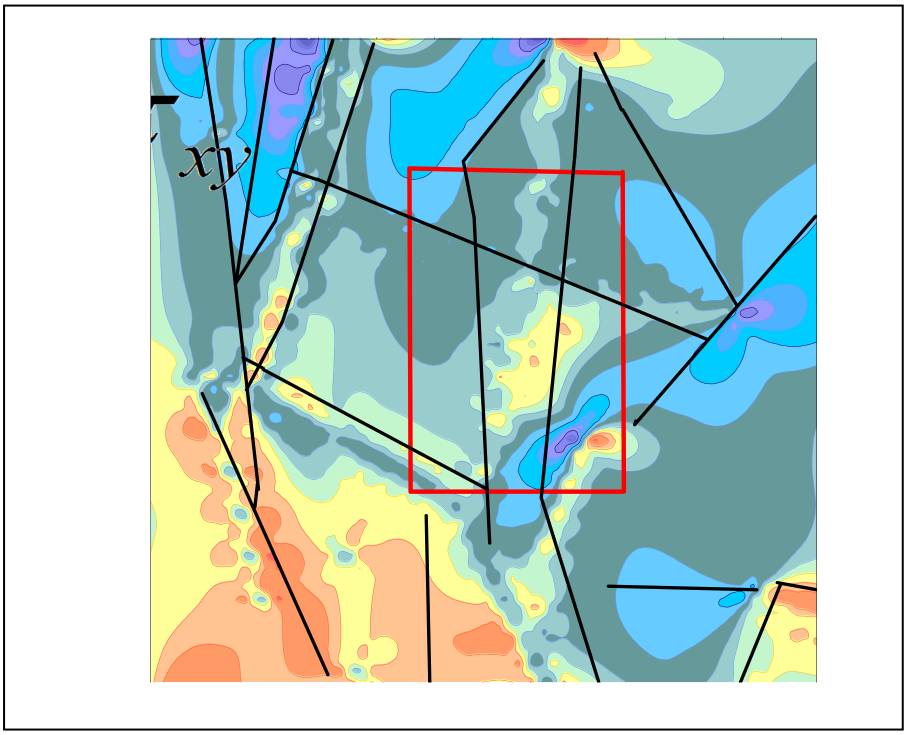

*Fig. 6.* **Distribution of shear stress $\tau_{xy}$ in «Eniseiskiy»**

On this basis, we have identified the two most probable directions of development of new active geodynamic zones affecting of «Eniseiskiy» area. They are displayed in Fig. 7 by dotted black lines. These are new the most probable faults in the area of «Eniseiskiy». They should be considered when assessing the environmental safety of HLRW repository. Fig. 7 displays the distribution of the stress intensity $\sigma_i$ and new vectors of filtration rates in the area of «Eniseiskiy» site.

Directions of the vectors correspond to the movement of groundwater in the weakened zone. Vectors of gradients working stresses are directed into the zones of tectonic disturbances (fig 7). Thus, these zones are reservoirs for groundwater flow. Filtration water can also be caused by activation of faults, i.e. run "trigger mechanism" tectonic activity. The faults are the channels of the intensive filtering groundwater, contributing to extensive migration of radionuclide in the geological environment, with the change of tectonic stresses.

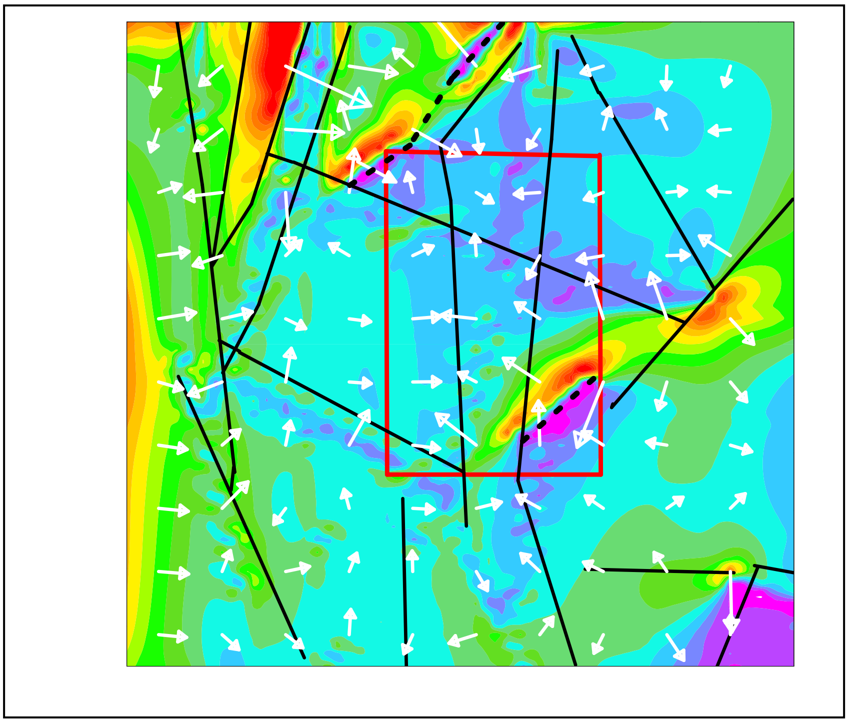

*Fig. 7.* **The distribution of stress intensity in the area «Eniseiskiy» and vectors of filtration rate**

## Summary

Summarizing the foregoing, we can give the following conclusions and recommendations to improve methods of prediction of degradation of the geological environment in relation to the task of choosing the least dangerous area for disposal of high level radioactive waste:

1. Zones of high concentration of stress intensity $\sigma i$ are the zones of an unstable state of the geological environment within which are more likely to develop of the tectonic destruction of the structural-tectonic blocks with subsequent destruction of the artificial and natural isolation barriers.
2. It is necessary to consider the major relationship between the laws of tectonic stress and the potential threat of mass transfer of radionuclide in the process of groundwater filtration, when choosing the area of placing HLRW cemeteries.
3. Kinematical principles of tectonic destruction of the geological environment in combination with the obtained values of stress intensity and shear stress $\tau_{xy}$ provide an opportunity to build a predictive scheme to destroy the structural blocks as successive iterations of the promotion of active faults with the redistribution of stress field and the

changing of SDS of rock masses, accompanied by changes in the hydrogeological conditions of the chosen area.

4. Correction of this model is possible, based on the observations of contemporary activity of the major tectonic faults within the area of a radius of 30 km using the methods of space geodesy.

**References**


1. Morozov V.N., Tatarinov V.N. Tectonic processes development with time in the areas of HLRW disposal from expert assessment to prognosis. // Int. Nuclear Energy science and Technology, Vol. 2. No, 1/2. 2006. Pp. 65-74.
2. Morozov V.N., Tatarinov V.N. Methods of selecting areas of the earth's crust to accommodate the environmentally hazardous waste. // Geoecology. M. 1996, № 6, p. 109-120.
3. Belov S.V., Morozov V.N., Tatarinov V.N., Kamnev E.N., Hammer I. Study of the structure and geodynamic evolution of Niznekansky granitoid massif in connection with the disposal of high level radioactive waste // Geoecology. M. 2007, № 3. p. 227-238.
4. Morozov V.N., Gupalo T.A., Tatarinov V.N. Forecast insulating properties of the rock mass in the placement of radioactive materials in mines // Mountain Gazette. 1999, № 6. p. 99-105.
5. Morozov V.N., Kolesnikov I., Belov S.V., Tatarinov V.N., Stress-deformed state of Niznekansky granitoid massif – as the area of possible disposal of radioactive waste. // Geoecology. M. 2008, № 3, p 232-243.

# APPLICATION OF GEOGRAPHIC INFORMATION SYSTEMS (GIS) IN ANALYSIS OF GEOLOGICAL RISK FACTORS AND ASSESSMENT OF GEOHAZARDS IN DAUGAVPILS AND ILŪKSTE DISTRICTS

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**Abstract.** *This article deals with the main aspects of geological and geomorphological hazards (geohazards) assessment by presenting review of GIS-based methodology for identification and analysis of environmental hazards of such type to which the Daugavpils and Ilūkste districts are exposed. It includes (1) critical review of the availability and state of the art in data sources about geological risk factors, (2) a description of using geomatics methods for obtaining thematic layers of risk factors and techniques of their combining and overlaying, and (3) an analysis and assessment of summary geohazard risk. Such a complex GIS-based studying of geohazards has not been performed before in the territory under study, nor has it been attempted in Latvia. At the same time obtained results allow highlighting areas exposed to geological risk within the Daugavpils and Ilūkste districts, hence providing relevant information for spatial planning of these territories.*

**Keywords:** *Geographical Information System, geohazard assessment, geological risk factors.*

## Introduction

The analysis and identification of natural geological and geomorphological hazards (geohazards) associated with natural processes is of topical interest to the scientific community and at the same time adequate assessment of such risk is very important for authorities dealing with territorial planning [1]. Hence analysis of geological risk factors and assessment of potential hazards related to these factors is one of the prerequisites in terms of rational management and sustainable using of territories in the world [2, 3, 4]. Despite the fact, that unlike some of European countries, Latvia rarely suffers from natural hazards, such as damaging earthquakes or floods of high magnitude, though information about potential geohazards is very important to assist decision-making in spatial planning and designing of land use in our country too [5]. Obtaining of such information on the one hand allows to mitigate the risks and threats caused by possible occurring of endogenic or exogenic geological processes or natural disasters like floods, which endanger buildings, objects of infrastructure and people; and on the other hand information about geohazards is important considering the demands of EU legislation documents in the field of environmental management and territorial planning [6, 7]. Thereby, in order to ensure planning of development and management of territories at municipal level in Latvia, and simultaneously to prevent risks associated with geological or geomorphological hazards, it is necessary to aggregate geological information and to develop unified methodology allowing to assess the geological risk.

In recent years, a different approaches has been used in assessment of the risk of geohazards in Latvia, e.g. mapping of selected risk factors and preparing analogue geological maps, cartographic analysis and overlaying methods. However, there are little studies on the integration of geological and geomorphological risk factors in Geographic Information Systems (GIS) to identify the areas susceptible to geohazards in Latvia, though adequate and timely GIS-based assessing the expected consequences of geomorphic processes and hazards is the goal of many international research works. Review of literature dealing with the issues of geohazards and applications for multicriteria evaluation of geological risk factors [8, 9, 10], reveals that during the past two decades in many countries GIS-based methods became the main tool for effective risk assessment purposes. This tendency is determined, first of all, by the geospatial character of data describing factors of geological and geomorphological risk, hence allowing to transform them into GIS data, and secondly, by possibility to integrate such data that handle spatial information about geographic distribution of risk factors in GIS and to use this software tools for multicriteria geospatial analysis. Considering that, authors worked out GIS-based methodology adopted for physiogeographic and geological conditions of Latvia, which allows to estimate the potential geohazards risk at local scale as well as for the whole territory of each municipality. Such a complex GIS-based studying of geohazards has not been performed before in the territory under study, nor has it been attempted in our country.

## Materials and methods

Research and developing of methodology presented in this paper had been carried out by using of tools of ArcGIS software, as well as by other means and techniques of geomatics. In addition aggregation and analysis of the information, and field survey was carried out in order to obtain necessary input data or to verify results of the research.

First of all, factors of geological and geomorphological risk which potentially can affect the Daugavpils and Ilūkste districts were identified. Review of scientific publications and special literature dealing with issues of geological and geomorphological risk [11, 12, 2] reveals, that commonly a term “geohazard” includes great diversity of different processes, however, as the major categories are mentioned geological hazards, like mass movements or karst processes, hydrometeorological and fluvial hazards like floods and river channel changes, geomorphological hazards like accelerated soil erosion by water and geophysical hazards like earthquakes or volcanoes. The more general definition given by Zelčs and Markots [5] describes geological risk as probability that exogenic or endogenic geological processes can cause or human activities can enable the negative impact of these processes on environment, human life, health or property, as well as potential consequences of such undesirable processes which pose risk for a certain time period. Considering this definition and content of term “geohazard”, as well as geographic location of territory under study, its physiogeographic features and geological structure, the following geological and geomorphological risk factors potentially exposing the territories of the Daugavpils and Ilūkste districts to geohazards were identified: flood hazard, seismic hazard, karst hazard, wind erosion and aeolian processes hazard, landslide and soil erosion geomorphological hazard, coastal erosion hazard.

Thereafter desk-based studies, aggregating and analysing of the data about the geographic distribution of these hazards were carried out. For this purposes search through the internet resources of responsible institutions like planning departments of municipalities, as well as examination of reports of field studies, expeditions, and analogue geological maps [13] available in the Geological Fund of the Latvian Environment, Geology and Meteorology Centre had been done. Information about location of tectonic faults and historical records of earthquakes was obtained on the basis of published information sources [14, 15]. The obtained information allows to get understanding about the state of the art in data sources of geological risk factors and to locate areas of each risk factor for further GIS-based studies.

GIS tools and other means and techniques of geomatics were used for digitizing and preparation of thematic layers of raster and vector formats, converting and integrating GPS data into GIS, creating digital elevation model of the Daugavpils and Ilūkste districts and preparing of maps. Geospatial data of discrete type were represented as polygons (e.g. areas potentially affected by floods, karst, wind erosion, coastal erosion) or polylines (tectonic faults and zones of historically recorded earthquakes) of *.shp format. Geospatial data of continuous type (e.g. risk of landslides and accelerated soil erosion by water) were

represented as ESRI Grid raster with pixel size 10 x 10 m. For deriving these raster data the digital elevation model was prepared, which in turn were created from digitized contour lines by tool *Topo to Raster*. For this purpose contour lines in topographic maps (coordinate system СК-42) at scale 1:10,000 and elevation interval of 2 m was digitised by applying the standard procedure.
Considering a range and large space of territories affected by flooding, traditional methods, e.g. conventional topographic survey or GPS mapping, cannot be used for identification of inundated areas. For these purpose geomatic methods as using of remote sensing and GIS was chosen as the most appropriate. On the basis of hydrological data about mean and maximal flood level altitudes, standard procedure of interpolation and derived contour lines construction from points of known elevation and local topography indicated in maps was performed. Vector polygons representing inundated territories at different flood level were created by geospatial analysis and digitizing GIS data layers from topographical maps (scale 1:10 000 with contour interval 1 m) using ArcGIS software. Computed inundated territories shape conformity to real situation was validated by comparing ones with remotely sensed data, field survey GPS, and oblique aerial photography. The first of tasks, i.e. processing of remote sensing data, was carried out by use of LANDAST false-colour image of territory under study taken during spring floods in 1979 (Fig 1.). Situation fixed in this image illustrates dimension of inundation triggered by mean annual flood level. The second and third of tasks were performed during the floods in 2010, when conformity of digitised flooded territory was verified *in situ* by *Real Time Kinematic* GPS LEICA GX 1230 2 GG and simultaneously by oblique aerial photography taken from motorised delta-glider.
Comparison of computed inundated territory by means of GIS with remotely sensed image, data of high accuracy GPS field survey and oblique aerial photos indicates that obtained data layers confirm to real situation and well delineates the flood hazards polygon.
After the preparing of geospatial GIS data representing each factor of geological risk, vector data were converted into regular raster layers in order to range them and combine into one summary layer of geohazards. It estimates total geological risk in each pixel from data, collected by a combination of GIS mapping techniques, physical GPS survey and remote sensing (LANDSAT images and oblique aerial photography) on the six elements of risk. The individual relative value of each factor of geological risk was estimated according to approved methodology [2], which arranging the risk factors in order of increasing of possible loss and the probability for an individual hazard event. Subsequently, it allows to range risk factors and to evaluate its relative contribution to total risk (Table 1.).

*Table 1.*

**Relative values of geological risk factors in diminishing sequence**

| **Geological hazard factor (and abbreviation )** | **Individual relative value (dimensionless)** |
|---|---|
| Flood hazard (FL) | 6 |
| Seismic hazard (SE) | 5 |
| Karst hazard (KA) | 4 |
| Wind erosion and aeolian processes hazard (AE) | 3 |
| Landslide and soil erosion geomorphological erosion hazard (LS) | 2 |
| Coastal erosion hazard (CO) | 1 |

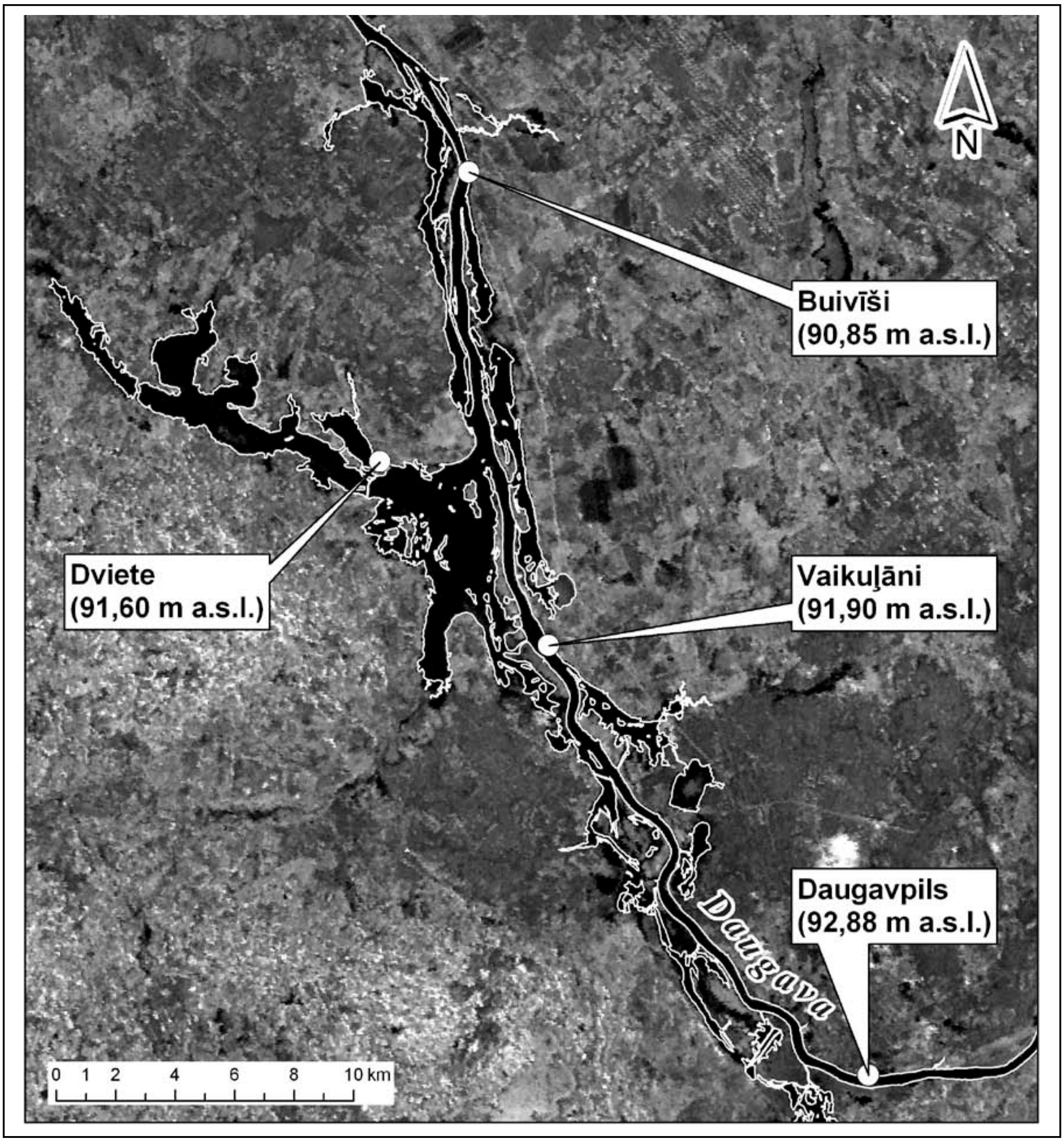


*Fig. 1.* **Comparison of really inundated territory (LANDSAT raster image in background, flooded territory is coloured in black due to near-zero reflectance in IR band on false colour image) with GIS-computed (white lines). Circles represent hydrological stations and their name. Figures in callouts indicate flood levels recorded at these hydrological stations at the same date when satellite image was taken**

The operation of combining of separate risk factors into summary layer was performed by ArcGIS extension *Spatial Analyst*, by tool *Raster Calculator* according to Map Algebra syntax expression (1):

$$SUM_{hazard} = FL + SE + KA + AE + LS + CO \qquad (1)$$

Finally, the data obtained during geospatial analysis and thematic layers were aggregated in the map of geological risk, which can be used for purposes of territorial planning of the Daugavpils and Ilūkste districts.

## Results and discussion

Obtained results, first of all, show that information and data about geological risk factors within the Daugavpils and Ilūkste districts is fragmented, not enough systematised and is available only in analogue format (printouts and maps). In additional it is necessary to point out that there is no geohazards data in digital format, and for user it is not possible to obtain this information via internet. Moreover, the degree of detailed elaboration considering the scale of maps does not allow using them for purposes of spatial and territorial planning at municipal or local level. Summarising aforementioned it necessary to remark that state of the art in data sources stored in the Geological Fund of the Latvian Environment, Geology and Meteorology Centre actually is beneath contempt in context of urgent necessity of GIS-based analysis of nature hazards and decision support for hazard mitigation.

The results of integration and geospatial data reveal, that considerable part of the territory of the Daugavpils and Ilūkste districts are exposed to the risk of mass movement processes, mainly landsliding formation, and to the risk of accelerated soil erosion by water. In particular the steep slopes within the Latgale upland, Augšzeme upland and the largest river valleys potentially are exposed to the geomorphological risk (Fig 2.). The lower values of geological risk are associated with coastal processes and wind erosion and aeolian processes hazard. The coastal processes affect very narrow zones along the littorals of the largest lakes, e.g. the Lake Sventes, the Lake Riču etc. The aeolian processes can become activate within the area of inland dunes in central part of the Daugavpils district, though this area at the present is afforested and possible risk relates only to the case of total forest clearance.

However, the highest degree of geological risk is associated with flooding, because during the floods of high levels and high magnitude (period of recurrence 1 or 5 times par 100 y), to the risk of inundation are exposed from 20% to 40% of territory of local rural municipalities, e.g. Dviete local municipality. Simultaneously, high degree of geohazards is associated with seismotectonic processes, which geographically are located in form of wide zone orientated from north-west to south-east. This zone encompasses large areas of both the Daugavpils and Ilūkste districts, and within it historically were recorded earthquakes of 4.7 magnitude according to Richter’s scale. In combination with risk related to presence of objects of infrastructure with potential threats to environment, e.g. oil products and gas pipelines, waste dumps, gasoline stations and depositories, railway lines, this factor of geological risk determines relatively high degree of geohazards in both municipalities.

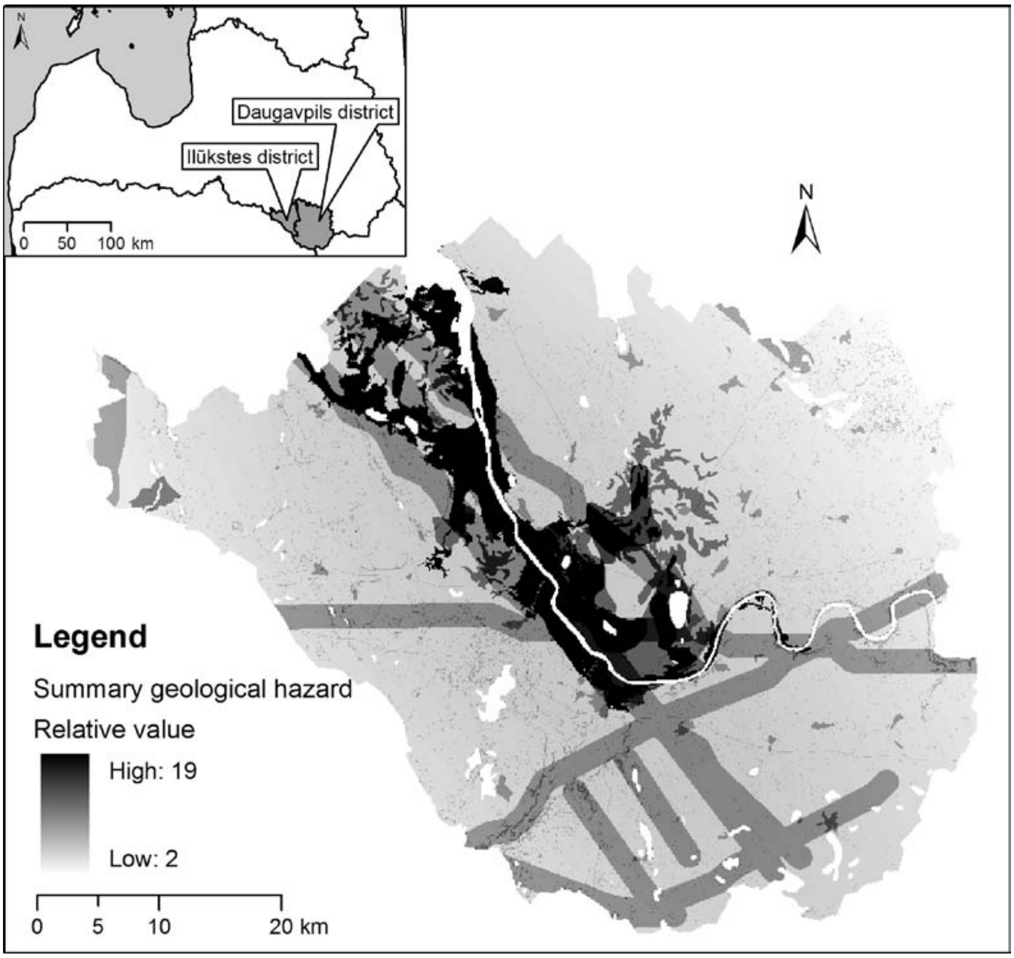

*Fig. 2.* **The map of summary geological hazard within the Daugavpils and Ilūkste districts**

## Conclusions

The results of the given research based on GIS analysis of geological risk factors and assessment of geohazards demonstrates, that highest risk of geohazards in the Daugavpils and Ilūkste districts is associated with floods of high magnitude, because this natural disaster potentially can affect more than 20% of territory in some local municipalities, thus determining high possible economical losses and negative impact on environment.

The seismotectonic risk associated with possible earthquakes exceeding a 4.0 magnitude according to Richter's scale is among those principal geological risk factors which in combination with the technogenic risk can harmfully affect the infrastructure and environment in large areas in the Daugavpils and Ilūkste districts.

The second-grade geological risk factors are coastal processes, wind erosion and aeolian processes hazards, due to small scale of expression as well as presence of protective cover of forest vegetation in the areas potentially exposed to hazards of these exogenic geological processes.

Despite the fact that geomorphological hazards like mass movement processes and soil erosion by water potentially can affect large areas, at the present moment this factors are impeded by presence of natural vegetation cover. Considering the potential risk of landsliding and linear erosion, several territories in the Daugavpils and Ilūkste districts should be afforested to prevent reactivation of these processes.

Application of GIS software and means of geomatics allow to assess very effectively geohazards and potential geological risk, thus enabling wide opportunities for using of these digital data in form of electronic tables or GIS maps by governmental municipal and private institutions for purposes of spatial and territorial planning. Simultaneously digital format of information depicting geographic distribution of geological risk makes it accessible to society via internet.

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**References**

1. Campus, S., Barbero, S., Bovo, S., Forlati, F. Evaluation and Prevention of Natural Risks. Taylor & Francis, UK, 2007, 470 pp.
2. Smith, K., Petley, D.N. Environmental Hazards: Assessing Risk and Reducing Disaster. 5th edit. Routledge, New York, USA, 2009, 416 pp.
3. Crozier, M., Glade, T. Hazard assessment for risk analysis and risk management. *In*: Alcántara-Ayala I., Goudie A. (eds.), *Geomorphological Hazards and Disaster Prevention*. Cambridge Univ. Press, Cambridge, UK, 2010, pp.221-232.
4. Higgitt, D. Geomorphological hazards and sustainable development. *In*: Alcántara-Ayala I., Goudie A. (eds.), *Geomorphological Hazards and Disaster Prevention*. Cambridge Univ. Press, Cambridge, UK, 2010, pp.257-268.
5. Zelčs, V., Markots, A. Ģeoloģiskās informācijas izmantošana teritorijas attīstības plānošanā. Valsts ģeoloģijas dienests, Latvijas Universitāte, Rīga, 1999, 123 lpp.
6. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy (Water Framework Directive). Official Journal of the European Communities, 2000. L 327, vol. 43, 22 December 2000, pp. 1- 72.
7. Directive 2007/60/EC of the European Parliament and of the Council of 23 October 2007 on the assessment and management of flood risks (Floods Directive). Official Journal of the European Union, 2007. L 288, vol. 50, 6 November 2007, pp. 27 -34.
8. Chen K., Blong R., Jacobson C. MCE-RISK: integrating multicriteria evaluation and GIS for risk decision-making in natural hazards. *Environmental Modelling & Software*, 16 (4), 2001, pp. 387-397.
9. Fedeski, M., Gwilliam, J. Urban sustainability in the presence of flood and geological hazards: The development of a GIS-based vulnerability and risk assessment methodology. *Landscape and Urban Planning*, 83 (1), 2007, pp.50-61.
10. Van Westen, C.J. GIS for the assessment of risk from geomorphological hazards. *In*: Alcántara-Ayala I., Goudie A. (eds.), *Geomorphological Hazards and Disaster Prevention*. Cambridge Univ. Press, Cambridge, UK, 2010, pp.205-220.
11. Glossary of Environment Statistics: Studies in Methods. Series F, No. 67, United Nations, New York, 1997, 78 pp.
12. Landesman, Y.L. Public health management of disasters: The practice guide. American Public Health Association, NW, Washington, DC,2001, 122 pp.
13. Karte "Pazemes ūdeņu aizsardzība un ģeoloģiskā riska teritorijas". Krāj.: *Ģeoloģiskas informācijas sagatavošana valsts nacionālā plānojuma vajadzībām*. 2.sēj. Valsts Ģeoloģijas dienests, Rīga. 1998, 35 lpp.
14. Nikuļins, V. Latvijas vēsturisko zemestrīču seismotehniskā pozīcija. *Latvijas ģeoloģijas vēstis*, 1996.Nr.1. - Rīga, Valsts ģeoloģijas dienests, 31.-36.lpp.
15. Nikuļins, V. Latvijas seismotektoniskie apstākļi un seismiskā bīstamība. Promocijas darba kopsavilkums. LU Akadēmiskais apgāds, Rīga, 2007, 106 lpp.

**Anotācija.** *Rakstā apskatīti galvenie ģeoloģiski ģeomorfoloģiskā riska (ģeoloģiskā riska) novērtēšanas aspekti, izklāstot GIS bāzētu metodoloģiju šāda veida vides apdraudējuma identificēšanai un analīzei Daugavpils un Ilūkstes novados. Raksts iekļauj, pirmkārt, pārskatu par ģeoloģiskā riska faktorus raksturojošās informācijas un datu pieejamību un situāciju šajā jomā; otrkārt, ģeomātikas metožu aprakstu riska faktoru tematisko slāņu ieguvei un paņēmienus šo datu apkopošanai un apstrādei; un, treškārt, summārā ģeoloģiskā riska novērtējumu un analīzi. Šāda kompleksa GIS bāzēta pieeja ģeoloģiskā riska izpētē līdz šim nav tikusi izmantota nedz pētījumu teritorijā, nedz arī Latvijā. Iegūtie rezultāti vienlaicīgi arī ļauj izcelt tos apgabalus, kuri ir pakļauti ģeoloģiskajam riskam Daugavpils un Ilūkstes novados, tādējādi nodrošinot nozīmīgu informāciju šo pašvaldību teritoriju plānošanas vajadzībām.*

# EXPERIENCE ANALYSIS AND SAMPLE DISTRIBUTION PROBLEMS IN LOCAL LEVEL LANDSCAPE MONITORING

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**Abstract.** *After summarizing experience of various countries in the field of landscape monitoring, it appears that the real changes of landscape have to be observed in a large scale (not smaller than 1:10,000) in order to avoid generalization of small landscape elements. Usually there are several levels of distributing the places of monitoring: 1) the level of sample area, when monitor territories are stratified by landscape types; 2) the level of investigation site that is distinguished inside the sample area for the more detailed research; 3) the level of transect or field investigation site, sometimes created in order to multiply the statistical data for some special aspect of monitoring. The paper offers an original method of distributing the landscape sample areas in Lithuanian territory, differing from most methods based on random choose of sample areas though thorough analysis of the analogous methods abroad was performed.*

**Keywords:** *landscape monitoring, sample areas, best representation principle, land cover structure, natural landscape types.*

## Introduction

Landscape is a result of interaction between many natural processes and functional interests influencing use and protection of territory, it's a creation of natural forces and society's land management efforts. Current Lithuanian landscape contains reflections of various past social-economical reforms recorded in landscape mosaics and land use structure. Especially sudden as seen from our modern perspective, appears landscape structure changes that have taken place in Lithuania after regaining the Independence and after approving certain programmes of land restitution. The latter stimulated fragmentation of owned land, bringing our country somewhat back to the interwar period, only with the traces of soviet land management and signs of some new elements in our landscape. Such a situation requires objective and scientifically grounded monitoring of landscape state and spatial structural change especially seeking to ensure sustainable formation of landscape.

In order to ensure correctness of data collection for landscape state and spatial structure change, it is important to have a methodology that could represent landscape changes in the main landscape types and could generate a reliable basis for comparison of Lithuanian landscape change with the other countries' respective data.

In Lithuania, landscape structure analysis was being performed mostly in national and local levels, as well as in several areas of special interest like coastal, karst region, and protected areas. For national and regional level landscape change fixation a land cover data, such as CORINE (scale 1: 100.000) was used.

However, at the local level Lithuanian experience quite less, where the aerial photographs (giving images in scale of 1:10.000 or larger) should be used as a basis, complemented by specific local field investigations in linear transects. These change fixations could be highly valuable for assessment of landscape stability and for basing ecological optimisation means, as well as legal regulations of territory use.

## Methods

A study of experience of landscape monitoring in other European countries was conducted in order to offer and adapt a methodology of landscape spatial structure changes in local level for Lithuania. Attention was focused on the selection of sample areas, monitoring indicators and data collection methodology.

It is notable, that some European countries like UK, Sweden, Denmark, Austria, Estonia, Finland have much deeper and longer experience in landscape monitoring, having started their legally approved activities as early as in 80s or even earlier as in case of Denmark where the programme of the monitoring of the smaller biotopes was initiated even in late 70s [1].

***Problem of sample area selection***. Most of mentioned countries in their landscape monitoring systems do not distinguish national, regional and local levels. On other hand, every country has its own point of view how to implement their respective landscape monitoring programme, following the attitude towards landscape admitted in that country, the depth and character of landscape knowledge, research traditions and technological equipment. Western countries possess more ecosystemic attitude towards landscape, therefore, they are strongly investigating biodiversity of landscapes, or particular species, that serve as indicators [2,3]. Quite often for such a kind of monitoring the elements that indirectly reflect the biodiversity spread are used, namely land cover. It is the landscape element that reveals the main aspects of human influence to landscape, therefore this indicator fits well in Lithuanian case as well, especially because here the prevalent concept of landscape is more morphological than bioecological.

Important characteristic of landscape monitoring is the necessity of sufficient technological facilities and mathematical process of data, as well as maximum objectivity of monitoring. Usually there are several hierarchical levels in the monitoring system, because selected sample areas that are wider, like buffer areas, contain one or several sites of investigation where data is collected in much detailed level. Sample area is usually related to the representation of some landscape or habitat type, whereas site that is inside it is a main feeder of data in local level. In this sampling process there can be several variations in different countries, sometimes appearing even lower level of monitoring in case it is needed to collect more data, namely field data collection site or transect.

In national monitoring programme of Sweden (in 2003) 500 randomly selected sample areas were defined in three main landscape types: 1) agrarian territories, 2) wetlands, and 3) northern mountainous region. Size of each sample area is 5x5 km, but inside it there was a smaller site of intensive monitoring distinguished [4].

Similarly, but proportionally less (100) samples were selected according to the Austrian landscape monitoring programme's sub-programme SINUS (1996-2000), the size being 5x5 km of each. 80 sample areas were selected in eight agrarian landscape classes, differentiated according to cultural type, relief, geology. Each landscape type was represented by 10 sample areas distributed in the territory in random way. The other 20 sample areas of the same size were selected subjectively in areas of the greatest interest. In every sample area, were distinguished two sites of detailed monitoring (1x1 km each) [5, 6].

There are 58 landscape types in four regions monitored in Finland using sample areas selected one in each type. Each sample area, being of 1x1 km in size was divided into four parts in order to enlarge statistical volume, and besides that, contained 20 transects of 50 m in length [7]. Norway created its own methodology dividing the whole country by 18x18 km quadrangles, 1000 sample areas selected systemically within them. This monitoring system was matched with already functioning agrarian landscape monitoring programme 3Q [7].

Estonian experience differs from the mentioned countries by methodology of selecting areas for landscape monitoring. According to the landscape monitoring sub-programme of Environment monitoring programme, approved in 1996, 6 protected areas were selected with

3 km wide buffer zones. Thus landscape monitoring was conducted both inside and outside of protected areas, additionally with field observations in 84 sites. Landscape monitoring covers about 10% of Estonian territory.

In 1995 German Federal Nature protection agency created and tested the system of ecological area sampling, according to which 1x1 km size samples were selected in the whole country stratified by land classes and land cover types. In later stages, inside of these sample areas, smaller sites of observation are selected with the purpose of recording plants and animals in the biotope.

Denmark can boast with the quite early (started in late 70s) programme of smaller biotopes, having 32 sample areas of 2x2 km size, where detailed investigations are performed [10].

British landscape monitoring system being technically strong represents landscapes of the country in detail, their specialists indicate some important points for successful monitoring: 1) clearly defined observation territories, 2) objectivity in sample area selection, 3) representation of landscape, 4) equal and unchangeable size of sample areas. Besides that, it is important that field observations in landscape monitoring must not take much time so that the fixation of all the sites was taken with the least difference in time. Successful monitoring includes optimal staff and equipment transfer, or generally, logistics, as well as ensured quality control and data reliability [7].

***Problem of indicators and data collection methodology***. In most of mentioned countries, landscape monitoring is related to the collection of information about biological constituents, but alternatively there can be other indicators more related to the culture influence on landscape structure, like indicators in already mentioned Sweden programme such as land cover, lengths of linear elements, density of point objects, frequency of indicative or key species, indexes of captured insects' abundance, proportions of various landscape elements (species, vegetation types, tree crowns) [4].

Austrian SINUS landscape monitoring in 1x1 km sites includes indicators like land use, patch origin, defined matrix-patch model, hemerobiotic state and species richness. Austrian project BINKL (1998-2001) was devoted to distinguish indicative species of organisms that could be applied in describing changes in different agrarian landscape classes [7].

In Finland's 58 landscape sample areas, monitoring indicators are related to landscape structure changes and evaluation of captured insects species diversity. Norwegian 3Q programme's monitoring indicators are numerous and belong to several groups like landscape spatial structure (including patch type area and occupied part, fragmentation, diversity and heterogeneity indexes, terrestrial and water bodies boundaries indexes, urbanization density, etc.), spatial structure of agricultural lands (land use types, fragmentation indexes, field shape, field boundaries indexes, point objects indexes), biodiversity, evaluated by Shanon diversity index, cultural heritage (historical buildings, cultural monuments and sites, historical boundaries, roads and paths, and their indexes), connectivity indexes, as well as data on noise near roads, etc [7]. Estonian landscape monitoring programme comprise two main groups of landscape diversity indicators, namely measured (area statistics) and estimated like boundary neighbourhood indexes, diversity metrics [8, 9].

## Results and discussion on new methodology

In the process of creation of Lithuanian landscape monitoring system, there are the same tasks raised like sample area number and location selection, indicator system creation, data collection periodicity.

A distinctive feature of Lithuanian landscape monitoring system that was offered for Environment protection agency under Ministry of Environment of Lithuanian Republic is the principle of representativity instead of random selection method. The optimal number of sample areas for the country like Lithuania (somewhat smaller than Austria) was chosen 100, the size being of 2.5 $km^2$ (~1.5x1.5 km). The representation principle implied that the sample areas were distributed among main natural landscape types proportionally to the area occupied by these types. Proportionality was corrected in a way that unique and small area occupying landscape types (spit, delta) received greater weight coefficient determining number of sample areas, than the most popular landscape types, like clayey plains or morainic hills (Table 1).

*Table 1.*

**Landscape monitoring sample area distribution in the main natural landscape types of Lithuania**

| No | Natural landscape types | Represented area (total area of Lithuania is ~65300 $km^2$), $km^2$ | Part of Lithuanian territory, %. | Number of attributed sample areas (direct proportion) | Number of attributed sample areas (corrected proportion) |
|---|---|---|---|---|---|
| **A** | **B** | **E** | **F** | **G** | **H** |
| 1. | Clayey plains | 23862.4 | 36.10 | 42 | 22 |
| 2. | Clayey downy plains | 11002.5 | 16.64 | 19 | 17 |
| 3. | Morainic hills | 9974.4 | 15.09 | 17 | 16 |
| 4. | Sandy plains | 5527.3 | 8.36 | 10 | 13 |
| 5. | Valleys | 3966.6 | 6.00 | 7 | 11 |
| 6. | Lake terrains | 2535.1 | 3.83 | 4 | 9 |
| 7. | Spit | 101.4 | 0.15 | 0 | 5 |
| 8. | Delta valley and delta | 238.4 | 0.36 | 0 | 4 |
| 9. | Sandy coastal plain | 189.1 | 0.29 | 0 | 3 |
| | **Total** | **57397.2** | **86.83** | **100** | **100** |

Particular locations of sample areas in the destined for them landscape types were selected once again by application of representation principle, not a random generation of coordinates, that is a popular way in other countries‘monitoring systems to achieve objectivity of location selection. In our case, representation principle was an expression of objectivity obligation. A special computer programme was created (by A. Kryžanauskas) in order to find locations in a chosen landscape type that in their land cover structure were most similar to the summarized land cover structure of the respective landscape type. The principle of the programme work was the „striding“ of the sample area shape (quadrangle of 1.5x1.5 km) across the landscape type and automatically calculating its inner structure and presenting the result in a data base table. Depending on size of the landscape type, positions of the sample shape tested inside the landscape type area were several hundreds to several tens of thousands, the total possible sample area positions tested being 67,758 (Table 2).

Later analysis enabled to calculate and sort tested positions of the striding sample shape and to select the best representing ones. Data of each sample shape’s land cover (in our case CORINE land cover data of 2006 was used) structure was compared to the land cover structure of the respective natural landscape type by calculating a relative distance between these structure using the following formula (1):

*Table 2.*

**Number of tested positions of sample shape striding across the different landscape types**

| No | Natural landscape types | Number of sample areas | Number of tested positions of sample areas |
|---|---|---|---|
| 1. | Clayey plains | 22 | 27518 |
| 2. | Clayey downy plateaus | 17 | 11265 |
| 3. | Morainic hills | 16 | 10605 |
| 4. | Sandy plains | 13 | 5550 |
| 5. | Valleys | 11 | 8884 |
| 6. | Lake terrains | 9 | 2555 |
| 7. | Spit | 5 | 407 |
| 8. | Delta | 4 | 237 |
| 9. | Coastal Plain | 3 | 737 |
| | **Total** | **100** | **67758** |

$$D = \sum_{j} \left| z_j - Z_j \right| \qquad (1)$$

where D – relative distance of the land cover structure in a sample shape from the respective landscape type measured in %, j – running number of the land cover type (the total number of land cover types according to CORINE is 30); $z_j$ – percentage of *j* land cover type in a sample shape, $Z_j$ – percentage of *j* land cover type in a respective landscape type.

As the land cover structure of the sample shapes is much less diverse as that of the whole landscape type, an additional index, namely number of land cover types, was introduced into the sample selection process, preference giving to those with the largest meaning of this index. In fact, sample shapes with the largest number of land cover types contain only 50 to 70 percent of the total number of land cover types found in hosting them natural landscape type.

Regional representation (principle of equal spread of sample areas) was also taken into account, meaning that we avoided selection of sample areas in one region or in several close regions trying to find sample areas with the best representation characteristics in the most distant landscape regions.

To generalize, the final choice for the locations of the sample areas was determined by the position the sample shapes being the most similar in land cover structure (the least distant from the natural landscape land cover structure), having richest diversity of land cover types, and representing different regions of the same natural type landscapes (Fig. 1).

Landscape condition and structure change investigation in local level are important for substantiating directions of landscape protection, formation and management, as well as for preparation of territorial planning document of different rank. Especially important is the knowledge of landscape spatial structure and state in ecologically sensitive natural complexes, as e.g. in nature frame territories, areas of specific problems, and protected areas, that require introduction of specialized and adequate use conditions, regulations for economical activities and their limitations.

Additional analysis has revealed that most of the selected hundred sample areas fall into the areas of mentioned sensitive character. Thus, ignoring the overlapping, we might state, that 62 sample areas will be able to represent parts of Lithuanian nature frame (legally approved network of geoecologically important territories of Lithuania), 23 of them will describe landscape changes in regional and national parks (protected areas), 14 will describe nature reserves, and 2 will represent biosphere polygons.

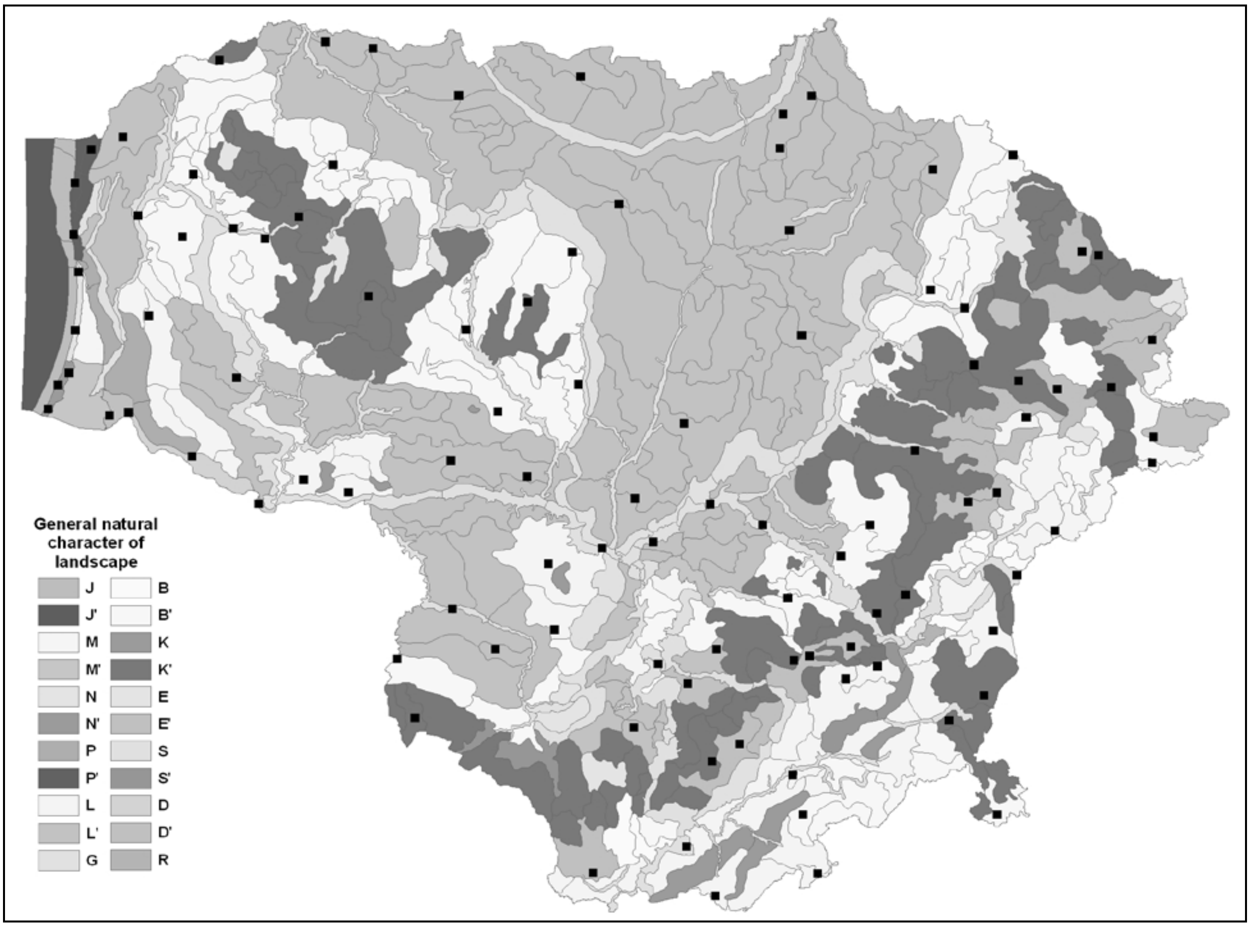


*Fig. 1.* **Landscape monitoring sample areas (black squares) in different natural landscape types of Lithuania (map according to [11])**

Natural character types of landscape: J – marine landscape in the coastal zone (at a depth of < 20 m); J‘ – underwater plateaus and troughs; M – shallow lagoon (at a depth of < 2 m); M‘ – deep lagoon; N – smoothened spit; N‘ – rugged spit; P – lagoon coastal plain; P‘ – sandy coastal plain; L – continental sandy plains; L‘ – clayey plains; B – sandy downy plateaus; B‘ – clayey downy plateaus; G – morainic hills; K – sandy hills; K‘ – morainic hills; E – troughs with lakes; E‘ – lake terrains; S – valleys; S‘ – old valleys; D – delta valley; D‘ – delta; R – erosion washes.

## Conclusions

Experience from countries having longer experience in landscape monitoring, including the local level one, show the main methodological tasks that has to be resolved, namely territorial distribution of sample areas, system of indicators to be monitored, ways of collecting the data, ways of processing and generalization of collected data. There are also some principles that each country must develop for distinguishing monitoring sites, namely strict definition of monitoring area, objectivity, representation, size of sample areas, periodicity of data collection.

Adapted to Lithuanian case, the principles of landscape monitoring using local level monitoring sites could comprise the following points: 1) number of monitoring sites is 100; 2) territorial distribution represents main landscape character types; 3) size of monitoring sites – 2,5 $km^2$; 4) indicator system is tied with landscape cover structure with additional evaluation of vegetation state.

In the process of sample area selection, a principle of representation instead of random selection method was offered. Thus the choice for the locations of the sample areas was determined by the most similar to the natural landscape type land cover structure, richest

diversity of land cover types (as the way of approximation to the landscape type richness), and considering the even territorial distribution of most representative sample areas.
The offered landscape local level monitoring sample areas will reliably represent landscape state condition and spatial structure change not only in the context of the whole Lithuanian territory, but also the situation in ecologically sensitive landscape complexes like Nature frame (62 sample areas), protected areas (39 sample areas) and several areas of specific problems like karst region, coastal region, etc.

**References**


1. Gulbinas, Z., Pileckas, M., Petravičiūtė, R. Kraštovaizdžio monitoringo organizavimo problematika. 1. Šiaurės Europos šalių patirtis [Problems of landscape monitoring organization. 1. Experience of Northern countries]. *Geographical Yearbook* 36(1), 2003, p. 225-236 (in Lithuanian).
2. Sepp, K., Mikk, M., Mänd, M., Truu, J. Bumblebee communities as an indicator for landscape monitoring in the agri-environmental programme. *Landscape and Urban Planning, Volume 67, Issues 1-4, 15 March 2004*, p. 173-183..
3. Jonason, D., Milberg, P., Bergman, K.-O. Monitoring of butterflies within a landscape context in south-eastern Sweden. *Journal for Nature Conservation, Volume 18, Issue 1, January 2010, Pages 22-33*
4. Löfgren P., Fridman J., and Ringvall A., Ståhl G. Sweden's new national landscape monitoring program, SLÖ, 2002, Internet access: http://www2.dmu.dk/1_Viden/2_Miljoe-tilstand/3_natur/nordlam/nldocs/wsNov01T3/PLofgren.pdf
4. Wrbka, Th. Landscape and Vegetation monitoring in Austria, 2000. Internet access: http://www2.dmu.dk/1_Viden/2_Miljoe-tilstand/3_natur/nordlam/NLmeetings/wsOct00T2.asp
5. Banko, G., Zethner, G., Wrbka, Th., Schmitzberger, I. Landscape types as the optimal spatial domain For developing landscape indicators, 2002. Internet access: http://webdomino1.oecd.org/comnet/agr/landscape.nsf/viewHtml/index/$FILE/AustriaBanko.PDF
6. Developments in strategic landscape monitoring for the Nordic countries. Groom, G. (Ed.), 2004. Internet access: http://www.norden.org/pub/miljo/miljo/sk/ANP2004705.pdf
7. Aaviksoo, K., Meiner, A. Satellite monitoring of Estonia landscapes. 2000. Internet access: file:///C:/Documents%20and%20Settings/DV/Local%20Settings/Temporary%20Internet%20Files/Content.IE5/Q4L5M5PY/KAaviksoo%5B1%5D.ppt#281,18,WHY MASKS?
8. Aaviksoo, K., Muru, K. 2008. A methodology of the satellite mapping and monitoring of protected landscapes in Estonia. Estonian Journal of Ecology, 57(3), p. 159-184
9. Monitoring Information. [online]. [cited 12 February 2009] Workshop on Integration of Partial Coverage and Full Coverage Landscape, 2000. Available from internet: http://www2.dmu.dk/1_Viden/2_Miljoe-tilstand/3_natur/nordlam/NLpubl/wsOct00T2_rpt.pdf
10. Lietuvos Respublikos kraštovaizdžio erdvinės struktūros įvairovės ir jos tipų identifikavimo studija [Study of landscape spatial structure diversity and its types' identification of Lithuanian Republic]. 2006. Internet access: http://www.am.lt/VI/index.php#r/1144 [last access 2011-03-01].

# USE OF PLANTS TO REMEDIATE SOIL POLLUTED WITH OIL

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**Abstract.** *In the present investigation the growing and development ability of various annual and perennial plants to grow on model peat substrate artificially polluted with oil products in the range of concentrations from 1 to 5% was evaluated. The highest tolerance towards peat contamination by oil products has been demonstrated by three annual crops (maize, oat and lupine). These plants were tested for phytoremediation of polluted black soil from the area of oil refinery plant (Mazeikiai, Lithuania), which was treated by association of oil oxidizing bacteria up to residual concentration of the oil products of 4.5 %. The maize plants revealed the highest remediation ability: oil content in the soil decreased by ~ 1.5 times in one month plant vegetation.*

**Keywords:** *oil oxidizing bacteria, phytoremediation, rizosphere, soil microbiot*

## Introduction

As a result of human industrial activity, a large quantity of soil becomes polluted with a wide spectrum of petroleum products. Integrated technology, which includes soil treatment by the association of oil oxidizing bacteria followed by plants vegetation, allows to clean up heavy polluted soils. The use of phytoremediation as a secondary or polishing in situ treatment step minimizes land disturbance and eliminates transportation and liability costs associated with offsite treatment and disposal [1]. Using phytoremediation include cost effectiveness, aesthetic advantages, and long-term applicability.

Phytoremediation mechanisms include physical, chemical, and biological processes to remove, degrade, transform, or stabilize contaminants within soil. Microbial degradation is considered as the most significant mechanism for decontamination soils polluted with hydrocarbons [2-8]. The rhizosphere of most plants promotes a wealth of microorganisms that can contribute significantly to the degradation of petroleum hydrocarbons during phytoremediation especially within plant root zone.

Root exudates containing sugars, alcohols, and organic acids can amount to 10 to 20% of plant photosynthesis annually [1] and provide sufficient carbon and energy to support large numbers of microbes. Due to these exudates, microbial populations and activities are 5 to 100 times greater in the rhizosphere than in bulk soil. Root exudates are the link between □roducē and microbes that leads to the rhizosphere effect. The type and amount of root exudates are depend on plant species and the stage of plant development

Efficiency of the final remediation stage depends on the number of factors e.g. type of soil, its nutrition quality and tolerance of plants towards pollutants. The goal of this work was to select several plants growing in moderate climate with enough tolerance toward oil pollutants and to estimate their phytoremediation ability on the second stage of integrated bioremediation technology after treatment of polluted soil with association of oil oxidizing bacteria.

## Materials and methods

***Plant seeds.*** Certified seeds of annual and perennial plants, provided by the LUA Agency "Research Institute of Agriculture", were used for the experiments.

| | **Annual plants:** | **Latin name of the crop** |
|---|---|---|
| **1** | Field beans „Ada" | *Faba bona* |
| **2** | White mustard | *Sinapis alba* |
| | Lupine broad-leaved „Peršacvet" | *Lupinus* |
| **4** | Oat „Laima" | *Avena sativa* |
| **5** | Maize "Ostreg"C.V. (Ukraine) | *Zea mays* |
| | **Perrennial plants:** | |
| **6** | Red clover „Dīvaja"* | *Trifolium pratense* |
| **7** | Timothy „Teicis"* | *Phleum pratense* |
| **8** | Ryegrass „Spīdola"* | *Lolium perenne* |
| **9** | Lucerne „Skriveri"* | *Medicago sativa* |

*Plants of Latvian Selection

Before sowing, the germination of seeds was tested and the norm of the seeds needed for sowing was corrected taking into account the test results.

***Tolerance of annual and perennial plants towards oil products*** was tested in a model experiment on peat substrate PG-MIX 12-14-24. The contaminant for purposeful pollution of peat substrate was obtained by mixing of oil and mazut (1:1) and 3 polluted substrates with 1, 3 and 5% of oil products were prepared. Experiments were made in triplicate in 0.5 l vegetation vessels placed at the experimental space in outdoor conditions. Germination of seeds in the polluted substrate was established at $3^{rd}$ and $6^{th}$ day after sowing. The quantity of survived plants was evaluated at the end of the experiment ($14^{th}$ day), then the plants were taken out from the vegetation vessels, and the green mass of the plants overground part was determined.

***The phytoremediation test*** was carried out on the polluted black soil (TS) from the area of oil refinery plant (Mazeikiai, Lithuania) treated by association of oil oxidizing bacteria. Residual concentration of oil products was 4.5 % and 2.6 %. The latter soil sample was obtained by dilution of soil sample containing 4.5 % of oil products with clean black soil. In the case of contaminated soils, additives, stimulating plants development were introduced before seeds sowing. Experiment was done in 3 l pots placed in outdoor conditions. For maize and oats 15 seeds were sown into each pot, for lupine – 20. All experiments were done twice. To avoid roots overheating during vegetation pots were placed into trenches in such a manner that soil level in pots was at the ground level. The area was covered by agrofilm to prevent seed washing out in the case of heavy rains. As additives, stimulating development of soil microbiota and plants, the potassium humate (certified product of Russia) and Lignosilicon (synthesized in LS IWC and certified in Latvia) were used. In the control experiment plants were sown in the clean black soil, which was then watered with potassium humate.

***Concentration of petroleum hydrocarbons in*** soil was determined by gas-liquid chromatography (GLC) in accordance with ISO 16703 standard.

***Characterization of soil microbiota*** was performed using rhizospheric and bulk soil probes taken off from vegetation vessels after 4 weeks of maize growth. Collected root samples of three maize plants with adhered soil were placed into sterile distilled water for 20 min, periodically shaking roots. Then, decimal dilutions of soils suspension in sterile water were prepared and plated in duplicate. The total **heterotrophic bacteria** count in bulk and rhizosphere soils samples was determined using Tryptone Glucose Yeast Extract Agar (Sifin, Germany). EMB (Sifin, Germany) and malt agar were used for enumerating **Gram-negative bacteria and fungi**, respectively. Incubation was performed at 28 °C during 48h for inoculated TGA and EMB plates, and 72h – for malt agar plates, respectively.

**Community-Level Physiological Profiles (CLPPs)** were determined using EcoPlates (Biolog, USA). For this purpose dilutions of soil samples were prepared in sterile 0,85% NaCl. 150 µl of appropriate dilution was added to each well. Measurement of bacteria growth on 31 different substrates (Table 1) was performed in dynamics, at 590 nm with a Model Expert Plus Microplate Reader (ALYS, Labware, Lausanne). EcoPlates were incubated at 28 °C during 7 days, with periodical shaking.

*Table 1.*

**Carbon sources in EcoPlate**

| No | Substrate | No | Substrate | No | Substrate |
|---|---|---|---|---|---|
| 1 | Control – Water | 11 | 2-Hydroxy Benzoic Acid | 22 | D-Glucosaminic Acid |
| 2 | B-Methyl-D-Glucoside | 12 | L-Phenylalanine | 23 | Itaconic Acid |
| 3 | D-Galactonic Acid γ-Lactone | 13 | Tween 80 | 24 | Glycil-L-Glutamic Acid |
| 4 | L-Arginine | 14 | D-Mannitol | 25 | D-Cellobiose |
| 5 | Pyruvic Acid Methyl Ester | 15 | 4-Hydroxy Benzoic Acid | 26 | Glucose-1-Phosphate |
| 6 | D-Xylose | 16 | L-Serine | 27 | A-Ketobutyric Acid |
| 7 | D-Galacturonic Acid | 17 | α-Cyclodextrine | 28 | Phenylethyl-amine |
| 8 | L-Asparagine | 18 | N-Acetyl-D-Glucosamine | 29 | α-D-Lactose |
| 9 | Tween 40 | 19 | Γ-Hydroxybutyric Acid | 30 | D,L-α-Glycerol Phosphate |
| 10 | i-Erythritol | 20 | L-Threonine | 31 | D-Malic Acid |
|  |  | 21 | Glycogen | 32 | Putrescine |

***Plant root system*** was analyzed using scanner STD-1600+ with software Win Rhizo 2002C.

## Results and discussion

5 annual and 4 perennial plants were chosen on the basis of literature data. Tolerance of these plants towards artificial contamination of peat soil is characterized in the figures 1 and 2. Tolerance is defined here as the ability of a plant to grow in hydrocarbon contaminated soil and it does not necessarily mean the plant is fully healthy in these conditions.

The maize plants showed the best tolerance towards oil pollution. Thus, even on the background of 5 % of oil pollution the maize plants development was suppressed not significantly (Fig. 1). Oats and lupine plants are more affected than maize but their tolerance was rather good at the same high level pollution. Mustard plant had the poorest tolerance at all pollution levels (1, 3 and 5 % of oil products).

Among perennial plants, timoty plant showed the best tolerance at all levels of oil contamination (Fig. 2). Development of other plants at the same level pollution was suppressed more significantly.

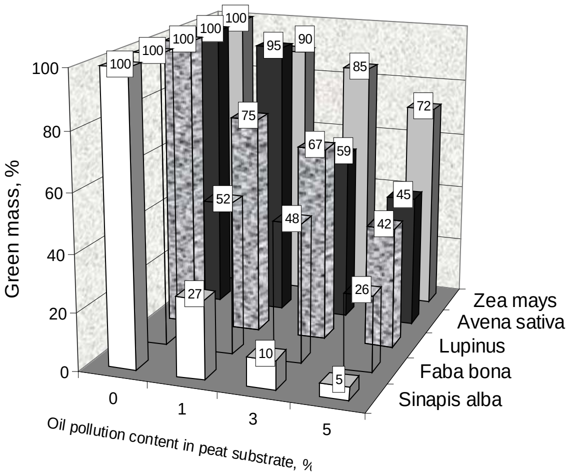


*Fig. 1.* **Tolerance of annual plants towards artificial contamination soil by oil products in terms of green mass of plant overground part (relative % on control plants)**

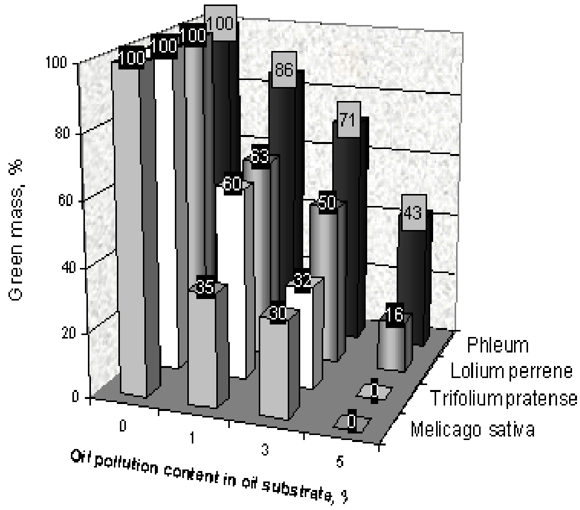


*Fig. 2.* **Tolerance of perennial plants towards artificial contamination soil by oil products in the first season of plant growth.**

Estimation of plants phytoremediation ability was performed on annual crops. Three annual crops (maize, oat and lupine) showed the highest tolerance to peat pollution by oil products were tested for phytoremediation of soil with technogenic pollution which was treated with association of oil oxidizing bacteria on the first stage of the integrated bioremediation technology.

Maize and oats developed well on the treated soil, which had residual concentration of the oil products of 2.6 and 4.5%. The growth of plants in variants with polluted soil differed from that for control (clean soil with humate) plants insignificantly.

The characteristics of underground parts of plants are presented in the table 2 and figure 3. Results obtained have shown that LSi applied as a soil amendment promotes development of maize plant root system stronger than potassium humate.

*Table 2.*

**Characteristics of underground parts of 4 weeks old maize plants grown on treated soil (residual oil content 4.5%) in the presence of growth activators**

| Soil sample | Root dry mass, mg | Average root length, cm | Average root diameter, mm | Root volume, $cm^3$ |
|---|---|---|---|---|
| Control soil | 37.3 | 174.7 | 0.40 | 0.22 |
| TS with addition of LSi | 77.1 | 242.9 | 0.48 | 0.44 |
| TS with addition of potassium humate | 53.4 | 196.3 | 0.49 | 0.38 |

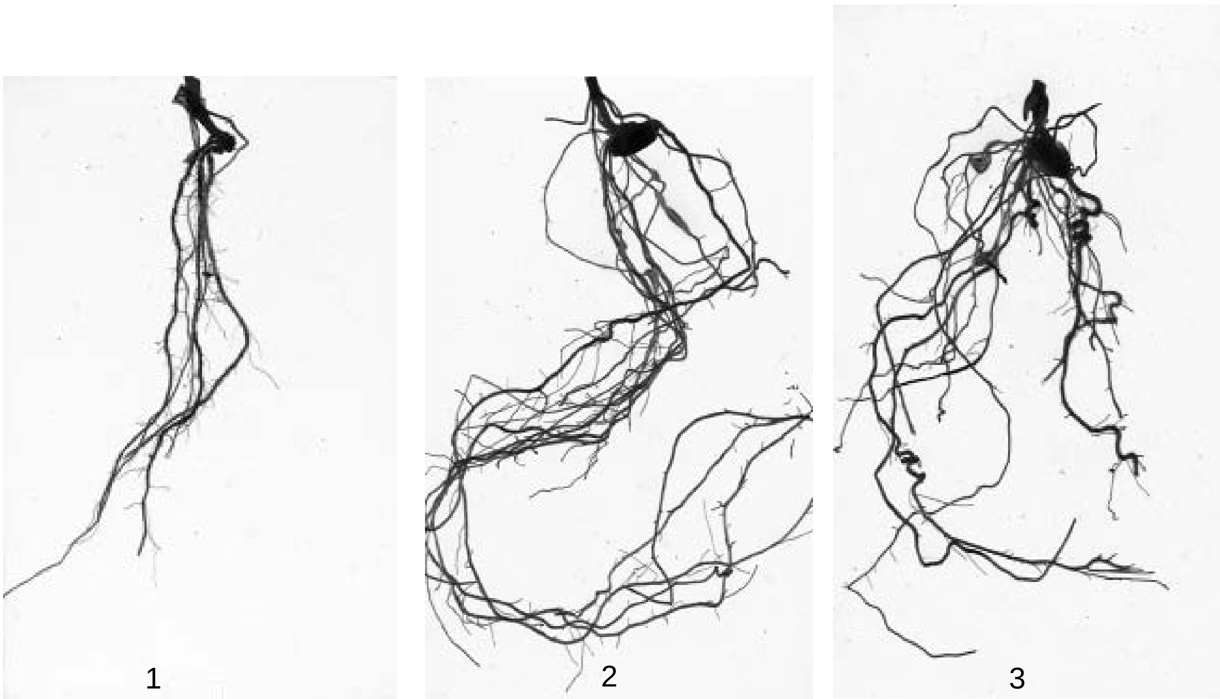


*Fig. 3*. **WinRhizo images of 4 weeks old maize roots:**
1 – Control plant was grown on clean black soil with addition of potassium humate; 2 – the plant was grown on TS (residual oil products content 4.5%) with addition of LSi; 3 - the plant was grown on TS (residual oil products content 4.5%) with addition of potassium humate

Intensive development of maize root system grown on soil treated by associations of oil oxidizing bacteria are in good conformity with the results of analysis of oil products content in planted soil before and after vegetation (Table 3 and 4).

*Table 3.*

**Influence of plants vegetation on oil products content in polluted soil treated with oil oxidizing bacteria (TS) with initial oil concentration of 2.6 %. Duration of experiment 4 weeks**

| Soil sample | Average content of oil products in soil for different plants, % | | |
|---|---|---|---|
| | Maize | Oats | Lupine |
| Unplanted TS used for the experiment (0 weeks) | 2.6 ± 0.2 | | |
| Unplanted TS with addition of potassium humate (4 weeks) | 1.9 ± 0.05 | | |
| Planted TS with addition of potassium humate (4 weeks) | 1.2 ± 0.1 | 1.7 ± 0.1 | 1.2 ± 0.1 |
| Planted TS with addition of LSi (4 weeks) | 1.3 ± 0.1 | 1.0 ± 0.1 | 1.3 ± 0.1 |

*Table 4.*

**Influence of plants vegetation on oil products content in polluted soil treated with oil oxidizing bacteria (TS) with initial oil concentration of 4.5 %. Duration of experiment 4 weeks**

| Soil sample | Average content of oil products in soil, % for different plants | | |
|---|---|---|---|
| | Maize | Oats | Lupine |
| Unplanted TS used for the experiment (0 weeks) | 4.5 ± 0.4 | | |
| Unplanted TS with addition of potassium humate (4 weeks) | 4.0 ± 0.4 | | |
| Planted TS with addition of potassium humate (4 weeks) | 3.8 ± 0.3 | 4.0 ± 0.4 | 3.9 ± 0.4 |
| Planted TS with addition of LSi (4 weeks) | 3.1 ± 0.2 | 3.2 ± 0.3 | 3.8 ± 0.4 |

Vegetation of maize plants on the treated soil (oil products content of 4.5%) in the presence of LSi resulted in the statistically significant decrease in oil products content in comparison with initial unplanted soil and unplanted soil after its exposition for the same experiment duration. In the case of oil products content in soil of 2.6%, all plants grown in the presence of both activators show the statistically significant decreasing effects.

***The soil microbiota analysis*** was performed for unplanted and planted with maize TS samples (initial oil products content of 4.5%). Comparison of the total count of heterotrophic microorganisms showed that in the variants with maize, it varied for various media in the range of 3.1 x $10^7$ to 5.8 x $10^8$ cfu/g d.w.(Fig. 4). It attributed to the both, bulk and rhizospheric soil samples. The number of culturable Gram-negative bacteria, grown on EMB agar, was found to be very similar for maize rhizosphere and variants without vegetation and planted with maize bulk soil (Fig. 4).

The concentration of fungi also was rather similar in all tested samples and varied in the range 1.2 x $10^5$ ÷ 7.7 x $10^5$ cfu/g dw, however, in rhizospheric soil from the variant with LSi application it was significantly higher (1.4 x $10^7$ cfu/g d.w.) (Fig.4).

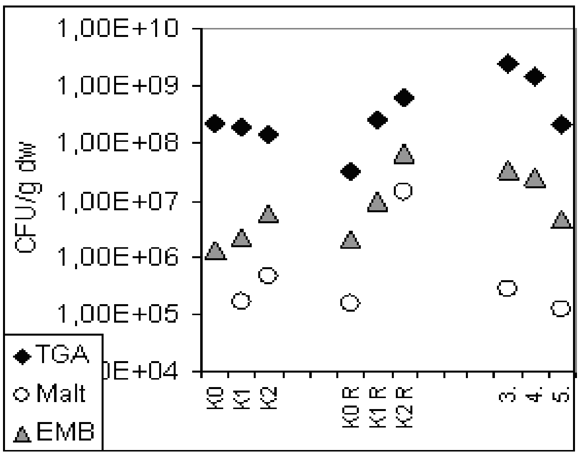


*Fig. 4.* **The number of colony forming units (CFU) in bulk and rhizosphere soils samples, determined using three different medium.**

TGA – Tryptone Glucose Agar for heterotrophic bacteria count, EMB – Eosine Methylene Blue – for culturable Gram-negative bacteria count, Malt agar – for fungi count

**K0 and K0 R** - bulk and rhizospheric soil, respectively, from variant, where maize plants were grown for 4 weeks on clean black soil with addition of potassium humate; **K1 and K1 R -** bulk and rhizospheric soil, respectively, from variant, where maize plants were grown for 4 weeks on TS (initial oil content of 4.5%) with addition of humate; **K2 and K2 R -** bulk and rhizospheric soil, respectively, from variant, where maize plants were grown for 4 weeks on TS (initial oil content of 4.5%) with addition of LSi; **3, 4** – unplanted TS (initial oil content of 4.5%) with addition of LSi and humate, respectively after 4 weeks outdoor exposition; **5 –** initial TS (oil content of 4.5%) used for the experiment.

***The measurement of growth intensity of microbial communities*** at the early stage, i.e. after 16h of cultivation, has revealed a significant difference in growth activity between bulk and rhizosphere microorganisms sampled from K1 and K2. Thus, rhizosphere microorganisms actively grew, using such substrates, as N-Acetyl-D-Glucosamine, B-Methyl-D-Glucoside (Fig. 5 - arrows). In turn, microorganisms from bulk soil did not exhibit growth activity during the first 16h of cultivation.

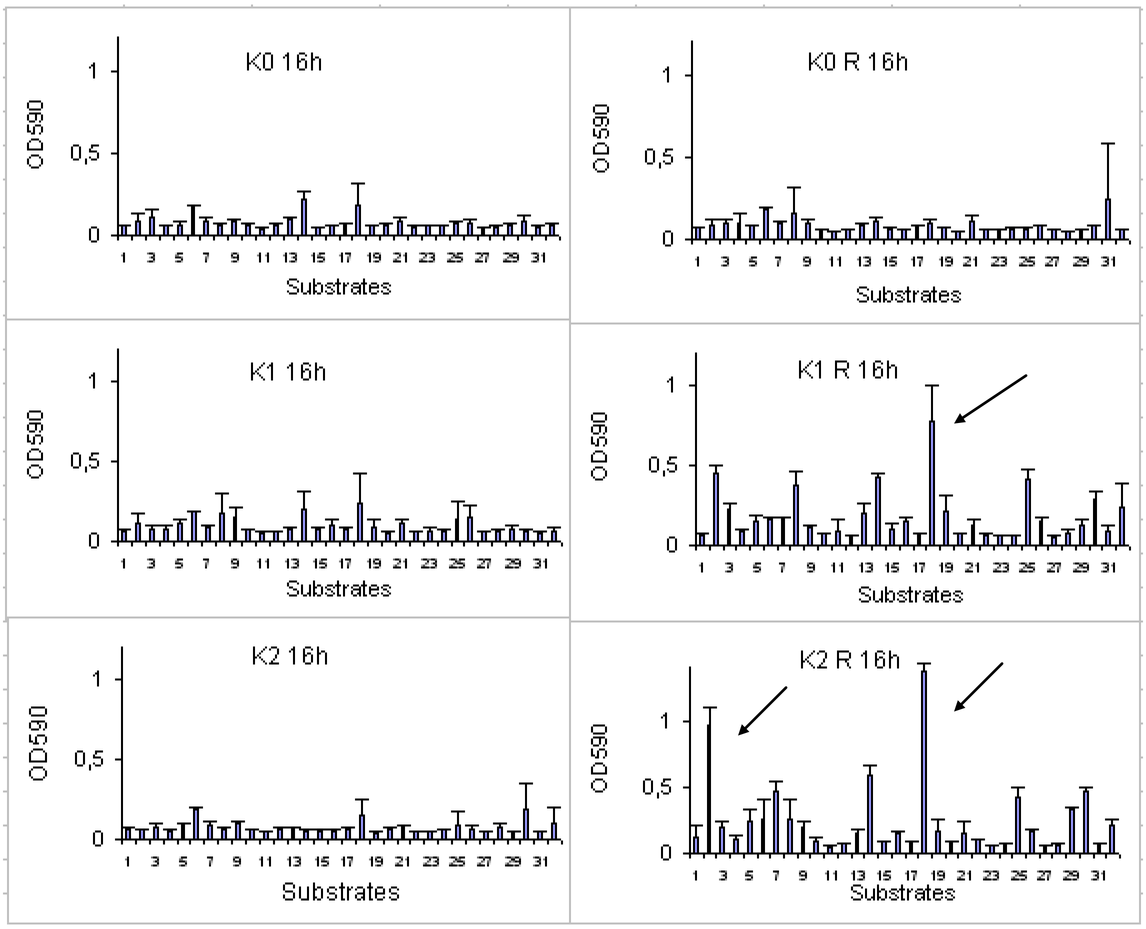


*Figure 5.* **16h growth of soil microorganisms on Biolog EcoPlate substrates. Value are means (n=3). Bars represent standard deviation. Description of carbon sources is shown in the subdivision 2.5). Samples description is shown in the legend to the Fig.4.**

These results are in a good agreement with the data on the number of total heterotrophic bacteria in plant rhizosphere in comparison with bulk soil (Fig. 4).

## Conclusions

- In two weeks model experiments rapidly developing annual plants revealed higher tolerance towards oil contamination than perennial plants
- The tested annual plants can be arranged according their tolerance towards oil contamination of the peat substrate as follows:
  maize > oats >> lupin > beans > mustard.
- Tested perennial plants can be systemized according their tolerance towards oil contamination of the peat substrate as follows:
  timothy > rye-grass > red clover > alfalfa
  Due to slow biomass accumulation by perennial plants, the conclusions about their applicability for phytoremediation should be done during at least two vegetation periods.
- The significant activization of microbiota in rhizospheric zone of plants grown on polluted soil in comparison with bulk soil was exemplified by vegetation of maize plants on soil treated with oil oxidizing bacteria (residual oil content of 4.5%).
- Maize vegetation decreased oil content in treated soil by 1.3-1.6 times during 4 weeks of vegetation.
- Application of LSi showed a stronger positive effect on phytoremediation in comparison with the traditional soil amendment – potassium humate.

## Acknowledgments

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## References

1. Schnorr, J.L., Licht, L.A. McCutcheon, S.C., Wolfe N.L. and Carriera, L.H. Phytoremediation of Organic and Nutrient Contaminants, Environ. Sci. Technol., 29, 1995, p. 318 – 323.
2. Aprill, W. and Sims, R.C. Evaluation of the use of prairie grasses for stimulating polycyclic aromatic hydrocarbon treatment in soil, Chemosphere, 20, 1990, p. 253 - 265.
3. Banks, M.K. Lee, E. Schwab, A.P. Fate of Benzo[a]pyrene in the Rhizosphere of *Festuca arundinacea*, Journal of Environmental Quality, 28,1999, 294 - 298.
4. Binet, P. J. Portal, M. and Leyval, C. Dissipation of 3-6-ring polycyclic aromatic hydrocarbons in the rhizosphere of ryegrass, Soil Biol. Biochem., 32, 2000, p. 2011 - 2017.
5. Liste, H.H and Alexander, M. Accumulation of phenanthrene and pyrene in rhizosphere soil, Chemosphere, 40(1) 2000, p. 11 - 14.
6. Reilley, K.A. Banks M.K., and Schwab, A.P. Dissipation of polycyclic aromatic hydrocarbons in the rhizosphere, J. Environ. Qual., 25, 1996, p. 212 - 219.
7. Miya, R.K. and Firestone, M.K. Phenanthrene-degrader community dynamics in rhizosphere soil from a common annual grass, J. Env. Qual., 29, 2000, p. 584 - 592.
8. Miya, R.K. and Firestone, M.K. Enhanced Phenanthrene Biodegradation in Soil by Slender Oat Root Exudates and Root Debris, J. Env. Qual. 30, 2001, p. 1911 – 1918.

# SELECTION OF MICROBES AND CONDITIONS THAT INDUCED BIO-CRACKING OF BRANCHED HYDROCARBON SQUALANE

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**Abstract.** *Biological oil hydrocarbons degradation is a complicated process, influenced by hydrocarbons properties, microorganisms and environmental conditions. The aim of this work was to select microbial strain, capable of degrading heavy branched hydrocarbons for further application in environment remediation and bio-cracking. Also, it was necessary to select optimal conditions (temperature, pH, concentration and etc.) for selected microbial strain degrading heavy branched hydrocarbons. Since crude oil and its products are mixtures of various hydrocarbons, at the first step of selection the ability of the strains to degrade individual hydrocarbons was investigated. Squalane was used as a test substrate. 10 microbial cultures belonging to genus Arthrobacter and obtained from culture collection of JSC "Biocentras" were used for the investigations. Gas chromatography analysis revealed that Arthrobacter sp NJ5 strain had the highest effectiveness (67%) in degradation of heavy branched oil hydrocarbon (Squalane) to shorter chain intermediates. So, Arthrobacter sp NJ5 could be applied in bio-cracking. For the application in industry, more detailed analyses are needed.*

**Keywords:** *Arthrobacter , bio-cracking, heavy branched hydrocarbon squalane.*

## Introduction

As oil industry continuously grows and consumption rates of fuels are getting higher, oil derived pollutants are blocking up the environment [1, 2]. Hydrocarbons, that are the main oil components (up to 98 %), consist of carbon and hydrogen. Oil hydrocarbons differ in their structure and molecular mass [3, 4]. According to their structure hydrocarbons are divided into several classes: alkanes, cycloalkanes, aromatic hydrocarbons and alkenes [3, 5, 6, 7]. A different class of polar hydrocarbons are the asphaltenes.

If an oil spill occurs, the volatile light fractions evaporate, while the higher molecular mass hydrocarbons can remain in the environment for a long period of time. Since heavy hydrocarbons have complex structures their degradation can be prolonged and ineffective. The most problematic are polyaromatic and branched oil hydrocarbons (that have more than 28 carbon atoms), tar and asphaltenes [8, 6]. These hydrocarbons under normal conditions are thick or hard, therefore, they are almost unavailable for oil-oxidizing microorganisms to degrade. Indeed, oil-oxidizing microbes, that can degrade heavy hydrocarbons, have been poorly investigated.

Biological oil hydrocarbon degradation is a complicated complex process influenced by the nature of hydrocarbons, environmental conditions and by microorganisms themselves [6]. Claude E. ZoBell was one of the first researches, who in 1946 reported, that most of the microorganisms found in nature could use hydrocarbons as the sole source of carbon and energy for their reproduction and growth [9]. The most of microorganisms that degrade hydrocarbons are bacteria [7]. For example, bacteria belonging to *Pseudomonas, Achromobacter, Arthrobacter, Micrococus, Nacardia, Vibrio, Acinetobacter, Bacillus, Corynebacterium, Flovabacterium* genus are known to degrade hydrocarbons [10, 11, 12].

Other reseachers have reported, that the amount of oil-oxidizing microbes becomes greater when their environment is polluted with hydrocarbons [13, 14, 15, 16].

Oil-oxidizing microorganism growth and biological degradation length depends on many environmental factors. The main factors determining the effectiveness of degradation are: the hydrocarbon mixture composition, physical properties, temperature, nutrients availability, pH, microorganisms [17, 6].

Heavy oil fraction degradation process, when short chain hydrocarbons are created, is called cracking. Over the last years an alternative to chemical and thermal cracking was introduced, that uses biological processes, called bio-cracking. A few laboratories have started experiments in 2009 with *Achromobacter, Leptospirillum, Pseudomonas, Sulfolobus* and *Thiobacillus sp* bacteria in order to use them in bio-cracking [18]. If researches were successful and bio-cracking technology was created, it would be ecological and effective in extracting lighter fractions of hydrocarbons from the useless heavy crude oil.
The aim of this work was to select microbes and evaluate conditions that induce bio-cracking of the branched hydrocarbon – squalane.

## Materials and methods

**Heavy branched hydrocarbons**. Heavy branched hydrocarbon squalane ($C_{30}H_{62}$) was selected as substrate. According to IUPAC nomenclature this compound is known as 2,6,10,15,19,23-hexamethyltetracosane.
**Microorganisms.** The following strains of hydrocarbon degrading bacteria belonging to *Arthrobacter* genus were used: sp N3, NJ1, NJ5, NJ9, NJ6, Pr82, Mž811, Kl1, M1 and M2.
**Media.** Nutrient agar (Oxoid, Basingstoke, UK) was used for plating microbial strains, and nutrient broth (Oxoid, Basingstoke, UK) was used for the subculture and preculture of the strains. To investigate the ability of the strains to degrade squalane, a mineral medium was used. The mineral medium had the following composition (g/l): 0.1 $(NH_4)_2HPO_4$; 0.2 $NH_4Cl$; 0.25 $K_2HPO_4$; 0.25 $KH_2PO_4$; 0.02 $MnSO_4$; 0.01 $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$; 0.01 $CaCl_2$ and 0.05 $(CH_3COO)_2Zn$.
**Biodegradation of squalane.** The ability of strains to degrade squalane was investigated in a mineral medium. Cultivation was carried out under sterile conditions in 250 ml flasks with 50 ml of mineral medium. Heavy branched hydrocarbon squalane ($C_{30}H_{62}$) was used as substrate, wich concentration was 0.2 g/l. After inoculation with 10% of volume blank flasks were incubated on a rotary shaker at 30 ºC and 200 rpm. The same cultivation conditions were applied for the testing of correlation between squalane degradation intensity, temperature, medium pH and squalane concentration.
Squalane degradation dependency on medium pH was investigated at pH values of: 4; 5; 6; 7; 8; 9.
Squalane degradation dependency on temperature was estimated at 5; 20; 30; 40; 45°C; and dependency on concentration was investigated with 0.025; 0.2; 1; 2; 3.5; 5 mg/ml of squalane. After 48 h incubation, the cultures were extracted with equal volume of tetrachlormethane for IR spectroscopy or hexane for GC..
**Infrared spectroscopy of squalane.** Samples were quantified by petroleum analyzer AN-1 at $1/\lambda=2930$ $cm^{-1}$ wave length. IR absorption is directly proportional to the concentration of hydrocarbons.
**GC analysis of squalane.** Samples were quantified by GC system (GC-2010 Plus, Shimadzu, Japan) equipped with a flame-ionization detector and MXT-1 capillary column (Siltek treated stainless steel). Operation conditions were as follows: nitrogen was used as the carrier gas; the injector temperature and detector temperature were 330 and 350°C, respectively; the column oven temperature was kept at 40°C for 1 min and then raised to 320°C at a rate of 10°C $min^{-1}$`.
**Biomass measurement.** Bacterial growth was measured as optical density (OD) at 600 nm (with spertrophotometer (UV 1601 Shimadzu).

## Results and discussion

The heavy branched hydrocarbon used for experiments – squalane, is a poorly degradable substrate. It is known since our previous research that Arthrobacter species degrades oil hydrocarbons, therefore we have choosen the following strains of *Arthrobacter sp* N3, NJ1, NJ5, NJ9, NJ6, PR82, MŽ811, KL1, M1 and M2 for testing degradation of heavy branched hydrocarbon squalane.

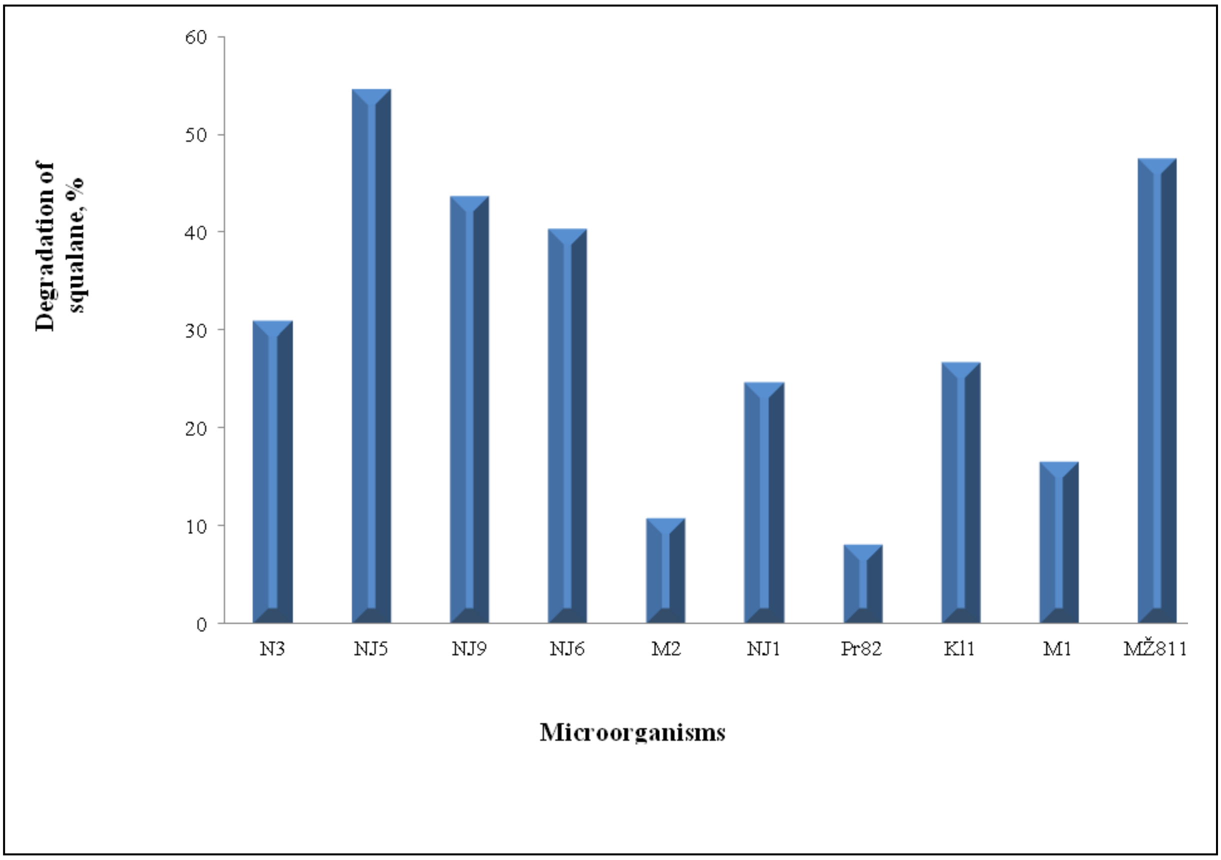


*Fig. 1* **The effect of hydrocarbon degrading bacteria on squalane biodegradation**

*Fig.1* results show that the greatest degradation of squalane occurred using strain *Arthrobacter sp* NJ5, which was chosen for the later experiments.
It is known, that bacterial biomass growth and substrate degradation effectiveness depends on the inoculum's age. Usually microorganisms are taken for biological degradation, when they are in their exponential growth phase, and when their reproductional processes are at peak [2]. Therefore, after selection of the best squalane degrading bacterial strain, correlation between inoculums' age and squalane degradation was investigated (*Fig. 2*).
Experiments were carried out in order to determine the influence of different cell phase (exponential and stationary) on squalane degradation levels.
Substrate degradation level depends on the inoculums growth time. The greatest squalane degradation (54.5 %) occured when substrate was inoculated with 18-hour old inoculum, which was in its stationary phase.
After that, the effect of initial medium pH, temperature and substrate concentration of squalane degradation with *Arthrobacter sp.* NJ5 strain was investigated.

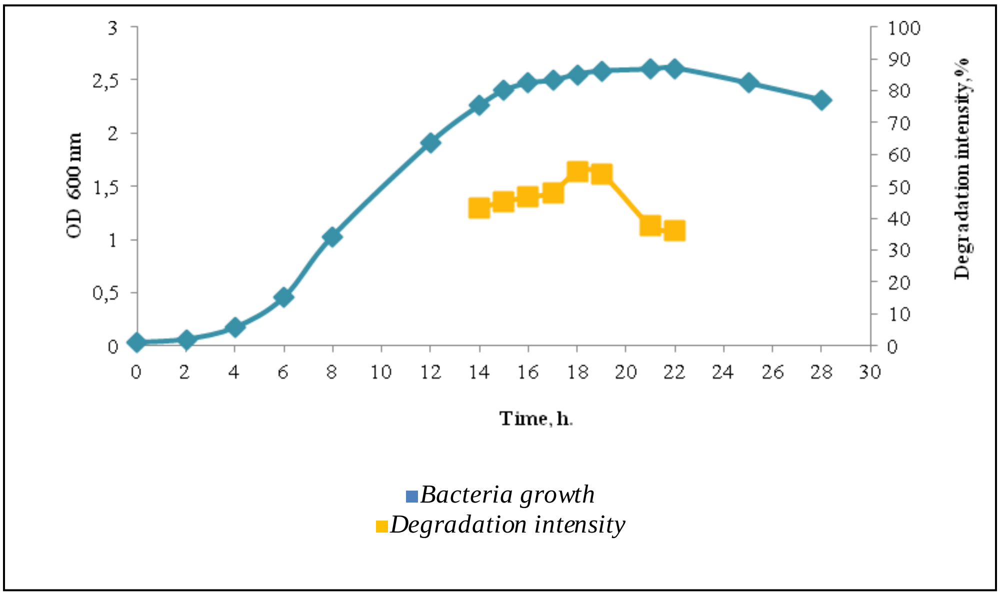


*Fig. 2* **NJ5 inoculums age influence on squalane degradation intensity**

During the selection of an optimal mediun pH, the maximum substrate degradation was achieved at pH range 6-7, while the more alkaline or acidic medium has prevented effective squalane degradation (*Fig. 3).*

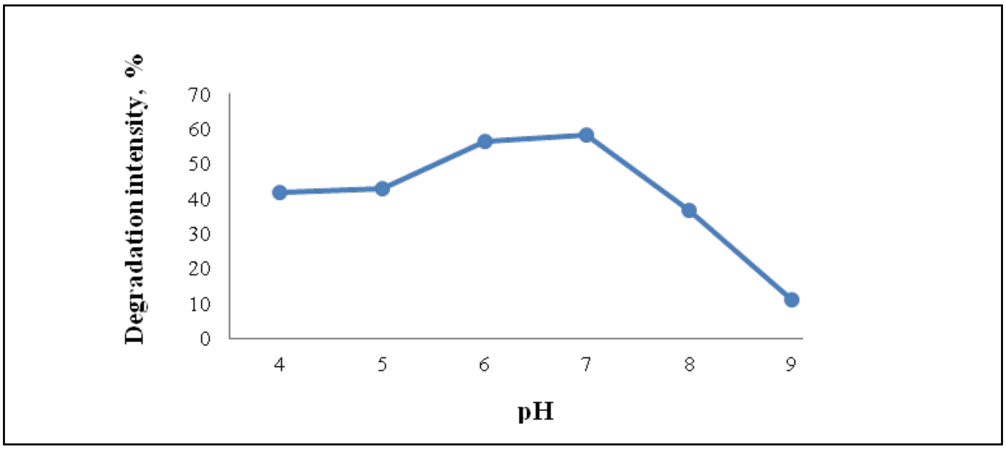


*Fig. 3* **Dependency of squalane degradation by *Arthrobacter sp* NJ5 strain on medium pH**

Microbiological hydrocarbon degradation process effectiveness is influenced by the substrate concentration as well, which can be inhibitory or even toxic to oil-oxidizing microorganisms [1, 5]. Therefore, the sp NJ5 strain oxidizing properties were tested against the hydrocarbon substrate. Results revealed that, when substrate concentration in medium was increased from 0.025 to 2.0 mg/ml, substrate degradation level has risen, but higher concentrations (up to 5.0 mg/ml) slowed down the intensity of degradation. The best substrate degradation was observed when the initial squalane concentration was at 2.0 mg/ml (*Fig. 4).*

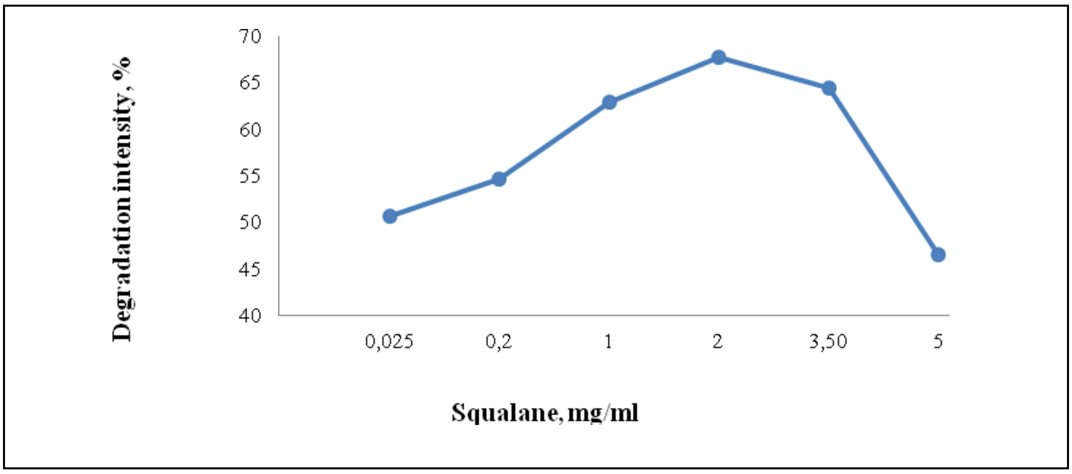


*Fig. 4* **Dependency of squalane degradation on squalane concentration**

After determining the dependency of degradation on squalane concentration, temperature regime was selected for the most efficient pollutant degradation. It was found that the rise in temperature from 5 to 35°C promotes degradation of substrate and it is highest at 35°C; however, degradation level drops at 35-45°C temperatures' interval (*Fig. 5).*

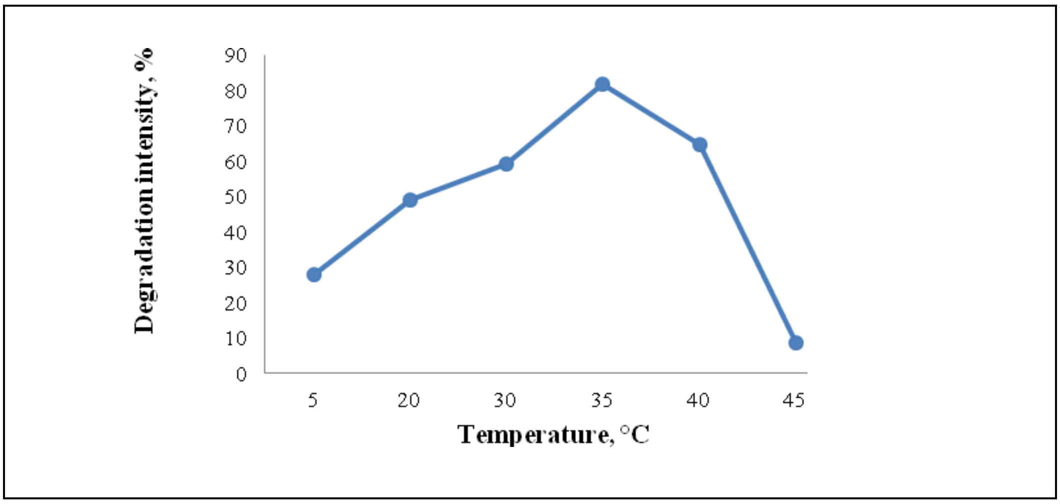


*Fig. 5* **Dependency of squalane degradation on temperature**

Gas chromatographic analysis was carried out to investigate quantitative and qualitative changes of squalane during biodegradation by selected strain sp NJ5. In biodegradation experiment initial concentration of squalane and inoculate in mineral medium was 1mg/ml and 10 %, respectively. Inoculated flasks were incubated at 35°C and 200 rpm for 48 h. Control test was performed at the same conditions, except the inoculate. Results of qualitative analysis are shown in (*Fig. 6).*
As it is seen from chromatograms, during incubation squalane was degraded into compounds with smaller molecular weight (1–7 peaks in *Fig.6*.b) in comparison to the control (*Fig. 6*a). After exposure to NJ5 strain only 0.33 mg/ml of squalane was found, i.e. 67 % of substrate was degraded (Table 1). Using IR spectroscopy for squalane determination, 62.8 % of substrate was found degraded. Both methods showed very similar results.

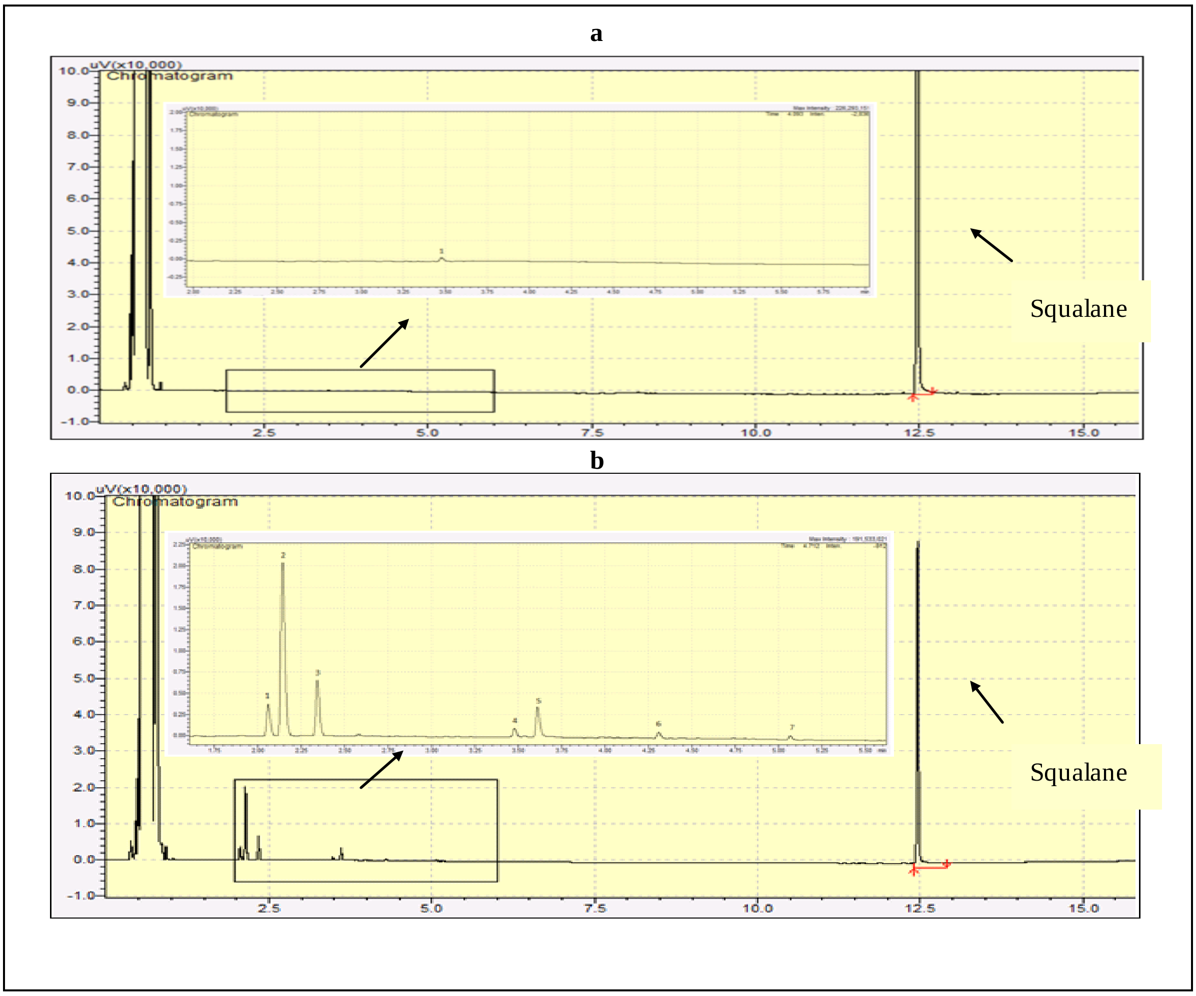


*Fig. 6* **Gas chromatograms of squalane (a – control test; b – after biodegradation by sp. NJ5 strain)**

*Table 1.*

**Results of squalane GC chromatograms before and after degradation**

| **Peak** | ***Peak retention time, s*** | ***Peak area*** | ***Peak height*** | ***Concentration*** |
|---|---|---|---|---|
| **Control** | | | | |
| Squalane | 12.470 | 670256.3 | 344508.2 | 1.03163 |
| **Sampler after degradation** | | | | |
| 1 | 2.058 | 5294.7 | 3626.3 | – |
| 2 | 2.141 | 33223.8 | 20118.5 | – |
| 3 | 2.342 | 9495.4 | 6488.8 | – |
| 4 | 3.478 | 1473.9 | 1031.9 | – |
| 5 | 3.611 | 5552.1 | 3540.7 | – |
| 6 | 4.308 | 1151.5 | 775.9 | – |
| 7 | 5.067 | 666.2 | 463.3 | – |
| 8 squalane | 12.464 | 210463.1 | 89248.8 | 0.33095 |

## Conclusions

10 strains of *Arthrobacter* were investigated, and one of them - sp NJ5 showed the best results in heavy branched hydrocarbon squalane degradation activity. The highest substrate degradation level (54.5 %) was reached using 18 hour old inoculate culture, which was in stationary growth phase. The best squalane degradation (58.3 %) was ocurred using *Atrhrobacter sp* NJ5 strain when the initial medium pH was 7.0. What is more, when the initial squalane concentration was 2.0 mg/ml, the highest substrate degradation level (67.7 %) was reached. Also it was determined, that the optimal squalane degradation temperature is 35ºC.

Therefore, the selected *Arthrobacter sp* NJ5 strain can be used for biological environment remediation from heavy oil hydrocarbon fractions. As the selected *Arthrobacter sp* NJ5 strain is effective in degrading the heavy branched hydrocarbons into smaller compounds (67 %), and can be used in bio-cracking. However, for the further employment in industry more detailed research is needed.

### References

1. Hasanuzzamana, M.; Ueno, A.; Ito, H.; Ito, Y.; Yamamoto, Y.; Yumotoc, I.; Okuyama, H. Degradation of long-chain n-alkanes (C36 and C40) by *Pseudomonas aeruginosa* strain WatG. *International Biodeterioration & Biodegradation*, 2007, nr. 59, p. 40-43.
2. Margesin, R.; Schinner, F. Biodegradation and bioremediation of hydrocarbons in extreme environments. *Appl Microbiol Biotechnol,* 2001, nr. 56, p. 650–663
3. Jankevičius, K.; Liužinas, R. Aplinkos biologinis valymas. Vilnius: *Apyaušris*, 2003. ISBN 9955-609-00-1
4. Wauquier, J.P. Petroleum refining. Paris: *Editions Technip,* 1994. ISBN-2-7108-0686-X.
5. Okoh, A.I. Biodegradation alternative in the cleanup of petroleum hydrocarbon pollutants. *Biotechnology and Molecular Biology Review*, 2006, nr. 2, p. 38-50. ISSN 1538-2273.
6. Singh, A.; Ward, O. P. *Biodegradation and bioremediation*. Canada: Springer, 2004. ISBN-3-540-21101-2.
7. Environmental Biotechnology. Hydrocarbon Degradation. http://www.molecular-plant-biotechnology.info/environmental-biotechnology/hydrocarbon-degradation.htm
8. Kato, T.; Haruki, M.; Imanaka, T.; Morikawa, M.; Kanaya, S. Isolation and characterization of long-chain-alkane degrading *Bacillus thermoleovorans* from deep subterranean petroleum reservoirs. *Journal of Bioscience and Bioengineering,* 2001, nr. 91, p. 64-70.
9. ZoBell, C. E. Action of microorganisms on hydrocarbons. *Bacteriol. Rev.*1946. 10:1-49.
10. Atlas, R.M. Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiological Reviews*, 1981, nr. 45, p. 180-209.
11. Ollivier, B.; Magot, M. 2005. *Petroleum microbiology.* American Society for Microbiology: ASM press.p. ISBN 1-55581-327-5.
12. Stroud, J.L.; Paton, G.I.; Semple, K.T. Microbe – aliphatic hydrocarbon interactions in soil: implications for biodegradation and bioremediation. *Journal of Applied Microbiology*, 2007, nr. 102, p. 1239–1253
13. Brock, T.D.; Madigan, M.T.; *Biology of Microorganisms (Sixth Edition)*. New Jersey: Prentice Hall, 1991. ISBN-0-13-083817-9
14. Roberts, E.R. 1995. Bioremediation of petroleum contaminated sites. CRC press.p. ISBN 0-87371-832-1.
15. Saadoun, I.; Munir, J.M.; Hameed, K.M.; Shawaqfah, M. Microbial populations of crude oil spill polluted soils at the Jordan – Iraq desert (The Badia region). *Brazilian Journal of Microbiology,* 2008, nr. 39, p. 453-456. ISSN 1517-8382.
16. Van Hamme, J.D.; Singh, A.; Ward, O.P. Recent advances in petroleum microbiology. *Microbiology and molecular biology reviews*, 2003, nr. 67, p. 503–549.
17. Montiel, C.; Quintero, R.; Aburto, J. Petroleum biotechnology: Technology trends for the muture. *African Journal of Biotechnology*, 2009, nr. 12, p. 2661. ISSN-1684–5315.
18. Chatterjee, S.; Chattopadhyay, P.; Subhasita, R.; Sukanta, K.S. Bioremediation: a tool for cleaning polluted environments. *Journal of Applied Biosciences*, 2008, nr. 11, p. 594–601.

# DEVELOPMENT OF MUNICIPAL WASTE MANAGEMENT

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***Abstract.*** *This paper is based on an empirical work done by author on a series of case studies such us document studies and analyzing the best practices examples. The objective of this research is to find out barriers to reach regional waste management plan demands in three municipalities: Salacgriva, Saulkrasti and Ikskile. Author gives proposal with some recommendations for development of municipal waste management as well.*
*There are several views and attitudes of local stakeholders such us municipality, waste producers, waste collectors and mediators on how to manage collection and transportation of solid waste in practice as well as on public involvement in the process.. Passivity of stakeholders to realize theirs needs and requirements mainly depend on the limited human and financial resources, but often political will, skepticism or lack of knowledge. A lot of problems could be solved faster and easier, if there existed better communication and collaboration among local stakeholders.*

**Keywords:** *municipality, sustainable waste management, stakeholder's collaboration.*

## Introduction

Recycling of the waste is being seen as a solution of European Commission to Member States on how to solve problems with the significant increase waste amounts. This approach is preferred mainly, because of the huge costs involved in waste landfill as well as their irreclaimable impacts to environment and the fear of society about unknown impacts on people's health. Essential issues are also the reduction of human consumption and protection of natural resources by reusing and recycling of waste and using it as raw material. Reusing and recycling activities have an important role in the developed countries, because it creates large part of their work place share, reduce price of raw materials and necessity to import them and it is an effective way to realize environmental protection (Marion, 2002).
European Union Landfill Directive sets targets for all Member States on reduction of waste arising and development of waste recycling and recovery as well encourages use of recycling materials and renewable energy, to meet nature protection requirement and to prevent wasteful use of land (Directive 1999/31/EK).
At an average from EU27 Member States only 40% of municipal waste are recycled or composted in 2008 and there are big differences among each state's environmental performance in practice. For example, in Germany and Netherlands municipal waste was landfilled only 1 % from total amount; Sweden and Austria - 3% to compare with Estonia - 75%, Latvia -93% and Lithuania- 96%. In its turn, in Bulgaria activities of recycling taken as whole was very insignificant and almost all collected municipal waste was landfilled (CEWEP, 2010 (11)).
The amount of municipal waste generated and landfilled in kg per person varies significantly across Member States also. This variation is mainly due to different consumption behavior. If we compare Structural Indicator in previous mentioned countries then municipal waste generated and landfilled (kg per capita) are the following: Germany 587 kg per capita and 2 kg per capita; Netherlands - 616 and 4; Sweden - 485 and 7, Austria - 591 and 4, Estonia - 346 and 214, Latvia - 333 and 307, Lithuania - 360 and 326, Bulgaria - 468 and 450 (Eurostat 2010). Of course, such high public activity and participation in waste sorting and recycling can be achieved also with strong waste management policy and high landfill taxes, for example, Sweden has landfill taxes 110-160 euro per tonne, Austria 60-130, Netherlands from

16, 79 for non- hazardous up to 107.79 for hazardous waste, Lithuania 14, 5 (CEWEP, 2010 (9)) and Latvia 25 -35 euro per tonne (Landfills: Daibe, Getliņi, Kivites webpages).
Partly thanks to impact of day's economical situation, which has contributed to reduction of the average of household consumption expenditure (total in money and in kind) of inhabitants of Latvia (average per household member monthly, LVL) from 232.06 LVL in 2008 to 195.27 LVL in 2009 (CSP) as well as historical traditions of composting the biological waste in their private territory, inhabitants of Latvia are often making so comparably low amount of produced waste per one person. However this indicator and inhabitant's density of Latvia in average 34.6 persons per $km^2$ in 2010 (CSP) shows, that in Latvia it will be very hard to realize energy recovery from municipal waste or it will be very expensive for local inhabitants, therefore the only cost - effective way how to reduce waste in landfill is recycling, reuse and composting.
The main waste management regulations applying setting waste management priorities in Latvia are Directive 2008/98/EC European Parliament and of the Council (19.11.2008) on waste and repealing certain Directives, National Waste management plan from 2006 to 2012 (29.12.2005) and Law On Waste Management (18.11.2010), which are setting major principles of sustainable waste management as follows 1) to minimize waste generation; 2) to maximize waste recycling and reuse; 3) to ensure the safe and environmentally sound disposal of waste.
The formulation of goals and priorities, determination of roles and jurisdiction, and the legal and regulatory policy framework determinate basely demands for waste management system and responsibility of municipality, however it do not give direct advice, how to achieve effective waste management, sustainable development and successful collaboration among stakeholders in local municipality depending on existing situation.
In practice there exist different views and attitudes of stakeholders on how to organize waste management. There are mainly two groups: passive, who have been felling comfortable in the existing situation and they do not see any need for change and formally waste management is provided; and active, who have been involved in public education on development of sustainable waste management in line with demands and rules of European Union and National level.

## Materials and methods

This research has focused on problems of small municipality waste management with number of 10 000 inhabitants. After the new administrative-territorial reform in 2008 in Latvia there are at least 70 municipalities of this size (www.raplm.gov.lv). The empirical work was made in three small municipalities: Salacgriva, Saulkrasti and Ikskile and major attention was paid to sustainable waste management implementation.
This paper included brief summary of following studies:

1) Individual case study research (Teibe, 2010 b), "Waste management research for Ikskile municipality, 2010", based on document studies, 16 interviews, 205 responds to questionnaire and individual observations;
2) Case studies (Teibe, 2010 d; 2010 c), Teibe I., Ozola G., Sturma A., Jakusenoka S. "Climate change adaptation policy planning guidelines for coastal municipality: Salacgrivas municipality. Nature environment sector" (2010 April-June), based on document studies, 18 interviews, 16 responds to questionnaire, individual and group observations; and Teibe I., Kirsona I., Ozola G. "Environmental communication action program guidelines for coastal municipality: Saulkrastu municipality. Household management sector" (2010 October -2011 January), based on document studies, 21 interviews, 93 responds to questionnaire, individual and group observations;

3) Individual case study (Teibe, 2010 a) "Environmental communication in waste management: inter – municipal partnership case", North Vidzeme Waste Management organization (ZAAO) - best practice example.

Waste management research focused on accessibility and effectiveness of provided services and infrastructure, inhabitant's willingness to participate and local shareholders (such municipal authorities, waste collector and transporter, waste producer and mediator) estimation of activities (Fig.1).

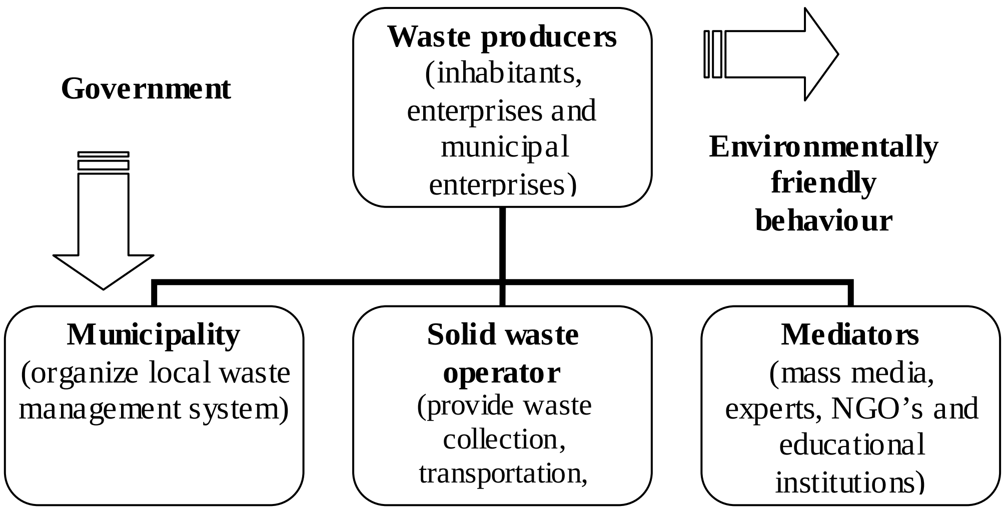


*Fig.1.* **Local stakeholders of waste management**

**Results**

Saulkrasti and Salacgriva are coastal municipalities. After administrative-territorial division municipality of Salacgriva consist to North Vidzeme's region, but municipalities of Saulkrasti and Ikskile belong to Pieriga's region.

Characterization of municipalities territorial in 2010:

1) Municipality of Salacgriva: total population 9522, total land area 63,6 km², population density 15 pers per km², defined 1 territorial area, where has been operating 1 solid waste operator;
2) Municipality of Ikskile: total population 9125, total land area 132,1 km², population density 69 pers per km², also defined 1 territorial area, where have been operating 3 solid waste operators in the full market competition;
3) Municipality of Saulkrasti: total population 6243, total land area 47,7km², population density 131 pers per km², in common with municipality of Ikskile, here defined 1 territorial area where have been operating 3 solid waste operators. One of the specific problems of municipality of Saulkrasti is that the amount of population increases from 3 till 5 times during the season. (May-October) (Information from municipality).

The process of waste management in these municipalities is being determined by local governments and local rules on waste management. According to these rules in whole territory there is determined order of waste management, administrative area division of solid waste management zones, requirements for waste collection, transport, handling and storage, as well as the procedures of the payments for the services.

The rule is binding for all persons in the administrative territory, who are performing regulated activities according to the conditions. The administrative responsibility in case violations also mentioned here.

Municipality of Salacgriva is participating in ZAAO. The main purpose to establish the pilot project ZAAO in the Northern part of Vidzeme of Latvia in 1998, was to remove the existing 104 legal and illegal dumpsites which were non – conformed with European Union and

National requirements as well as create a new, modern municipal solid waste landfill and introduce waste management system, which would cover Cesis, Limbazu, Valka and Valmiera districts. This territory was chosen mainly because here is situated National Park Gauja and the Biosphere Reserve of Northern Vidzeme, which require special environmental protection.
Today ZAAO is a largest full services waste operator in North Vidzeme region and the board is operated by 22 municipalities: Valmiera city and 21 counties, including municipality of Salacgriva.
When organisation ZAAO was established, every municipality participated with local investments in the organization share capital and entrusted centralize to ZAAO make and develop to local waste management system as well as provide educational activities. Today ZAAO can be considered as best practice in waste management in Latvia.
In the Pieriga's region there does not exist organization like ZAAO, therefore municipalities of Ikskile and Saulkrasti are organizing waste management depending on available human and financial resources, their understanding on how the wast management process should be organized according to National regulation on waste management.

***Municipalities***
In all municipalities, which have participated in empirical work, they have their own enterprise, which organizes municipal solid waste collection from all enterprises and households of municipality as well as public territories like parks, streets, graveyards etc. This company also must sign a contract with solid waste operator, which wants to provide collection and transporting services in this territory in accordance with law regulating public purchases and legislative demands and criteria from the municipal authority.
Every private household or waste producer according to local waste management regulation has to sign contract directly with solid waste operator ZAAO, in the municipality of Salacgriva, however, in the municipalities of Saulkrasti and Ikskile waste producers can choose the company among 3 operators, which will provide waste collection. In practice here even in one territory, street or private apartments house, municipal waste collection are providing all 3 operators. Here, the selection of operator is based on principle of full market competition: better price for the service, comfort of service application, offered services or company image.
In order to organize unsorted and recycled solid waste collection and transportation in the whole territory, municipality takes for the basis the knowledge about average amount of waste, which gives only a rough idea of waste generation, composition and types (LASA, 2007). But in practice no one of the three municipalities was able to actively monitor the amount of waste, therefore it was forcible to receive this information only from waste operators.
If to describe a total amount of collected waste in municipalities, (Fig.2), even though municipalities of Salacgriva and Ikskile are territories with quite similar number of inhabitants, respectively 9522 and 9125, here is significant difference between collected waste amounts. One of the reasons is population density (look before mentioned features of municipalities), in municipality of Salacgriva more pronounced private houses and separate located households, but in municipality of Ikskile a large part of population is living in apartment houses.
Second reason is that produced waste amount was determined also by average income level in the family, as municipality of Ikskile belongs to Pieriga region, where according to data of Central Statistical Bureau in 2009 "Consumption expenditure average per household member per month" was higher 230.57 LVL per person than in Vidzeme's region - 182,62 LVL per person (CSP).

And the third one, the collected waste amount is directly affected by the applied accounting method, as vehicles of solid waste operator of municipality of Salacgriva are weighted before landfill the data is more precise if compared to the municipality of Ikskile where largest part of the collected waste is calculated from contracts and the allowable mistake is aproximally +/- 20 % (waste operator information).

***Solid waste operators***

Each operator's tariffs of solid waste collecting and transporting by region are approved at the Public Utilities Commission, which is an independent state institution responsible for regulation of energy, telecommunications, post and railway sectors in accordance with the law On Regulators of Public Utilities and the corresponding normative acts in the regulated sectors. This information is open to public and review at website: http://www.sprk.gov.lv. Depending from each administrative territory distance from landfill Daibe, where are disposed all collected municipal solid waste in North Vidzeme, ZAAO have a variable transport rates confirmed by each municipality.

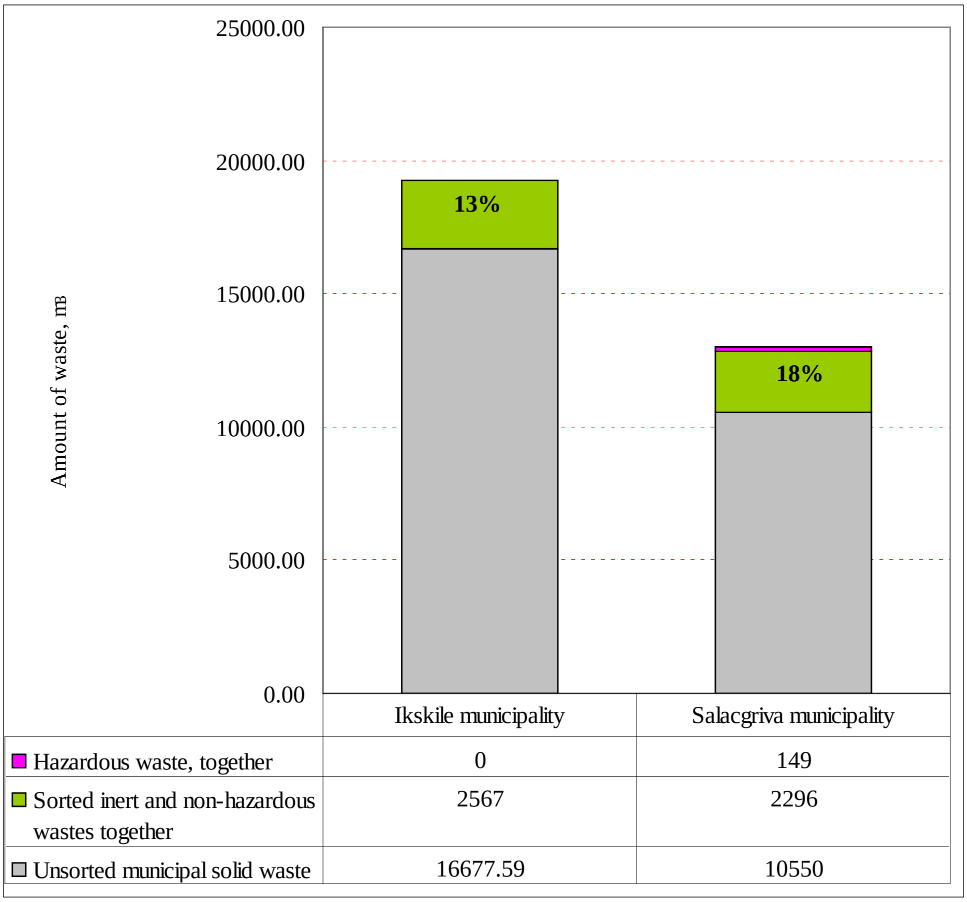


*Fig.2.* **Collected municipal waste in total: Ikskile and Salacgriva municipalities in 2009**

The municipality in cooperation with waste operator is organizing separate collection of municipal waste, including hazardous waste of households, in whole administrative territory under the National Waste Management Plan and Regional Plans (Law on Waste Management, 18.11.2010).

During the reporting period in 2009 in the municipality of Salacgriva were available 10 on street recycling EKO points for PET packaging, glass and paper in the different residential areas and 1 recycling EKO area for 12 different fractions in town according to tasks

mentioned by ZAAO (North Vidzeme Regional Waste Management Plan from 2006 till 2013). Each household can additionally purchase EKO bag for PET packaging, paper, metal and PE plastic sorting at their own territory and once per month to deliver over ZAAO or deliver by self to recycling EKO point or EKO area.
But from municipality of Ikskile part, there are 6 recycling points for PET packaging, glass and paper in mostly located in the town, multi apartment houses courtyards. For the present waste recycling area are still being arranged, therefore residents can bring their own vehicles to the other cities recycling areas if case the waste fraction can not pass recycling points. This is observed also on Figure 2 in total amount of collected municipal waste, such as lack of information about hazardous waste of households in municipality of Ikskile.
Municipal waste recycling is very weakly developed in municipality of Saulkrasti, mostly because here was very poor involvement in local waste management of cottager in the horticultural cooperatives. Due to irresponsible behavior of cottagers in the recycling points were receiving very poor quality materials, therefore waste sorting was suspended. However some pilot projects municipality had made again in the last season, such as recycling points for PET packaging in seacoast and had got a very good result.
The proportion of local municipalities of Ikskile and Salacgriva collected waste being recycled, composted or reused is shown in the 3rd Figure.

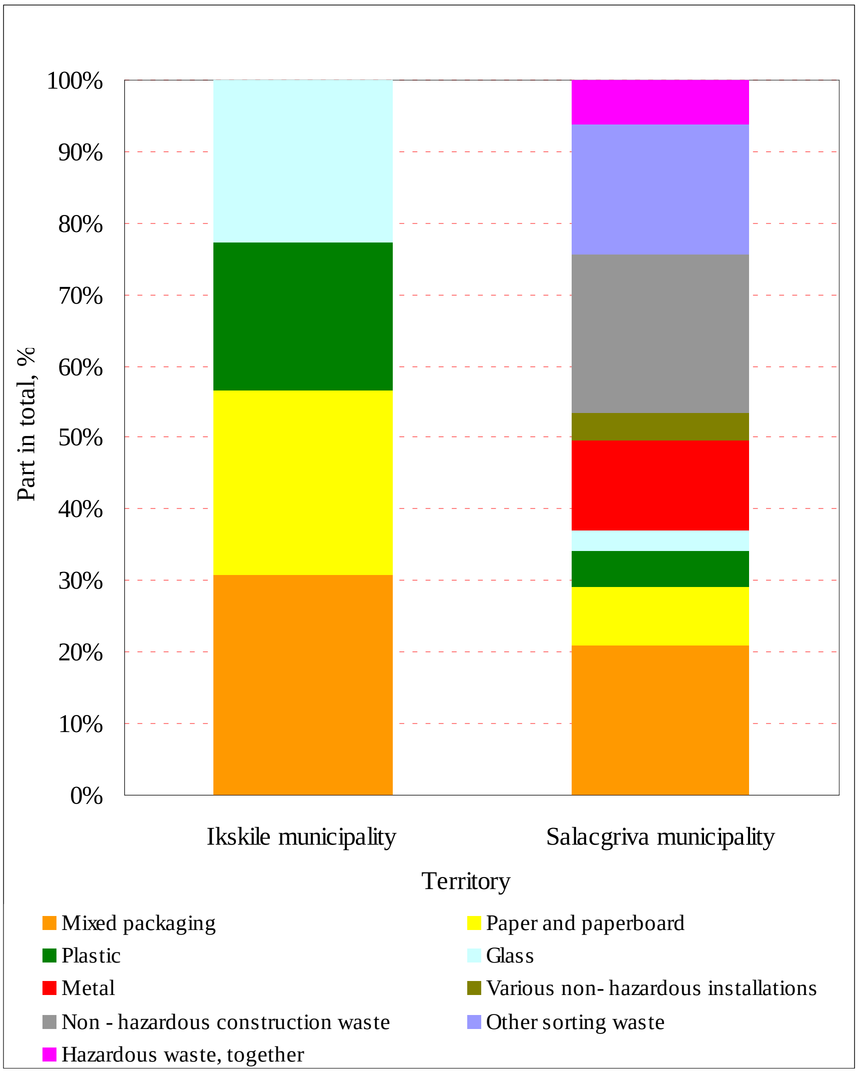


*Fig.3.* **Separate collected waste by fraction: Ikskile and Salacgriva municipalities in 2009**

These data evidence that the more possibilities of recycling are provided in the territory, the better information can be collected about municipal produced waste composition and quantity.

***Waste producers***

Within Empirical work in the municipalities of Ikskile and Saulkrasti was carried out sociological research to find out, what kind of waste management services inhabitants more often are using, data shown in Figure 4.

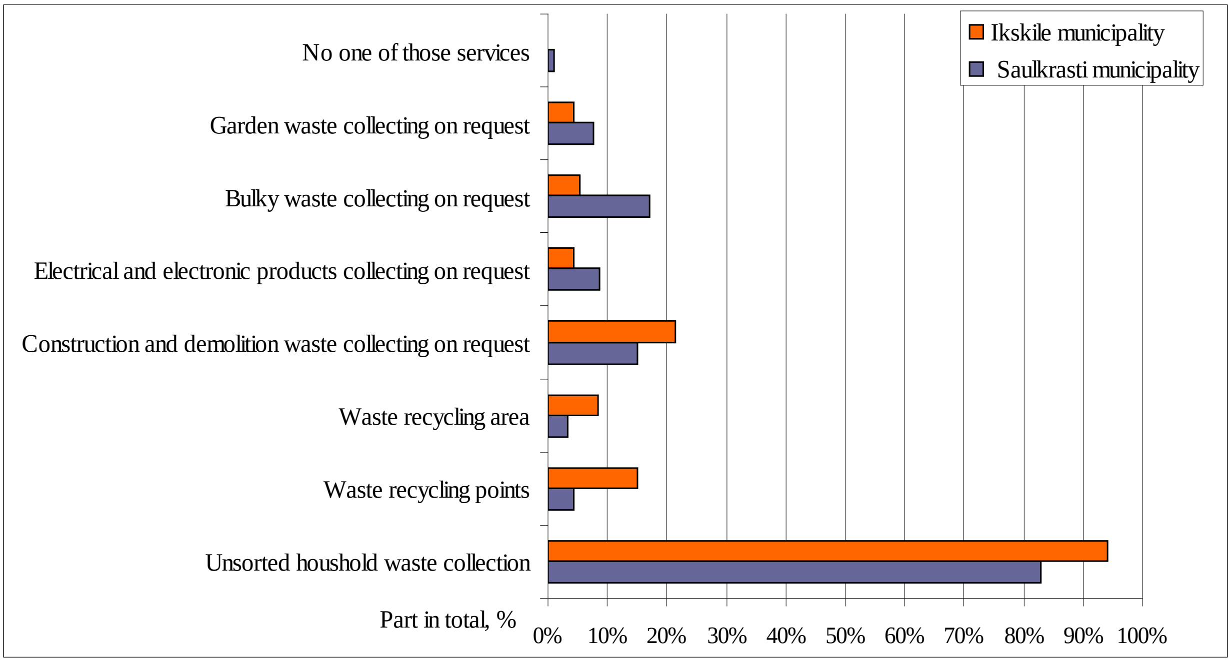


*Fig.4.* **Public partnership: Ikskile and Saulkrasti municipalities**

Respondents were indicated that the most commonly requested is the unsorted household solid waste collecting. Results indicate that there is very weak public participation in municipal waste recycling. From all respondents only 15 % from Ikskile and 5% from Saulkrasti are using local recycling points, much less than 8 % are ready to deliver the sorted waste to recycling areas in the other cities.

Residents in both municipalities have been more active in delivering of bulky and construction waste collecting on request, however green garden waste separation of the total waste stream has not gained popularity.

According to the results of sociological research the inhabitants gave an explication, why they have lack of motivation, mostly because they have not enough information about possibility and places where to bring recycling waste, quite often these containers had not been collected regularly or had been thrown together in to the same vehicle – sometimes together with unsorted municipal waste.

According to European Union Landfill Directive 1999/31/EK all Member States have to organize activities to reduce methane emissions from landfills due to the biological degradation of the many types of organic materials. Member States must put an effort to reduce greenhouse gasses, encouraging projects that turn the landfill gases into electricity as well as regularly controlling these emissions.

Therefore each country and local municipality should take measures and promote separate collection of biodegradable waste, such us sorting, recovery and recycling, but meanwhile local municipalities are not following these demands. In the best case residents have the possibility to deliver garden waste (leaves, grass cuttings and fruit) into composting area of municipality or hand over to waste operator like ZAAO by less tariff such unsorted waste. In their turn the collection and transportation of the kitchen waste from households and public catering places was very hardly assured in the visited municipalities.

***Mediators***

Environmental communication and education in the waste management sector is mainly provided by two companies: "Latvijas Zalais punkts" since 2000 and "Zala josta" since 2002. These are producers' responsibility systems in Latvia that deals with the implementation and coordination of the system for managing packaging waste and disposable tableware and cutlery, as well as waste electric and electronic equipment and goods harmful to the environment. Since 2005 there is established waste management coordinator "Zalais centrs" as well, but this company is responsibility only for environmentally harmful products disposal.

Companies "Latvijas Zalais punkts" and "Zala josta" have their own educational programs for public, for example "Latvijas Zalais punkts" has the "Green Dot School" program with an objective to increase the knowledge on ecological issues and to strengthen the sense of responsibility for the environment, promoting environmentally friendly life-style. This program has various educational framework and methods for children, schoolchild and students and any educational institution can participate here, only themselves must take the initiative to apply.

Basically local solid waste operators, which are dealing with waste collecting in the municipalities of Ikskile and Saulkrasti are quite passive educators, mainly due to competition. No one is ready to invest money and to provide service awareness or to realize some educational activities. Environmental communication from these companies is more like than campaign for collecting exactly one type of waste.

Within its capabilities in local municipalities are running formal and informal educators and institutions. For example, in municipality of Saulkrasti very active children are involved in Nature club in the primary school of Zvejniekciems, also in the local library there is available a small collection of literature on environmental issues, occasionally environment-related activities were also provided in the secondary school of Ikskile. Mainly with environmental education in these municipalities are operating enthusiasts or non-governmental organizations that care about the environment. However activities are not coordinated and have weak collaboration with other local interest groups and often with limited budget. But during the research there have been noted also the positive trends - more and more environmental projects are financed by local municipality.

The best practice example in the waste management sector in Latvia is ZAAO, which has done a significant investment in public involvement in environmental education since 2001. As an effective environmental communication instrument in ZAAO they are successfully using all four components: dissemination of environmental information, environmental education, public participation and collaboration and environmental friendly behavior (Ernsteins 2003).

In order to realize modern and environmentally friendly waste management systems and minimize the possible contamination into the environment, ZAAO is collaborating with four defined target groups: municipality, customers, society and educational institutions. Keeping in mind the defined target groups" needs, requirement and specific characteristic, environmental education and awareness activities, content and methods are developed. According to this model ZAAO is organizing environmental education in the waste management sector all over the North part of Vidzeme. All municipalities of this region are encouraged to participate and support ZAAO organized activities, which focused on public education, information and participation in protection of environment.

## Discussion

Results indicate that the responsible local authorities are not very interested to get deep knowledge into the environmental field, including waste management, although their understanding is necessary to build sustainable development of the municipality. Municipalities had inadequate information about real estates and inhabitants and have not monitored the involvement of local citizens in the waste management system. And basically it is not possible to assess how effectively system is working and manage it. The municipalities of Ikskile and Saulkrasti had not estimated types and quantities of municipal waste according to their producers, therefore it is hard to find out what kind of investments would be needed in order to attract funding for development of the system.
Special attention should be paid to involvement of inhabitants, meaning regular monitoring and administrative controlling, including work with the debtors. Result shows that these issues have not been paid enough attention by local municipalities, leaving the problem solving to waste operators.
One of the indicators that local government should follow to is average generated waste per capita in urban and rural areas. But in practice in such small municipalities have in prevalent only small and medium sizes enterprises, therefore the waste operators have not kept separate records on the amount of waste collected from residents and businesses. However, the random local government would to carry out such inspections, focusing on apartment houses where waste containers are kept in backyards and have publicly available and households where waste collected less than once a month or choose other criteria of inspection.
Such a common position and situation in regions are preventing implementation of regional waste management plan. In the future, these municipalities might be faced with a very expensive unsorted waste disposal costs, since the nearest landfill cells will be quickly filled and the waste disposal options will be limited or will be located quite far from territory. Following such a scenario will increase protest of inhabitants against the high waste collecting tariff and after that will follow illegal dumps in the environment.

## Summary

If the waste management laws, plans and regulations were introduced in municipalities from top to bottom mostly without awareness of each region's waste management situation and problems, except the North Vidzeme region, then in current situation the initiative should come from municipalities, from bottom to top, specifying the investments that would be needed for waste management development in the territory.
The first step in order to develop in municipalities for currently formally on-going waste management is to elaborate local framework of concept and plans. It being understood that the municipality has identified the internal and external resources and the criteria which are necessary for realizing the waste management in accordance with an order priority and as near as possible to waste producers; municipality has sufficient and timely qualitative and quantitative information about waste types, quantities and recycling in the whole territory and the potential of public participation and involvement; municipality fully controls and manages waste collecting and transporting processes within its territory and exercises continuous development of opportunities.

## Acknowledgment

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**References**


1. Atkritumu apsaimniekošanas likums. LR Saeimas pieņemtais likums, 18.11.2010// laikraksts „Latvijas Vēstnesis", Nr.183 (4375), 17.11.2010.) [stājas spēkā 18.11.2001.] Available at http://www.likumi.lv
2. Audit Scotland "Sustainable waste management", ISBN 978 1 905634 75 0, AGS /2007/7, September 2007, 45 p. Available at http:// www.audit - scotland.gov.uk (28.01.2011)
3. Centrālā statistikas pārvalde (CSP) /Central Statistical Bureau, Available at http://data.csb.gov.lv (04.02.2011)
4. Confederation of European Waste - to- Energy Plants (CEWEP), Recycling and Waste-to- Energy in combination for sustainable waste management, report of November, 2010. Available at http://www.cewep.eu/information/policy/m_554 (15.02.2011)
5. Confederation of European Waste - to- Energy Plants (CEWEP), Lanfill taxes and bans, report F September, 2010. Available at http://www.cewep.eu/information/data/landfill/index.html (15.02.2011)
6. Eiropas Parlamenta un Padomes Direktīva 2006/12/EK ( 2006. gada 5. aprīlis), par atkritumiem //Oficiālais Vēstnesis-2006.- Nr. 114 , 27.apr.- 9 – 21.lpp.
   Available at: http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32006L0012:LV:HTML (07.02.2011)
7. Ernsteins R. Environmental communication. Leonardo da Vinci Community Vocational Training Action Programme, Institute for Environmental Science and Management, University of Latvia. 2003.,96.p.
8. Eurostat, Municipal Waste Landfilled, kg per capital (Structural Indicator). Available at http://epp.eurostat.ec.europa.eu/portal/page/portal/waste/data/wastemanagement/landfill (03.02.2011)
9. Latvijas Atkritumu saimniecības asociācija, „Atkritumu saimniecība", Rīga, 2007. 132. lpp.
10. Marion S., Coggins C, Stovin V., Life cycle assesment and waste management, Volume 4, Istanbul, 2002 (2317 -2324 p.)
11. Direktīva 1999/31/EK (1999. gada 26. aprīlis) par atkritumu poligoniem. Available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31999L0031:LV:HTML (15.01.2011)
12. Par atkritumu apsaimniekošanas valsts plānu 2006.-2012.gadam, Ministru kabineta rīkojums Nr.860, 29.12.2005// Laikraksts „Latvijas Vēstnesis" Nr. 210 (3368), 30.12.2005, [stājas spēkā 29.12.2005.] Available at http://www.likumi.lv
13. Par Ziemeļvidzemes reģionālo atkritumu apsaimniekošanas plānu 2006.-2013.gadam. Ministru kabineta noteikumi Nr.797, 26.09.2006// Laikraksts „Latvijas Vēstnesis" Nr. 156 (3524), 29.09.2006.) [stājas spēkā 30.09.2006.]. Available at http://www.likumi.lv
14. Sabiedrisko pakalpojumu regulēšanas komisijā (Public Utilities Commission). Available at http://www.sprk.gov.lv/index.php?sadala=480 (06.01.2011)
15. Teibe I. "Vides komunikācijas attīstība atkritumu saimniecības sektorā: pašvaldību un mērķgrupu sadarbība" Rīga, 2010 a, 5.lpp. University of Latvia, Riga.
16. Teibe I. Ikšķiles novada atkritumu saimniecības izpēte 2010, 2010 b, 68.lpp. University of Latvia, Riga.
17. Teibe I., Ķirsona I., Ozola G. "Piekrastes pašvaldības vides komunikācijas rīcības programmas vadlīnijas: Saulkrastu novads, Mājsaimniecības vides pārvaldības sektora izpēte (2010, X -2011,I), 2010 c, 91 p., University of Latvia, Riga.
18. Teibe I., Ozola G., Šturma A., Jakušenoka S. „Klimata pārmaiņu adaptācijas politikas plānošanas vadlīnijas piekrastes pašvaldībai: Salacgrīvas novads. Vides sektors, Rīga, LU, 2010 d, 94 p., University of Latvia, Riga.

# COAGULATION OF WOOD POLLUTANTS FROM MODEL WASTEWATER BY ALUMINIUM SALTS

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***Abstract.*** *One of the stages of raw material preparation for plywood producing is hydrothermal treatment of birch wood. Wastewater from plywood hydrothermal basin is characterized by the high degree of contamination. The basic contaminating component of this wastewater is lignin, hemicellulose and extractive substances (LES), which are the main reason of a high level of chemical oxygen demand (COD) and color of water. The main objective of the present study is to investigate the influence of aluminium sulfate, aluminium chloride and poly aluminium chloride dose on coagulation of LES from model wastewater. It was established that the influence of coagulant dose on LES removal can be described by 3 regions: first region - the process of coagulation does not take place; second region is characterized by the sharp increase of efficiency of LES removal and the third region corresponds to decrease of efficiency of LES removal at the increase of coagulant dose.*

**Keywords:** *coagulation, model wastewater, aluminium salts, dose, hemicellulose, lignin.*

## Introduction

The problem of wastewater treatment of hydrothermal basins that contain plenty of contaminating components such as lignin, hemicellulose and extractive substances of wood (LES) is very actual for the enterprises of the plywood industry. These substances give the high value of chemical oxygen demands (COD) and degree of colouring to the water flows. Traditionally these enterprises have the centralized system of biological purification that for a number of reasons in modern conditions can not suit ecological norms on emission in water objects. Change in purification technology and introduction of the additional stage of the physical and chemical purification from oxidation-prone part of organic matters of wood raw material delignification is the most perspective direction of emission decline on regulated property. From the other side, wood originated pollutants can be of interest in practice [1,2].

The coagulation method of purification in combination with the mechanical method of separation of the educed phase can be used as most accessible, not requiring considerable investments, and effective enough method. This process is carried out by adding hydrolyzing coagulants to the processed water. Chemical coagulants normally destabilise colloidal particles by four distinct mechanisms: double layer compression, charge neutralisation, enmeshment in a precipitate and inter - particle bridging [3].

In recent years the usage levels of coagulation method with the use of aluminium salts are increased, and judging by prediction, will increase. The study of regularity of coagulation process is therefore actual, as a method of purification of specific streams. Taking into account that the most high indexes of quality of wastewater purification are reached by adding of strictly certain optimal dose, then one of the stages in technology is determination of working dose of coagulant. For this purpose the researches have an important role, conducted on the model systems that imitate wastewater from plywood industry of hydrothermal basin [4].

The aim of this work is to study the coagulation process of LES in the presence of aluminium sulfate, aluminium chloride and poly aluminium chloride.

## Materials and methods

The model solution was described by pH, density, LES content, COD and its color. The description of model solution is given in Table 1.

*Table 1.*

**The characteristic of the model solution**

| Parameters | Value |
|---|---|
| pH | 9.02 |
| Density ($kg/m^3$) | 995 |
| Optical density (490 nm) | 0.285 |
| Content of dry solids (mg/l) | 1400 |
| Colority (mg/lPt) | 746 |
| COD (mgO/l) | 1285 |

Aluminium sulfate ($Al_2(SO4)_3*16H_2O$), aluminium chloride ($AlCl_3*6H_2O$) and polyaluminium chloride (Polypacs-30) were used as coagulants and the working solutions were prepared by dissolving of coagulants in distilled water depending on dose required. The process of coagulation was performed by mixing equal volumes of the coagulant and model solutions. A volume of the mixed system was 100 ml, and a time of mixing – 2 min. The optimal terms of the LES removal in the presence of aluminium sulfate and chloride were studied, varying the dose of coagulant.

The efficiency of LES coagulation was defined after 2 hours of the system settling and filtration. The filtration was fulfilled through a paper filter "blue ribbon". The colloidal stability and coagulation of LES in the presence of aluminium salts was studied by spectrophotometry using Genesys(TM) 10 scanning spectrophotometer with scanning wavelength from 190 to 1100 nm. The residual concentration of LES and birch lignin in the filtrate was defined by measuring filtrate optical density (*A*) at the wavelength 490 and 280 nm, respectively, using the preliminary received correlation curves. The filtrate color was defined by the method of photometry at the wavelength of 436 nm; the results were reported in platinum-cobalt (PtCo) units, where a unit of color is equivalent to that produced by 1 mg/l of platinum in the form of the chloroplatine ion (ISO7887:1994). COD was determined by the oxidization of the received filtrate by adding potassium dichromate under the given reaction conditions. Calculation of the COD value from the amount of dichromate reduced (LVS ISO 6060:1989). A sludge volume index (SVI) gave information about dispersion system settling. By definition, the sludge volume index is the volume in ml occupied by 1 g of the settled dispersion after 30 min settling.

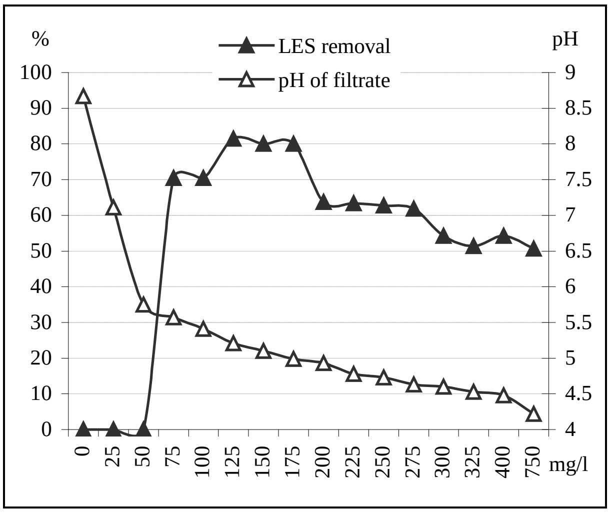
The efficiency of the model solution purification from LES, reduction of COD and color were calculated by using the following Eq. 1:

$$removal,\% = \left[\frac{(C_i - C_f)}{C_i}\right]*100 \qquad (1)$$

where $C_i$ and $C_f$ are initial and final concentrations of LES, COD and the color.

## Results and discussions

The study of influence of coagulant dose ($Al_2(SO_4)_3$, $AlCl_3$, Poly(AlCl) was conducted in a range 0 - 750 mg/l. Data, reflecting the values of efficiency of LES removal at the use of aluminium salts (Fig.1 a, b, c), show general character of regularity.

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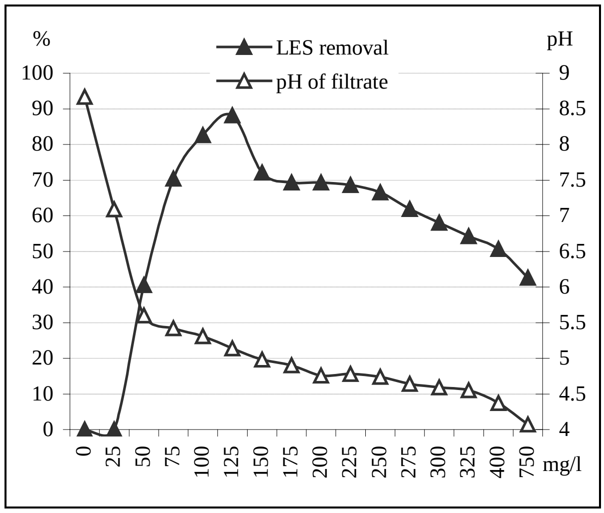
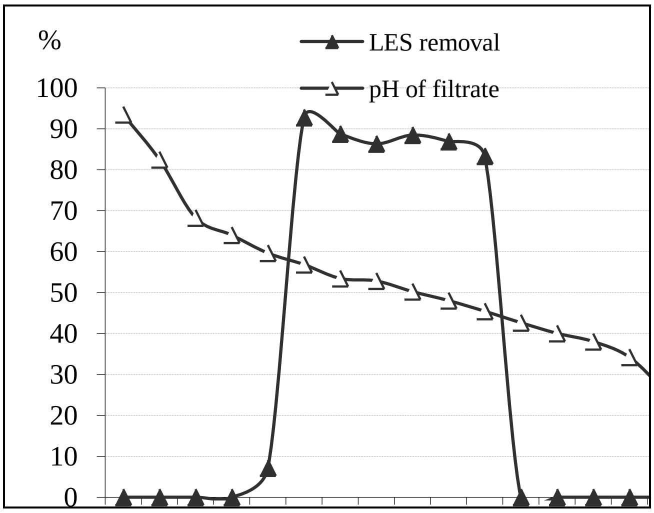



*b)*




*c)*

*Fig.1.* **The effect of coagulant dose on the removal of LES and pH values of systems after settling and filtration: (a) $Al_2(SO_4)_3$, (b) $AlCl_3$ and (c) Poly(AlCl)**

In all three cases the increase of coagulant dose results in decrease of the pH system, that is related to the process of hydrolysis of aluminium salts, as a result of that there is a formation of slightly soluble hydroxides and simultaneously the hydrogen ions accumulate in the system that give to it the acid values of pH and are able to slow fullness of hydrolysis.
As it is seen from the pictures (Fig.1 a, b, c), the influence of dose on a degree of the LES removal can be divided into 3 regions.
First region - the process of coagulation does not take place. This area is within the limits of doses of $Al_2(SO_4)_3$ to 50 mg/ l (Fig.1.a), doses of $AlCl_3$ is less than 25 mg/l (Fig.1.b) and doses of Poly(AlCl) which do not exceed 75 mg/l. This zone is characterized by conserving of LES colloid stability. The negatively charged particles of LES are stabilized due to forces of the mutual repulsion and hydrolysis products of aluminium salts with so small doses are incapable to neutralize the charges of LES particles.
Then the second region is characterized by the sharp increase of efficiency of LES removal: $Al_2(SO_4)_3$ is 50-175 mg/l (Fig.1.a), $AlCl_3$ is 25-125 mg/l (Fig.1.b) and Poly(AlCl) is 75-250 mg/l. On the curves of dependences there are maximums that correspond to the dose of 125 mg/l for $Al_2(SO_4)_3$, $AlCl_3$ and Poly(AlCl). The next values of LES removal are reached:

$Al_2(SO_4)_3$ - 81.4%, $AlCl_3$ - 88.1% and Poly(AlCl) - 92.7%. In this zone the degree of stability of LES particles intensively decreases and a capacity for settling of appearing coagulants increases. Thus the values of pH filtrates are 5.2, 5.1 and 6.8 for $Al_2(SO_4)_3$, $AlCl_3$ and Poly($AlCl_3$ ), respectively. According [5,6,7], coagulation of LES with aluminium salts in this pH region is possible to interpret as follows: the process of hydrolysis of aluminium salts is leading by formation of the hydrolyzed forms of aluminium $AlOH^{2+}$, $Al(OH)_2^+$ and dimeric structures $A1_2(OH)_2(H_20)_8$ with a charge $4^+$ for Poly(AlCl). The formation of phase of $Al(OH)_3$, the amount of which increases, begins and the density of its charge decreases as far as approaching to the isoelectric point of $Al(OH)_3$ (pH 6.5-7.8). The insoluble $Al(OH)_3$ formed from the hydrolysis of $Al_2(SO_4)_3$ appears at a lower pH (4.5-5.00 than that formed from $AlCl_3$ and Poly(AlCl) (pH 6.0-7.0).

The third region corresponds to decrease of efficiency of LES removal at the increase of coagulant dose. It is connected with the insignificant sizes, density of appearing LES coagulants and the speed of their settling. As a rule, it is related to lowering of alkaline reserve and pH system below than possible level, namely change of pH value from the isoelectric point of aluminium salts, and also according to literary data [5], it can be related to the recharge of LES coagulants in the interval of pH 4.0 - 5.0 (Fig.1.a, b) in presence of $Al_2(SO_4)_3$ and $AlCl_3$ due to the increase of concentration of the positively–charged products of hydrolysis of coagulants. Also it should be noted (Fig.1.c) in the range of pH $\leq$ 6.5 and doses of Poly(AlCl) > 275 mg/l is related to stoppage of LES settling. It is explained [7] that at the high doses of Poly(AlCl) in this area of pH there is a recharge of LES because of high content of hydrolysis products of Poly(AlCl) with a charge $4^+$, and the system saves sedimentation stability. It is necessary to mean that the increase of dose, comparatively with optimal, results not only in the overrun of coagulant but also to reduction of duration of useful work of sedimentation tanks.

In a table 2.there are data of efficiency of model solution purification from LES at the use of $Al_2(SO_4)_3$, $AlCl_3$ and Poly(AlCl) by a dose of 125 mg/l.

One of the important indexes of coagulation quality is a capacity of the coagulation system for settling. The sludge volume index (SVI) gives information about settling of the coagulation system. The lower sludge index is the better settling. Value of sludge index for about 140 ml/g is usually considered acceptable to the satisfactory setting [6].

*Table 2.*

**The efficiency of LES removal from model solution in the presence of aluminium coagulants at dose 125 mg/l**

| Coagulants | pH | LES removal, % | Lignin removal, % | COD removal, % | Color removal, % | SVI ml/g |
|---|---|---|---|---|---|---|
| $Al_2(SO_4)_3$ | 5.2 | 81.4 | 57.8 | 37.7 | 87.2 | 225 |
| $AlCl_3$ | 5.1 | 88.1 | 60.4 | 42.4 | 91.4 | 135 |
| Poly(AlCl) | 6.8 | 92.7 | 58.4 | 40.9 | 83.8 | 51 |

Presented data are practically comparable. However the maximal degree of purification is reached using $AlCl_3$ and Poly(AlCl). But it should be noted that Poly(AlCl) at the identical dose addition does not cause the displacement of the pH system in a acid environment. And it is its distinctive advantage in comparison with a $Al_2(SO_4)_3$ and $AlCl_3$, at the use of which pH filtrate is 5.0 on the average. In the working conditions of coagulation treatment of wastewater it can cause the necessity of the use of alkalizing reagents with the purpose of achievement of pH value of the purified water, corresponding to the norms of emission on local post-treatment of streams or centralized purifying stations (pH 6.2-7.2). Also it should be noted that a minimum value of SVI corresponds to the Poly(AlCl) that characterizes the ability of excreted coagulants of LES to be settled and consolidated more intensively.

## Conclusions

Represented data show the regularity of LES coagulation from model wastewater. It was established that:

1. the increase of coagulant dose results in decrease of the pH system;
2. the influence of coagulant dose on LES removal can be described by 3 regions:
   - ✓ first region - the increase of dose does not cause the LES removal;
   - ✓ second region is characterized by the sharp increase of efficiency of LES removal;
   - ✓ third region - the increase of dose relatively optimal unfavorably affects the efficiency of LES removal from model solutions due to the displacement of values of pH in acid environments and lowering of alkaline reserve.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### References


1. G. Shulga, J. Brovkina, T. Betkers, O. Aniskevicha, J. Ozoliņš. Relationship between composition of the lignin-based interpolymer complex and its structuring ability – Environmental Engineering and Management Journal, July/August 2008, Vol. 7. No.4. pp. 397-401.
2. G Shulga, V. Shakels, J. Brovkina, T. Betkers, J. Ozoliņš. Effect of rheological properties of the Lignin-based adhesive on aggregating of light-textured soil - Proceedings of 10th European Workshop on Lignocellulosics and Pulps, Stockholm, Sweden, August 26-29, 2008, pp. 356.
3. Mingquan Yan, Hailong Liu, Dongsheng Wang. Natural organic matter removal by coagulation: effect of kinetic and hydraulic power. Water Science and Technology: water supply, Vol. 9 (1), 2009, pp. 21-30.
4. J. Brovkina, G. Shulga, J. Ozolins. Recovery of lignin and extractive substances from the hydrolysate of model birch wood hydrolysis with aluminium salt. Chemine Technologija (Chemical Technology), Nr. 3-4 (56), 2010, p. 30-34.
5. Yu. M. Chernoberezhskii, D. Yu. Mineev, A. B. Dyagileva, A. V. Lorentsson and Yu. V. Belova. 2002. Recovery of Kraft Lignin from Aqueous Solutions with Oxotitanium Sulfate, Aluminum Sulfate, and Their Mixture. Russian Journal of Applied Chemistry, v. 75 (10), pp. 1730-1732.
6. С.Н. Линевич, С.В. Гетманцев. 2007. Коагуляционный метод водообработки, теоретичекие основы и практическое использование. Наука, Москва, 223 стр.
7. Barbara H. Wortley and Joe Steelhammer. (1990) Polyaluminum hydroxychloride application in neutral ph rosin sizing of paper. Mat. Res. Soc. Symp. Proc. v. 197, pp. 273-278.

# PRODUCTION OF BIOSURFACTANTS BY *ARTHROBACTER SP. N3*, A HYDROCARBON DEGRADING BACTERIUM

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**Abstract.** *Different screening methods, such as emulsification capacity and oil spreading assays, hydrocarbon overlay agar and modified drop collapse methods were used to detect biosurfactant production by hydrocarbon degrading Arthrobacter sp N3 strain. It was indicated that oil spreading assay was the most reliable method to detect biosurfactant production. To investigate biosurfactant production, batch cultivation of Arthrobacter sp N3 was carried out in a fermenter with complex nutrient medium supplemented by sunflower oil as a carbon source. The highest oil displacement activity was achieved when Arthrobacter sp N3 strain was cultivated in two stages (with aeration for cell production and without aeration for biosurfactant synthesis). Then, two forms of the biosurfactant (crude preparation and partially purified biosurfactant) were recovered from the culture liquid. Furthermore, the biosurfactant produced by Arthrobacter sp N3 strain was analyzed by thin layer chromatography and it was estimated that even a few compounds have surface activity. The effect of temperature and pH on biosurfactant activity was also studied. It was observed that no appreciable changes in biosurfactant activity occurred at temperature and pH values ranges of 4–125 ºC and 5–10, respectively.*

**Keywords:** *biosurfactant, Arthrobacter, fermentation, hydrocarbon degrading bacterium.*

## Introduction

Pollution caused by crude oil and its products is the most prevalent problem in the environment [1, 2]. Various physical, chemical and biological techniques are used to reduce its negative impact on human health, flora and fauna. Bioaugmentation, one of the most efficient biological techniques, is based on remediation of the contaminated environment by adding of hydrocarbon degrading microorganisms [3]. Unfortunately, biodegradation of hydrocarbons often is limited by bioavailability which is associated with their poor solubility in water and sorption to soil particles. Thus, to enhance hydrocarbon bioavailability, synthetic surfactants and biosurfactants are used [4, 5]. Biosurfactants have several advantages over synthetic surfactants: higher biodegradability, lower toxicity, higher specificity and effectiveness at the extreme temperature and pH values [3, 6].

The biosurfactant producing microbes are distributed among a wide variety of genera. For instance, bacteria that belong to such genera as *Bacillus, Pseudomonas, Sphingomonas, Rhodococcus* and *Arthrobacter* [7-12] and yeasts belonging to genera *Candida* and *Yarrowia* [13] have been reported to produce surface active compounds. Microorganisms produce the surface active compounds either extracellularly or these compounds are attached to microbial cells [6, 14]. In general, their structure includes hydrophilic and hydrophobic moieties. The major classes of biosurfactants include glycolipids (rhamnolipids, trehalolipids, sophrolipids), lipopeptides and lipoproteins, fatty acids, phospholipids, neutral lipids and polymeric biosurfactants [3, 6].

Biosurfactants often are used in processes of oil removal from contaminated sites and for enhancement of hydrocarbon biodegradation [2, 4, 5]. In some cases, not only biosurfactant itself but also biosurfactant producing microorganisms are applied for cleaning up of the hydrocarbon polluted environment [15].

Recently, increasing attention has been focused on the hydrocarbon degrading microorganisms with biosurfactant-producing capability [9]. Since these microorganisms are able to produce biosurfactants when grow on hydrocarbon compounds presented in polluted environment, they are highly promising for bioremediation purposes.

JSC "Biocentras" owns extensive microbial cultures collection with more than 200 strains of hydrocarbon degrading microorganisms. The strains were isolated from hydrocarbon polluted

environment around the world. Furthermore, in our previous work [16], we have discovered that some of these microorganisms have emulsification activity. So, these findings lead to the presumption that our microorganisms might be applicable for remediation of hydrocarbon polluted environment not only as hydrocarbon degraders but also as biosurfactant producers.
The aims of the present work were to determine capability of *Arthrobacter* sp N3 strain of producing biosurfactant, and to investigate biosurfactant production in batch cultivation. The biosurfactant was recovered from the culture liquid and its partial characteristic was determined.

## Materials and methods

**Microorganism**. Hydrocarbon degrading and biosurfactant producing *Arthrobacter* sp N3 strain obtained from the culture collection of JSC "Biocentras: was used.
**Media and cultivation conditions.** Nutrient agar (*Oxoid*, UK) was used for plating, and nutrient broth (*Oxoid*, UK) was used for the subculture and preculture of *Arthrobacter* sp N3 strain. For flask cultures, 750 ml Erlenmeyer flasks containing 100 ml of nutrient broth and 4 % (v/v) inoculums' culture were incubated with shaking at 200 rpm and 30 °C for 16-48 h. For biosurfactant production, batch cultivation was carried out in a 14 l benchtop fermenter BioFlo 110 (New Brunswick Scientific, USA) with 7 l of optimized complex medium. The medium was inoculated with 10 % (v/v) of 16 h-old seed culture. The fermenter was operated at 30 ºC and 200 rpm agitation, with or without aeration at 0.5-1 vvm and uncontrolled pH.
During the cultivation experiments, samples of culture liquid were removed periodically and analyzed for bacterial growth and biosurfactant production.
**Biosurfactant recovery.** Culture liquid of *Arthrobacter* sp N3 strain was centrifuged at 18500 x g for 20 min to obtain culture supernatant (named crude preparation). Then, two volumes of chilled acetone were added and, after keeping at 4 °C overnight, precipitate was collected by centrifugation at 3250 x g for 20 min. The biosurfactant from precipitate material was extracted with isopropanol, which was evaporated away leaving behind biosurfactant heaving an oil-like appearance. This product was named partially purified preparation of biosurfactant.
**Thin layer chromatography (TLC).** To determine chemical nature of biosurfactant, the TLC was conducted on Silica gel 60 glass plates (Fluka, Germany). The developing solvents systems were as follows: ***1***, n-hexane – diethyl ether – acetic acid (70:30:2, v/v/v); or ***2***, chloroform – methanol - water (65:25:4, v/v/v). After developing, the spots were revealed by: a) saturated iodine steam, for detection of lipids; b) spraying with 0.2 % w/v ninhydrin (in ethanol) and heating at 100 °C for 5 min for detection of compounds with free amino groups. To detect biosurfactant compounds, all spots were scraped off the plates, dissolved in n-hexane – 2-propanol (3:2, v/v) mixture and tested for surface activity by the oil spreading assay.
**Biosurfactant stability.** Stability studies were carried out using either crude preparation or partially purified biosurfactant. To determine thermostability, crude preparation of the biosurfactant was autoclaved at 121 ºC for 30 min, while partially purified biosurfactant was exposed at 4, 20, 30, 50, 75, 100 and 125 ºC for 1 h, after which the oil displacement area was measured. To study the pH stability, the pH of crude preparation of the biosurfactant was adjusted to different pH values (2 to 12) and oil displacement area was measured after 24 h exposure.
**Emulsification capacity measurement.** Emulsification activity was determined by the procedure described in our previous work [16]. The emulsification activity was given as a percentage of emulsified layer height divided by total height of the liquid column.
**Oil spreading assay.** The oil spreading assay was adapted from the method described by authors [11]. The 20 ml of distilled water was added to a Petri dish (10cm diameter) and

followed by the addition of 10 μl of crude oil to the surface of water. 10 μl of biosurfactant solution were then added to the oil surface. The diameter of clear zone formed on the oil surface was measured. Biosurfactant oil spreading (displacement) activity was defined as oil displacement area in $cm^2$.

**Drop collapse method.** A modified drop collapse method was carried out using microscope slides coated with crude oil. 10 μl of the sample tested were placed on the slides. Biosurfactant production was considered positive when the drop diameter was larger than those produced by distilled water and also by culture medium as negative controls.

**Blue agar plate method.** Pure bacterial culture was plated onto blue agar [17]. Anionic biosurfactant-producing colonies on blue agar plate are identified following the formation of dark blue halos around the colonies on a light blue plate background.

**Hydrocarbon overlay agar method.** Hydrocarbon overlay agar method [18] was performed with some modifications. Mineral agar plates [19] were coated individually with 100 μl of diesel fuel or fuel oil. Plates were inoculated with *Arthrobacter* sp N3 strain and incubated at 30 ºC for 48–72 h. Colony surrounded by an emulsified halo was considered being positive for biosurfactant production.

**Bacterial growth** was monitored by viable cell count which was determined by plating of serial dilutions of samples on nutrient agar plates and incubating at 30 °C for 24 h.

**Statistics.** All experiments were carried out in duplicate or triplicate. Calculations were performed with Origin software.

## Results and discussion

For investigation of *Arthrobacter* sp N3 strain ability to produce biosurfactants, various screening methods were performed. According to Satpute et al [18], combination of various methods is required for effective screening of biosurfactants since a single method is not suitable to identify all types of biosurfactants. As *Arthrobacter* sp N3 strain is being used as bioremediation agent for cleaning of hydrocarbon polluted environment, methods indicating biosurfactant activity toward hydrocarbons were preferred in this investigation.

Firstly, *Arthrobacter* sp N3 strain was examined for emulsification capacity. The experiment revealed that *Arthrobacter* sp N3 strain was positive in the emulsification test and showed 49.5 % activity.

Blue agar method is known as fast semi-quantitative method for detection of microbial cultures producing extracellular glycolipids or other anionic surfactants [18]. *Arthrobacter* sp N3 strain grew weakly on blue agar plates and produced no halos. This indicates that *Arthrobacter* sp N3 produces not glycolipids.

On the contrary, *Arthrobacter* sp N3 strain was positive for biosurfactant production in the hydrocarbon overlay agar method. The results (Fig. 1) indicated that *Arthrobacter sp N3* strain produced biosurfactant growing on both, diesel fuel and fuel oil.

Surface activity of the compounds produced by *Arthrobacter sp N3* strain was detected by modified drop collapse method, too. However, the method is more qualitative than quantitative [20].

Oil spreading assay was shown to be rapid and more sensitive for detection of surface active compounds [18, 20]. *Arthrobacter* sp N3 strain demonstrated oil displacement activity toward crude oil. Furthermore, it was observed that the oil displacement activity, as measured by the area of the clear zone on the oil-water surface, decreased proportionally with a decrease in concentration of the biosurfactant. Thus, oil spreading assay was found to be the most suitable for quantitative measurement of biosurfactant activity. The oil spreading assay was used to detect, quantify, and compare biosurfactant activities throughout all experiments in this work.

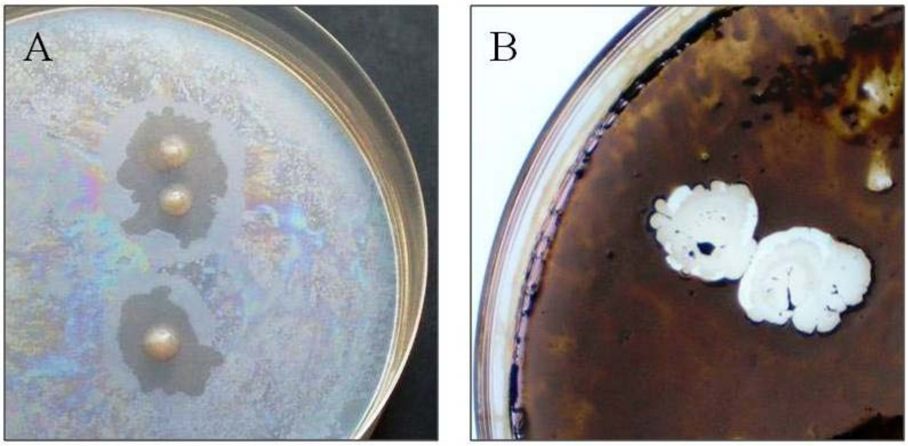


*Fig.1*. **Biosurfactant production by *Arthrobacter sp N3* strain grown on mineral agar with diesel fuel (A) and fuel oil (B)**

When *Arthrobacter* sp N3 strain was grown in shake-flask culture, it was observed that biosurfactant production depended on nutrient medium composition (data not shown). The highest oil displacement activity (88.2 $cm^2$) was determined in optimized nutrient medium with sunflower oil as carbon source. The medium was used for further experiments on biosurfactant production in a fermenter.

The batch cultivation of *Arthrobacter sp N3* strain was carried out in a fermenter with 7 l of medium containing sunflower oil by two different aeration modes: a) constant aeration; b) with and without aeration. The profiles of cell growth, pH changes and production of biosurfactant are shown in Fig 2.

With *Arthrobacter* sp N3 strain cultivated at constant aeration of 0.5-1.0 vvm and agitation of 200 rpm (Fig. 2A), the most intensive increase in bacterial cell count was detected during the first hours of cultivation. At 8 h of the cultivation, when stationary phase of cell growth was reached, cell count of $7.9 \cdot 10^9$ CFU/ml was obtained. Further microbial population increased slightly. The change in profile of pH was practically inconsiderable. However, surface activity of the culture liquid was much lower than expected. At the end of cultivation, only 19.6 $cm^2$ oil displacement activity was registered. It is likely that too intensive aeration and agitation inhibited synthesis of biosurfactant by *Arthrobacter sp N3* strain.

At the next stage of the investigation, *Arthrobacter sp N3* strain was cultivated in the fermenter under varied aeration and agitation conditions: the first 8 hours agitation of 200 rpm and aeration of 0.5-1.0 vvm were maintained; next, the culture was cultivated without aeration and agitation (Fig. 2B).

As shown in Fig. 2B, profiles of cell growth and pH changes were similar to these measured in batch fermentation with constant aeration (Fig. 2A.), on the contrary, biosurfactant production had different character. The first 8 hours, while fermenter was operated with aeration and agitation, *Arthrobacter sp N3* strain intensively grew but oil displacement activity was low. The oil displacement activity was gradually increased after 12 h. The highest oil displacement activity of 174.6 $cm^2$ was achieved at 24 hour of the cultivation. If to compare to shake flask culture, it is obvious that activity in the batch fermentation was about two times higher. Furthermore, the results confirmed that *Arthrobacter sp N3* strain growth and biosurfactant synthesis are separated processes: oxygen is needed for bacterial cells growth, while intensive aeration inhibited biosurfactant production.

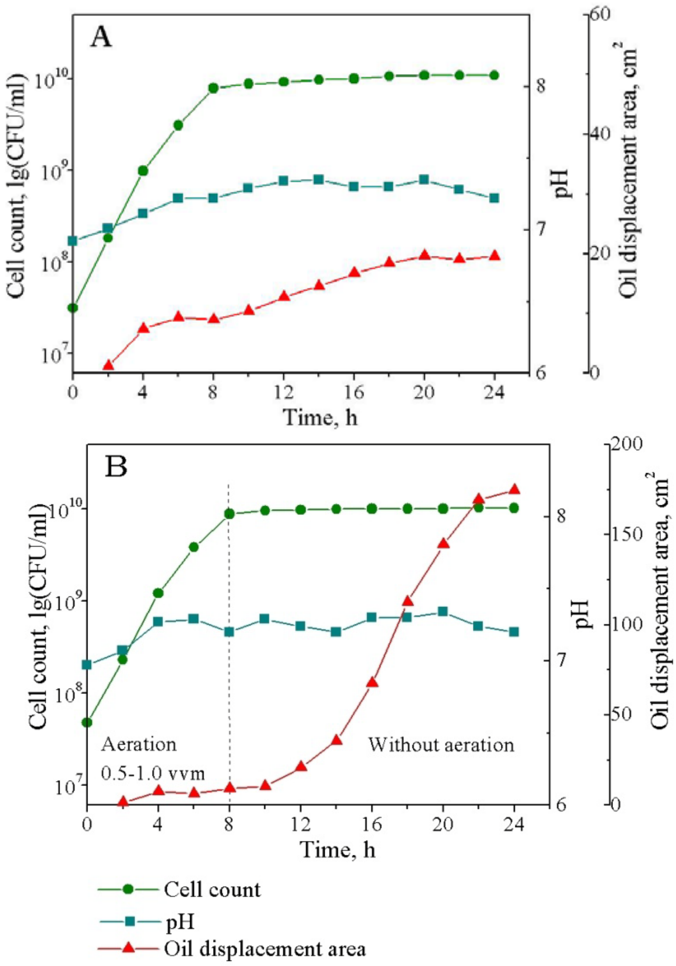


*Fig.2*. **Profiles of cell growth, biosurfactant production and pH changes during *Arthrobacter sp N3* strain batch cultivation carried out with constant aeration (A) and with and without aeration (B)**

The importance of aeration and agitation in producing of biosurfactant has been shown and by researchers [7, 13, 21]. For example, authors [13, 21] have reported that microbial growth and biosurfactant production increases when aeration and agitation rates are increased. On the contrary, Suwansukho et al. [7] have reported that aeration stimulated growth of *Bacillus subtilis* MUV4 strain but inhibited the biosurfactant production.

To recover biosurfactant from culture liquid, the effect of extraction and precipitation was investigated (data not shown). Based on the results obtained the procedure for biosurfactant recovery was developed. Following the procedure, the steps for the biosurfactant recovery are: centrifugation, acetone precipitation, 2-propanol extraction and evaporation. As a result, two types of the biosurfactants were obtained: crude preparation and partially purified biosurfactant.

The biosurfactants produced by *Arthrobacter* sp N3 strain, as shown by TLC analysis (Fig. 3), appear to be composed of a mixture of a few neutral lipids (Fig. 8A) and polar lipids (Fig. 8C). Moreover, purple colour of spots developed after visualization with ninhydrin (Fig. 8D) indicates that these surface active compounds have amino functional group, which is characteristic for lipopeptides and lipoproteins.

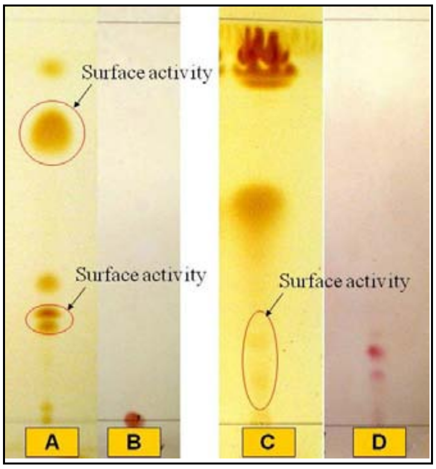


*Fig. 3*. **TLC of partially purified biosurfactant from *Arthrobacter* sp N3 strain, using solvent *system 1* (A and B) and solvent *system 2* (C and D).The plates were visualized by iodine steam (A and C) and ninhydrin (B and D)**

To evaluate the effect of environmental conditions on performance of biosurfactants produced by *Arthrobacter* sp N3 strain, the thermal and pH stability were studied.
The thermal stability of the biosurfactant was tested over a range of temperature (4-125 °C). The partially purified biosurfactant was shown to be thermostable (Fig. 4). Heating of the biosurfactant to 125 °C caused no significant effect on oil displacement activity. Furthermore, oil displacement activity of crude biosurfactant preparation was not lost after autoclaving at 121 °C for 30 min. Besides, the biosurfactant activity was 20 % higher than that was before the thermal treatment. The increase in oil displacement activity can be attributed to the fact that remaining in crude preparation bacterial cells were destroyed under thermal action and cell bound biosurfactant was released.

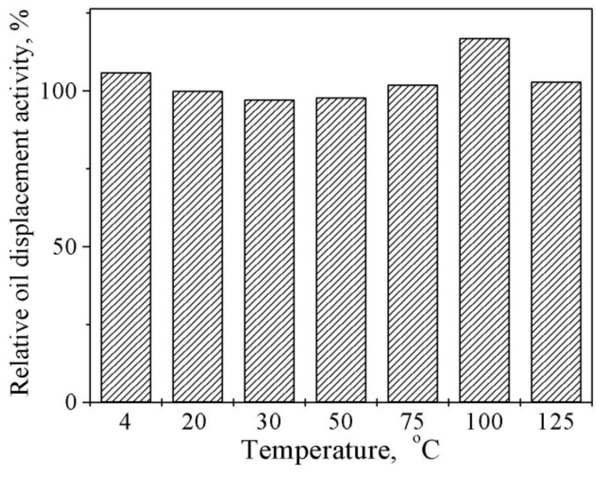


*Fig.4*. **Effect of temperature on the stability of the partially purified biosurfactant**

For pH stability, the pH value of crude preparation of biosurfactant was varied from 2 to 12. As seen in Fig. 5, no appreciable change in biosurfactant activity was observed in the pH ranges of 5–10. Precipitation of crude biosurfactant preparation occurred at pH below 5, which led to a decrease of biosurfactant activity about 43 %. Loss of biosurfactant activity at pH below 4 due to precipitation has been observed and by authors [8].

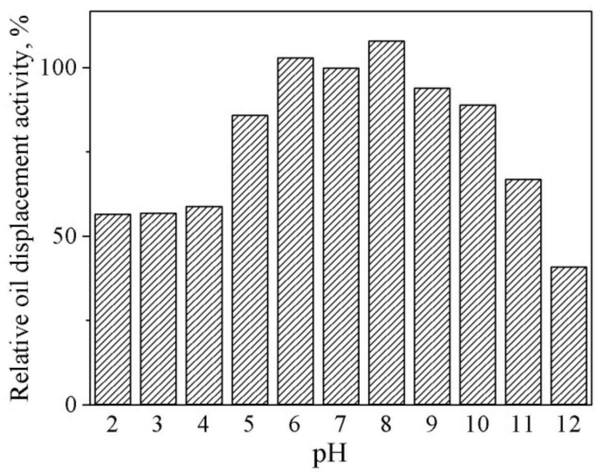


*Fig. 5.* **Effect of pH on the stability of crude biosurfactant preparation**

So, biosurfactants produced by *Arthrobacter* sp N3 strain has properties necessary for performance in oil polluted environment.

**Acknowledgment**

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## Conclusions

1. The ability of *Arthrobacter* sp N3 strain to produce biosurfactants was confirmed by hydrocarbon overlay agar and modified drop collapse methods, emulsification capacity and oil spreading assays. In addition, it was indicated that oil spreading assay is a reliable method to detect biosurfactant production.
2. Batch cultivation in two stages (with aeration for cell production and without aeration for biosurfactant synthesis) resulted in about 2-fold oil displacement activity, if compared to that in shake flasks culture.
3. Two forms of the biosurfactant (crude preparation and partially purified biosurfactant) were recovered from the culture liquid. Thin layer chromatography of the biosurfactants revealed that even a few compounds have surface activity.
4. Biosurfactants from *Arthrobacter* sp N3 strain were found to be stable at temperature and pH ranges of 4-125 ºC and 5-10, respectively.
5. Hydrocarbon degrading and biosurfactant producing *Arthrobacter sp N3* strain, as well as its biosurfactant, might be applicable in bioremediation of the sites contaminated with petroleum hydrocarbons.

### Bibliography

1. Caprino, L., Togna, G.J. Potential health effects of gasoline and its constituents. Environmental Health Perspectives. V.106, 1998, p. 115–125.
2. Millioli, V.S., Servulo, E-L.C., Sobral, L.G.S., de Carvalho, D.D. Bioremediation of crude oil-bearing soil: evaluating the effect of rhamnolipid addition to soil toxicity and to crude oil biodegradation efficiency. Global NEST Journal. V. 11, 2009, p. 181-188.
3. Kosaric, N. Biosurfactants and their application for soil bioremediation. Food Technology and Biotechnology. V. 39, 2001, p. 295-304.
4. Guo-liang, Z., Yue-ting, W., Xin-ping, Q., Qin, M. Biodegradation of crude oil by *Pseudomonas aeruginosa* in the presence of rhamnolipids. Journal of Zhejiang University SCIENCE. No. 8, 2005, p. 725-730.

5. Youssef, N., Simpson, D.R., Duncan, K.E., McInerney, M.J., Folmsbee, M., Fincher, T., Knapp R.M. In situ biosurfactant production by *Bacillus* strains injected into a limestone petroleum reservoir. Applied and Environmental Microbiology. V. 73, 2007, p. 1239-1247.
6. Gautam, K.K., Tyagi, V.K. Microbial surfactants: a review. Journal of Oleo Science. V. 55, 2006, p. 155-166.
7. Suwansukho, P., Rukachisirikul, V., Kawai, F., H-Kittikun, A. Production and applications of biosurfactant from *Bacillus subtilis* MUV4. Songklanakarin Journal of Science and Technology. V. 30, 2008, p. 87-93.
8. Makkar, R.S., Cameotra, S.S. Effects of various nutritional supplements on biosurfactant production by a strain of *Bacillus subtilis* at 45°C. Journal of Surfactants and Detergents. V. 5, 2002, p. 11-17.
9. Das, K., Mukherjee, A.K. Crude petroleum-oil biodegradation efficiency of *Bacillus subtilis* and *Pseudomonas aeruginosa* strains isolated from a petroleum-oil contaminated soil from North-East India. Bioresource Technology. V. 98, 2007, p. 1339-1345.
10. Bredholt, H., Josefsen, K., Vatland, A., Bruheim, P., Eimhjellen, K. Emulsification of crude oil by an alkane-oxidizing *Rhodococcus* species isolated from seawater. Canadian Journal of Microbiology. V. 44, 1998, p. 330-340.
11. Morikawa, M. Daido, H., Takao, T., Satoru, M., Shimonishi, Y., Imanaka, T. A new lipopeptide biosurfactant produced by *Arthrobacter* sp. strain MIS38. Journal of Bacteriology. V. 175, 1993, p. 6459-6466.
12. Pruthi, V., Cameotra, S.S. Short communication: production and properties of a biosurfactant synthesized by *Arthrobacter protophormiae* – an antarctic strain. World Journal of Microbiology and Biotechnology. V. 13, 1997, p. 137-139.
13. Amaral, P.F.F., Coelho, M.A.Z., Marrucho, I.M., Coutinho J.A.P. Biosurfactants from yeasts: characteristics, production and application. In: Biosurfactants. Sen, R. (ed.), Springler Sience, 2010, p. 236-249.
14. Maneerat, S., Dikit, P. Characterization of cell-associated bioemulsifier from *Myroides* sp. SM1, a marine bacterium. Songklanakarin Journal of Science and Technoogy. V. 29, 2007, p. 769-779.
15. Kumar, M., Leon, V., de Sisto Materano, A., Ilzins, O.A. Enhancement of oil degradation by co-culture of hydrocarbon degrading and biosurfactant producing bacteria. Polish Journal of Microbiology. V. 55, 2006, p. 139-146.
16. Celiešiūtė, R., Grigiškis, S., Čipinytė V. Biological surface active compounds application possibilities and selection of strain with emulsifying activity. Proc. of the 7th international scientific and practical conference: Environment. Technology. Resources. Rezekne, Latvia, 25-27 June 2009, p. 267-272.
17. Siegmund, I, Wagner, F. New method for detecting rhamnolipids extracted by *Pseudomonas* species during growth on mineral agar. Biotechnology and Technology. V. 5, 1991, p. 265-268.
18. Satpute, S.K., Bhawsar, B.D., Dhakephalkar, P.K., Chopade, B.A. Assessment of different screening methods for selecting biosurfactant producing marine bacteria. Indian Journal of Marine Sciences. V. 37, 2008, p. 243-250.
19. Čipinytė, V., Grigiškis, S. Selection of oil degrading microorganisms. Cheminė Technologija. V. 15, 2000, p. 65-69. (In Lithuanian).
20. Walter, V, Syldatk , C, Hausmann, R Screening concepts for the isolation of biosurfactant producing microorganisms. In: Biosurfactants. Sen, R. (ed), Springler Sience, 2010, p. 1-13.
21. Desai, J.D. and Banat I.M. Microbial production of surfactants and their commercial potential. Microbiology and Molecular Biology Rewiews. V. 61, 1997, p. 47-64.

# A STUDY OF MAJOR AND TRACE ELEMENT ACCUMULATION IN HUMIC ACIDS

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**Abstract.** *It has been widely studied recent as well as historic accumulation of elements in peat profiles depending on intensity of anthropogenic pollution and thereby peat profiles serve as archives for research of environmental change. Peat ability to accumulate major and trace elements depends on the character of element supply, potency of metal ions to bind functionalities in the peat structure, pH reaction, oxygen presence, presence of complexing compounds, inorganic ions and many other factors. The aim of this study is to assign major and trace element distribution in humic acids (HA) for two well characterized ombrotrophic peat profiles of Eipurs and Dzelve Bog and analyse factors affecting element concentration in peat humic acids. Elemental and functional analysis of the isolated HAs was done, using total reflection X – ray spectrometry, Elemental Analyzer Model EA – 1108, Thermospectronic Helios γ UV (Thermo Electron Co.) spectrophotometer, Total acidity method.*

**Keywords:** *humic acids, peat, trace and major elements, X-ray fluorescence spectroscopy.*

## Introduction

Major and trace element presence in peat are of importance as an indicator of peat genesis and organic matter humification processes and for industrial use of peat [1]. Upper peat layer of ombrotrophic type bog receive chemical elements only from atmosphere and thus reflect their presence in air [2]. Trace element accumulation in peat profiles has been used to reconstruct changes of human pollution and track down sources and characterize intensity of anthropogenic pollution. It has been widely studied recent as well as historic accumulation of many trace elements in peat profiles depending on intensity of anthropogenic pollution [3, 4, 5]. Peat ability to accumulate major and trace elements depends on the character of element supply (whether in particulate or ionic form) potency of metal ions to bind functionalities in the peat structure, pH reaction, oxygen presence, presence of complexing compounds, inorganic ions and many other factors [3, 4]. It has been hypothesized, that the main factor affecting metal accumulation in peat profile are humic substances [6, 7, 8, 9].

Humic substances (HS) are a general category of naturally occurring, biogenic, heterogeneous organic substances that can be generally characterized as yellow to black in colour, of high molecular weight, and refractory to degradation [10]. Humic substances consist of several groups of substances, that depending on their solubility, can be grouped as humic acid (HA) (the fraction insoluble in water under acidic conditions $pH < 2$, but is soluble at greater pH) and fulvic acid is the fraction soluble in water at all pH values [11]. In peat organic matter composition dominates humic acids. HS form most of the organic component of peat and they play a major role in the biogeochemical cycling of many trace elements [12] due to significant complex forming ability. The character of the complex formation between humic acids and major and trace elements is an object of intensive studies during last decades [13, 14, 15, 16].

Thus analysis of trace and major elements in humic substances might help to understand the character of their binding with natural organic matter and processes influencing their cycling in the environment. Knowledge on trace element concentrations in humic substances is also of importance considering their growing use in industry and agriculture. Until now trace and major element concentrations has been analysed in aquatic humic substances [17], sedimentary humic acids [18] and peat humic acids [8, 9].

The aim of this study is to assign major and trace element distribution between peat and peat humic acids from two well characterized ombrotrophic bog profiles and analyse factors affecting element concentrations in peat humic acids.

## Materials and methods

**Materials.** Analytical quality reagents (Merk Co., Sigma – Aldrich Co., Fluka Chemie AG RdH Laborchemikalien GmbH Co.) were used without purification. For preparation of solutions high purity water Millipore Elix 3 (Millipore Co.) 10 – 15 MΩcm was used throughout.

**Peat sampling and characterization, isolation of humic acids.** Peat profiles were obtained from well characterized [19, 20] ombrotrophic bogs Eipurs and Dzelve. Trace elements in 1 cm section of peat profile were determined after nitric acid digestion by GFAAS [21]. For isolation of humic acids, the obtained peat profiles were separated into layers by 10 cm layers and humic acids were isolated using the procedures recommended by the International Humic Substances Society (IHSS) [22].

**Characterization peat of humic acids.** Elemental analysis (C, H, N, S, O) was carried out using an Elemental Analyzer Model EA – 1108 (Carlo Erba Instruments). UV/Vis spectra were recorded on a Thermospectronic Helios γ UV (Thermo Electron Co.) spectrophotometer in a 1 – cm quartz cuvette. An automatic titrator tiroLine easy (Schott – Gerate GmbH) was used to measure carboxylic and total acidity of each humic acid. Ba hydroxide method [23, 24] was used to designate of the total amount of carboxylic groups and total acidity. Ba hydroxide method: in 10 ml of test tubes weigh 20 mg of humic acids, adding 10 ml of 0.1 *N* $Ba(OH)_2$ solution ($CO_2$ free) and place in a manual shaker for 24 hours. After a certain time to each shaken solution add one drop of phenolphthalein until samples coloured purple. Each solution is titrated with standardized 0.1 *N* HCl to pH 8.4 (solution remains colorless). Trace element (Ti, Sr, Se) concentrations were measured with total – reflection X-ray fluorescence spectrometry (TXRF) [25]. Samples of humic acid were prepared: 25 mg HA estimated with 1 ml conc. $HNO_3$ and boiled, until the solution completely evaporated. Using 1 ml burette was instilled 1 ml 50% $HNO_3$. The samples were cooled.

10 mg $l^{-1}$ of Ga internal standard (Sigma-Aldrich Co.) was added to each sample of 190 ml. To get complete results of X-ray fluorescence spectrometry, samples were applied three times on each quartz glass, samples were dried, using Labconco liofilizator. Analyzed samples were placed into total-reflection X-ray fluorescence spectrometer with a 1000 second measurement period.

## Results and discussion

The correlation matrix calculated for metals analyzed in the bog of Eipurs is presented in Table 1. The correlation matrix between metal concentrations in peat core and humic substances of Eipurs, was observed in the tightest correlation between element content of Fe, Zn, Cu and Ca. The element pairs Fe – Ca, Cu – Fe, Mn – Zn, As – Mn, Ca - Cu were all significantly correlated in humic substances of Eipurs bog. The element in peat core of Eipurs had strongest correlation among element pairs Fe – Ca, Mn – As, Zn – Pb, Cu – Ni, Ca – Ni, Pb – K, Ni – As (Table 1). It has been noticed that close correlations were between the element pairs of natural origin in peat core of Eipurs, for instance, Fe – Mn, K – Pb, Ca – As. Correlations such as Cu – Cr, Fe – Ni, Mn – Cu, Ni – Mn might be ascribed to industrial activity and long – range transport of pollutants. Comparison of distribution of metals between peat and its humic acid fraction reveals seeming similarity, however, if analyzing correlations between metal concentrations in peat and peat humic acids it becomes evident that there are tight correlations between metals in peat and in humic acid (for example in case of Cu and Fe), but for some elements (for example, As, K) these correlations are weak.

*Table 1.*

**Correlation coefficient matrix of major and trace element analyses in peat and humic acids (HAs) of Eipurs Bog**

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe - HA | **0.69** | | | | | | | | | | | | | | |
| Mn - P | **0.92** | **0.72** | | | | | | | | | | | | | |
| Mn -HA | -0.09 | 0.08 | 0.21 | | | | | | | | | | | | |
| Zn - P | -0.30 | 0.02 | 0.08 | **0.67** | | | | | | | | | | | |
| Zn - HA | -0.32 | 0.03 | -0.01 | **0.65** | **0.88** | | | | | | | | | | |
| Cu - P | **0.75** | *0.63* | **0.77** | -0.08 | -0.15 | -0.21 | | | | | | | | | |
| Cu - HA | *0.62* | **0.82** | **0.66** | -0.09 | -0.12 | -0.17 | **0.85** | | | | | | | | |
| Ca - P | **0.97** | *0.63* | **0.85** | -0.23 | -0.43 | -0.46 | **0.79** | **0.67** | | | | | | | |
| Ca - HA | *0.59* | **0.71** | 0.51 | -0.32 | -0.23 | -0.17 | **0.68** | **0.73** | *0.64* | | | | | | |
| Pb - P | -0.23 | 0.08 | 0.08 | **0.91** | **0.75** | **0.74** | -0.02 | 0.03 | -0.36 | -0.19 | | | | | |
| Pb - HA | -0.26 | -0.17 | -0.15 | 0.17 | 0.19 | 0.17 | -0.15 | -0.14 | -0.27 | -0.03 | 0.15 | | | | |
| Ni - P | **0.95** | **0.77** | **0.93** | -0.02 | -0.19 | -0.24 | **0.89** | **0.78** | **0.93** | **0.67** | -0.08 | -0.19 | | | |
| Ni - HA | -0.01 | 0.01 | -0.05 | -0.08 | -0.06 | -0.06 | -0.19 | -0.18 | -0.09 | -0.39 | -0.18 | -0.12 | -0.04 | | |
| As - P | **0.95** | **0.69** | **0.96** | 0.16 | -0.05 | -0.09 | **0.72** | *0.56* | **0.87** | 0.49 | 0.05 | -0.21 | **0.93** | 0.09 | |
| As - HA | 0.19 | 0.29 | 0.40 | **0.69** | *0.59* | *0.63* | -0.02 | -0.03 | -0.02 | -0.13 | *0.62* | 0.35 | 0.18 | 0.09 | 0.42 |
| | Fe - P | Fe - HA | Mn - P | Mn -HA | Zn - P | Zn - HA | Cu - P | Cu – HA | Ca - P | Ca - HA | Pb - P | Pb - HA | Ni - P | Ni - HA | As - P |

* *Correlation is significant at the 0.05 level (2-tailed)*

**** Correlation is significant at the 0.01 level (2-tailed)**

The absolute values of element concentration and their intervals determined in peat of Latvia are in general similar to that reported in Estonia, Sweden, Belgium, and other countries; at the same time, the data reflect the local processes affecting element concentrations in the peat mass. This may be related to major elements (Na, K), which are found in lower concentrations than, for example, in Norway, where sea salt aerosol – containing precipitation causes elevated concentrations of them, as well as to elements such as Ca, Mg, and Fe. In the peat bulk mass, which is of industrial importance, the trace element concentration is low, especially if compared with element concentrations in other countries. This aspect may be of importance considering the industrial uses of peat in agriculture.

Two studied bogs have very much differing botanical composition, variability of the peat decomposition degree (Fig. 1) and thus study of metal accumulation in their peat, properties and metal accumulation character in humic acids, isolated from peat can reveal the metal binding character during bog development and factors controlling it. A significant contribution to major and trace element binding in peat humic acids can provide their structural features and functional groups, reflected as in their elemental (C, H, N) and functional (COOH) composition (Fig. 1). The elemental composition of studied humic acids reflect their original material and is characterized with an increasing values of C in humic acids from peat with higher decomposition degree, but H and N content is fluctuating between values, common for peat humic acids and do not show any well expressed trends of changes within the peat profiles. Carboxylgroup concentration is lower in the humic acids from uppermost peat layers and can reach even values > 6 mEq $g^{-1}$ in humic acids isolated from peat with higher decomposition degree.

Concentration distribution of major and trace elements between peat and humic acids isolated from peat significantly differs depending on the element (Fig. 3): if concentrations of several elements (supposedly of natural origin such as Ca, Fe, K, Mn) in peat are higher than in humic acids, then concentrations of other elements (supposedly of anthropogenic origin such as Pb, As, Cr, Ni, Cu) are higher in humic acids than in peat. Comparison of element concentrations in humic acids found in our study and in other humic acids samples, including reference samples Waskish and Pahokee indicates the major importance of the source on the element on its presence in humic acids. Highest major and trace element concentrations were common for humic acids isolated from sea sediments. In humic acids isolated from peat, major and trace element concentrations depend on their presence in natural bog environment (for example, relatively high variability of Fe, Br, Zn, Ti), however concentrations of elements associated with recent human pollution are at relatively similar level. Major and trace element concentration changes in humic acids from peat profiles from studied bogs follow to general patterns: a) elements with increased concentrations in humic acids from upper layers of bog (Zn, Pb, Ni, Cr, Cu), b) elements with increased concentrations in humic acids from the bog bottom (Fe, Ca, Mn, Mg) and c) elements with elevated concentrations in bottom and upper layers in the humic acids in respect to their concentration in the middle part of the bog (K, As). Similar major and trace element accumulation pattern was previously found to be common for raised bogs and can be interpreted as accumulation of metals due to anthropogenic pollution in the upper layers, due to supply with groundwater from the bottom of the bog.

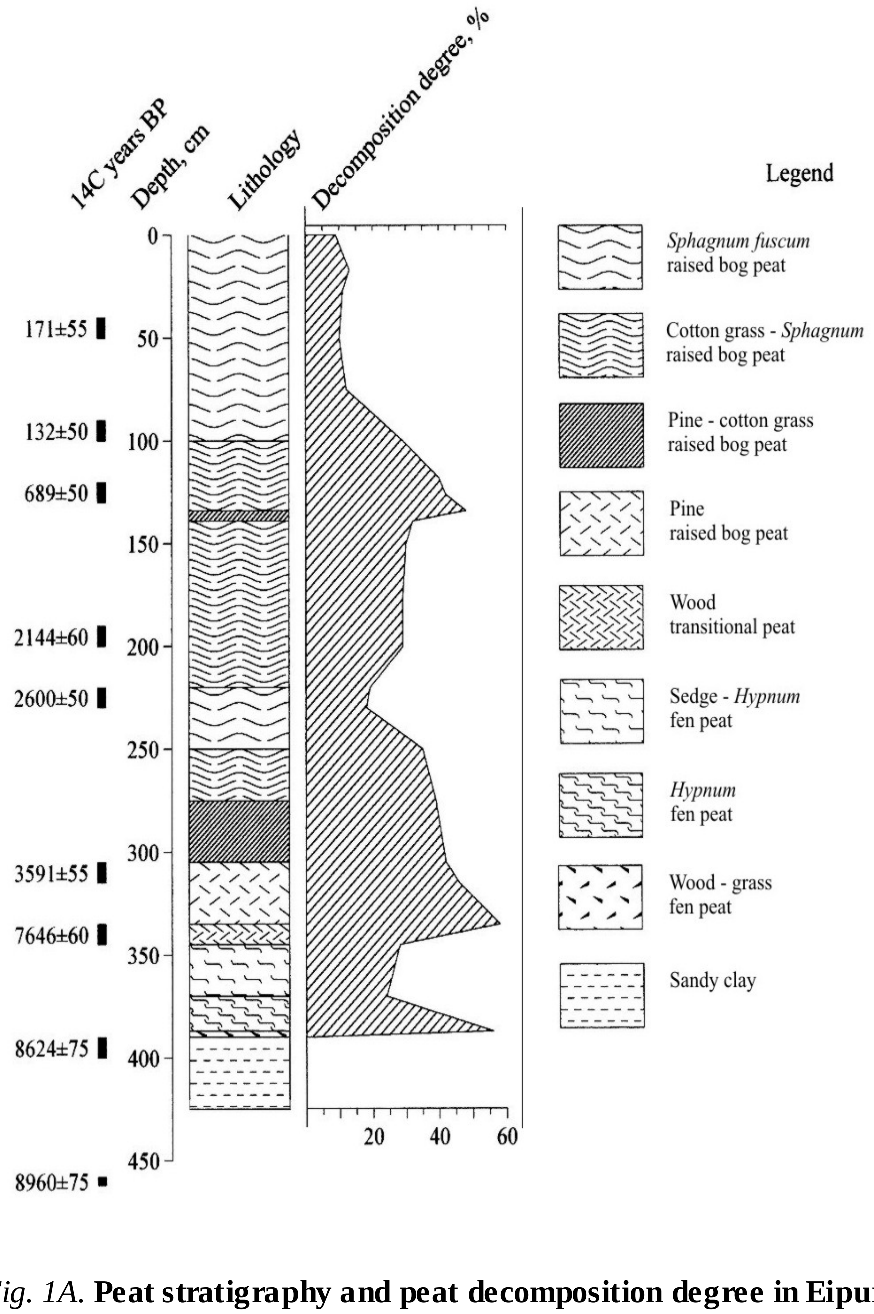


*Fig. 1A.* **Peat stratigraphy and peat decomposition degree in Eipurs bogs**

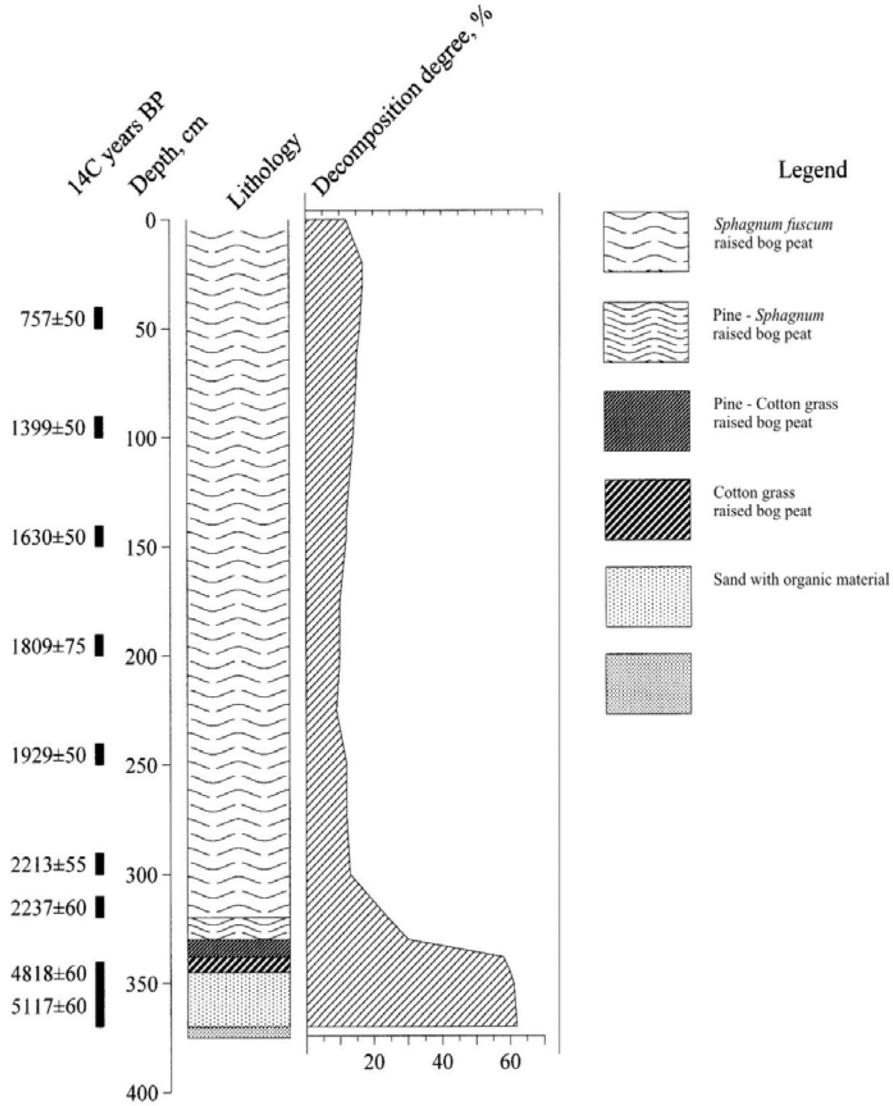


*Fig. 1B.* **Peat stratigraphy and peat decomposition degree in Dzelves bogs**

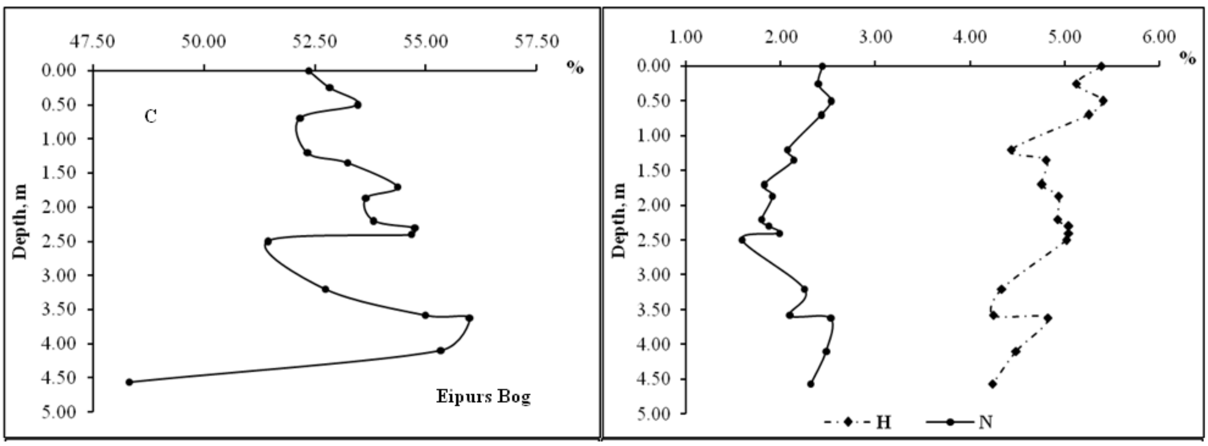


*Fig. 2A.* **Elemental composition of humic acids from Eipurs bogs**

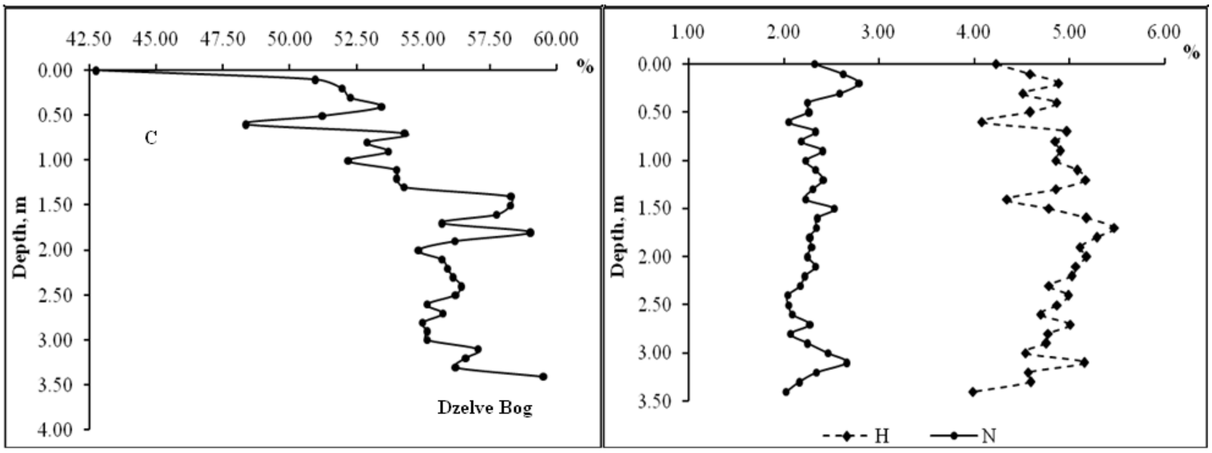


*Fig. 2B.* **Elemental composition of humic acids from Dzelve bogs**

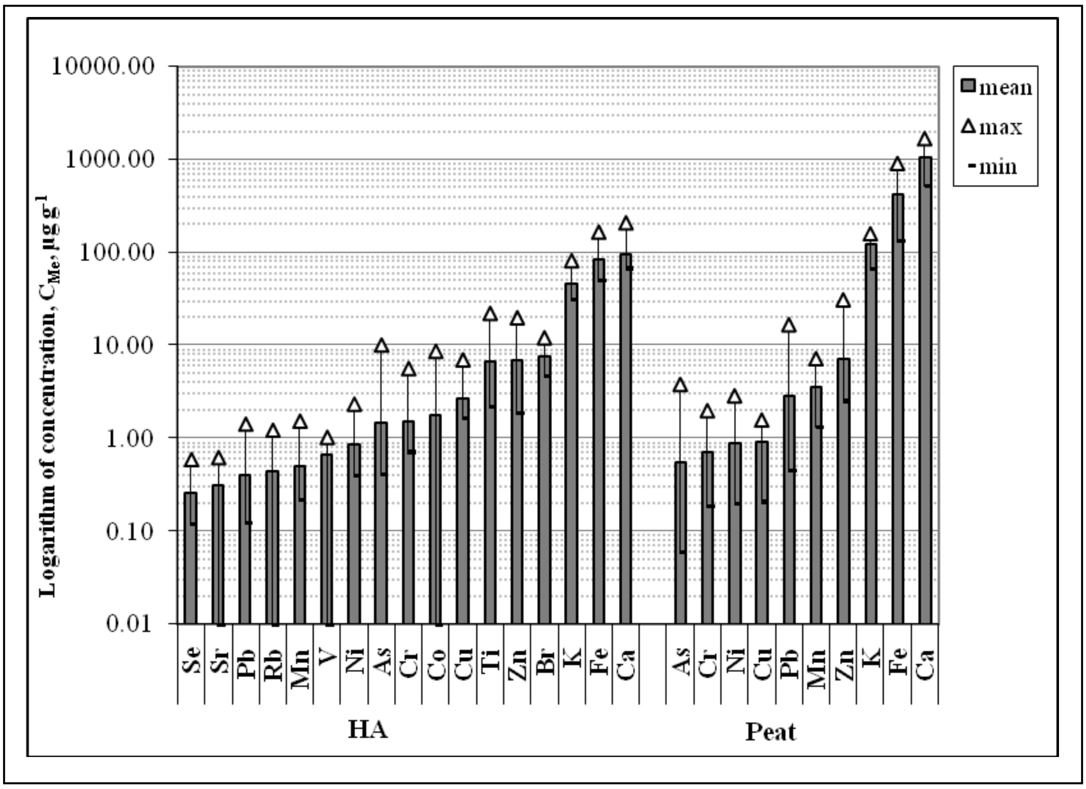


*Fig. 3.* **Concentrations (µg $g^{-1}$) of major and trace elements in peat and humic acids of Eipurs and Dzelve Bog**

## Conclusions

Eipurs and Dzelve Bog are located in lowlands, they are of similar origin (they developed due to ground paludification), but they have largely differing lithology. Both bogs are typical raised bogs and not presently, nor historically have not been affected by direct pollution sources. Data show that the iron concentration in peat bog Eipurs increases with increasing depth of peat, while metal (Fe, As, Ca, Cu) concentrations have high values of the depth range 3.5 m - 4 m in Eipurs bog peat and humic substances. Ammount of carboxylic groups in HAs significantly correlates with decomposition degree of peat. Fen peat and ombotrophic peat which formed from sedge and pine-cotton-grass shows higher decomposition level.

**References**


1. Fuchsman, C.H. Peat: Industrial Chemistry and Technology. Academic Press: N.Y., 1980.
2. Shotyk, W., Weiss, D., Appleby, P.G., Cheburkin, A.K., Frei, R., Gloor, M., Kramers, J.D., Reese, S., van der Knaap, W.O. History of atmospheric lead deposition since 12,370 $^{14}C$ yr BP from a peat bog, Jura Mountains, Switzerland. Science 281, 1998, p.1635 – 1640.
3. Shotyk, W. The chronology of antropogenic, atmospheric Pb deposition recorded by peat cores in three minerogenic peat deposits from Switzerland. The Science of the Total Environment 292, 2002, p. 19 – 31.
4. Orru H., Orru M. Sources and distribution of trace elements in Estonian peat. Global and Planetary Change 53, 2006, p. 249 – 258.
5. de Vleeschouwer, F., Gerard, L., Goormaghtigh, C., Mattielli, N., le Roux, G., Fagel, N. Science of the Total Environment 377, 2007, p. 282 – 295.
6. Gondar, D., Lopez, R., Fiol, S., Antelo, J.M., Arce, F. Characterization and acid–base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. Geoderma 126, 2005, p. 367–374.
7. Zaccone, C., Miano, T.M., Shotyk, W. Qualitative comparison between raw peat and related humic acids in an ombrotrophic bog profile. Organic Geochemistry, 38, 2007, p. 151 – 160.
8. Zaccone, C., Cocozza, C., Cheburkin, A.K., Shotyk, W., Miano, T.M. Distribution of As, Cr, Ni, Rb, Ti and Zr between peat and its humic fraction along an undisturbed ombrotrophic bog profile (NW Switzerland). Appl. Geochem. 23, 2008, p. 25 – 33.
9. Zaccone, C., Soler-Rovira, P., Plaza, C., Cocozza, C., Miano, T.M. Variability in As, Ca, Cr, K, Mn, Sr, and Ti concentrations among humic acids isolated from peat using NaOH, $Na_4P_2O_7$ and NaOH+$Na_4P_2O_7$ solutions. Journal of Hazardous Materials 167(1/3), 2009, p. 987 – 994.
10. Stevenson, F. J. Humus chemistry. N.Y.: J.Wiley, 1982.
11. Aiken, G.R. Isolation and concentration techniques for aquatic humic substances. In: Aiken, G.R. et al. (Eds.), Humic substances in soil, sediments and water, N.Y.: Wiley, 1985.
12. Falkowski, P., Scholes, R.J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K., Hogberg, P., Linder, S., Mackenzie, F.T., Moore, B., Pedersen, T., Rosenthal, Y., Tan, K.H. Humic matter in soil and the environment: Principles and Controversies. N.Y.: Marcel Dekker, 2003.
13. Tipping, E. Cation Binding by Humic Substances, Cambridge University Press, 2002.
14. Davies, G., Fataftah, A., Cherkasskiy, A., Ghabour, E.A., Radwan, A., Jansen, S.A., Kolla, S., Paciolla, M.D., Sein, L.T., Buermann, W., Balasubramanian, M., Budnick, J., Xing, B. Tight metal binding by humic acids and its role in biomineralization. J.Cham.Soc.Dalton Trans., 1997, p. 4047 - 4060.
15. Zhou, P., Yan, H., Gu, B. Competitive complexation of metal ions with humic substances. Chemosphere 58, 2005, p. 1327 - 1337.
16. Pourret, O., Davranche, M., Gruau, G., Dia, A. Rare earth elements complexation with humic acid. Chem. Geol. 243, 2007, p. 128 – 141.
17. Riise, G., Salbu, B. Major and trace elements in standard and reference samples of aquatic humic substances determined by instrumental neutron activation analysis (INAA). Sci. Total Environ. 81/82, 1989, p. 137 – 142.
18. Fengler, G., Grossman, D., Kersten, M., Liebezeit, G. Trace metals in humic acids from recent Skagerrak sediments. Marine Pollution Bulletin 28, 1994, p. 143 - 147.
19. Kuske, E., Silamikele, I., Kalnina, L., Klavins, M. Peat formation conditions and peat properties: a study of two ombrotrophic bogs in Latvia. In: Klavins, M. (Eds.), Mires and peat. Riga, University of Latvia Press, 2010, p. 56.
20. Silamikele, I., Nikodemus, O., Kalnina, L., Purmalis, O., Sire, J., Klavins, M. Properties of peat in ombrotrophic bogs depending on the humification process. In: Klavins, M. (Eds.), Mires and peat. Riga, University of Latvia Press, 2010, p. 71.
21. Krachler, M., Shotyk, W., Emons, H. Digestion procedures for the determination of antimony and arsenic in small amounts of peat samples by hydride generation – atomic absorption spectrometry. Anal. Chim. Acta 432, 2001, p. 303 – 310.
22. MacCarthy, P. A proposal to establish a reference collection of humic materials for interlaboratory comparisons", Geoderma 16, 1976, p. 179-181.
23. Tan, K.H. Principles of soil chemistry. Marcel Dekker, Inc., New York, NY, 1982.
24. Schnitzer, M. Organic matter characterization. In: Miller, R.H., Keeney D.R. (Eds.), Methods of soil analysis. *Agronomy series* No. 9. American. Society of Agronomy, Madison, W.I., 1982, p. 581 – 594.
25. Cabaniss, S.E. Synchronous fluorescence spectra of metal-fulvic acid complexes. Environ. Sci. Technol. 26, 1992, p. 1133 – 1139.

# PHOSPHORUS REMOVAL WITH GRASS IN AN APPLE ORCHARD UNDER INFLUENCE OF MULCH AND IRRIGATION

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**Abstract.** *Phosphorus leaching from intensive agriculture systems is one of major contributors responsible for pollution of ground-water and surface water bodies. The aim of this study was to determine the content of phosphorus in orchard lawn for reduction of phosphorus fertilizer application and to include the phosphorus from mown grass into P balance and turnover calculation. The investigation was done at the Latvia State Institute of Fruit–Growing in 2009. Three treatments were compared: control, mulch and fertigation. Inter-row strips were covered by grass vegetation. Grass samples were collected at the time of grass mowing. The removal of phosphorus was calculated as kilograms per hectare area. The concentration of phosphorus in the lawn and the height of grass growth were significantly influenced by the mowing time and the soil moisture treatment. These results can be a base for further studies of phosphorus turnover in an orchard, as well as for fertilizer planning and management.*

**Keywords:** *Malus domestica Mill., mineral nutrition, nutrient uptake.*

## Introduction

Phosphorus requirement of apple-trees is lower compared with field crops [1], but it is essential for the provision and transfer of plant genetic information. Phosphorus takes part in plant metabolism, respiration, photosynthesis, facilitates fertilization of flowers. Lack of phosphorus has negative effect on the growth and development of plant reproductive organs (seeds), as well as vegetative parts – trunk, leaves [2, 3]. Phosphorus is also important to sustain soil fertility. Stable, high quality yield can be obtained only providing plants with all necessary nutrients including phosphorous. The main task of fertilization is to compensate that part of plant nutrients which is necessary for plants to secure high yield of prime quality but which can not be provided by the soil. Fertilizing compensates the loss of nutrients from soil which are removed with the harvested yield, pruned branches, leached out from root zone as well as through other losses. Fruit growers constantly try to increase the quantity and quality of the yield which may lead to surplus addition of phosphorus to soil. Although phosphorus movement in soil is relatively slow [4] yet over fertilization can create environment pollution risk as well as unbalanced supply and chemical fixation of micronutrients.

Lack or surplus accumulation of phosphorus in soil greatly depends on the farming methods and growing technologies. It has been found that at farms where fruit remains are mashed and ploughed in (if possible), the total loss of phosphorus is significantly lower, because phosphorus returns to the circulation [5]. The rapidly increasing price of mineral fertilizers stimulates the producer, without loss of yield and income, to choose more rational growing technologies with a suitable fertilization system. If the mown grass is left in the orchard, not only the nutrients come back to the turnover, but also the content of humus in the soil will increase. Thus the buffer capacity of soil increases which in turn preserves nutrients from leaching, as well as improves soil aeration so influencing positively not only the growth of apple-tree roots, but also microbiological processes in soil, increasing and preserving sustainable soil fertility. This has become especially important during the latest years, with

serious concern for environment and development of organic and integrated fruit growing where mineral fertilizers are used as little as possible.
To provide the practical information for fertilizer planning it is necessary to clarify quantity of phosphorus found in the mown grass depending on technologies used for water supply – mulching of soil around trees or establishment of irrigation systems, which may significantly influence the grass biomass as well as concentration of phosphorus in grass.

## Materials and methods

The investigation was carried at the Latvia State Institute of Fruit-Growing, Dobele, in 2009. A field trial in three replications was set up on the basis of an orchard established in 1997, for cultivar 'Melba' on rootstock B9 (planting pattern 1.5 × 4 m). Three kinds of soil water treatment in tree strips were compared: (1) control - no water regulation; (2) sawdust mulch and (3) fertigation, e.g., drip irrigation with fertilizer additives. In the mulching treatment soil surface was covered with a 10 - 20 cm layer of sawdust which was renewed every three years. In the irrigation treatment 'Den' type pipelines with built-in drippers spaced 0.38 cm apart were used. The irrigation provided effective moistening of a 1 m wide zone in sandy loam soil, which makes about 25% of orchard area.
For the lawn sown in the inter-row strips *Lolium perenne* L. and *Poa pratensis* L. in proportion 1:3 were used. The tree strip in the control and drip irrigation treatments was 1 m wide, and during the growth season it was maintained free from grasses. The inter-row strips were 3 m wide. The grass during the experiment was mown regularly (3 - 5 times per season). The apple-trees were trimmed as a slender spindle. The average yield was 20 t $ha^{-1}$ annually.
Soil of the experimental plot was Pisocalcic Cutanic Luvisol (Hypereutric, Hyposkeletic, Clayic) [WRB, 2006], fine sandy loam/loam. Organic matter content in soil was 25 g $kg^{-1}$ (according to Tyurin method, wet combustion), soil reaction was pH 6.5 (in 1*M* KCl suspension, potentiometrically). Plant-available $P_2O_5$ was 300 mg $kg^{-1}$ and $K_2O$- 190 mg $kg^{-1}$, MgO- 162 mg $kg^{-1}$ (according to Egner - Rheem or DL method). This type is typical automorphic soil with relatively good water storage and water supply capacity.
Grass samples were collected during cutting, 3 times per season of 2009: May 20, June 21 and August 11. From the start of the growth season till May 19 the average air temperature was 13.6 $^{o}$C, precipitation 9.3 mm, till June 21 – 14.8 $^{o}$C and 93 mm, till August 11 – 18 $^{o}$C and 96 mm correspondingly. Grass samples were collected at distances of 0 – 15 cm, 15 – 30 cm and 30 – 45 cm from the grass-free tree strip. During each sampling the height of grass growth was measured.
Grass samples were dried, they were dry-matter content in % (ISO 6496). Chemical analyses of grass samples were carried out determining the phosphorus (colorimetrically) content in the ash extract, evaluate as % of dry matter (ISO 6491). The removal of nutrients was calculated as kilograms per hectare area (kg $ha^{-1}$).
The results of the investigation were analyzed using dispersion analysis ANOVA, as well as descriptive statistics (Descriptic statistic). To compare the data from two sample groups the Fisher criterion was used.

## Results and discussion

Soil moisture management positively influenced growth of grass in inter-row strips. The applied moisture treatments and mowing time significantly influenced the height of grass growth ($p$ <0.05) (Fig.1).

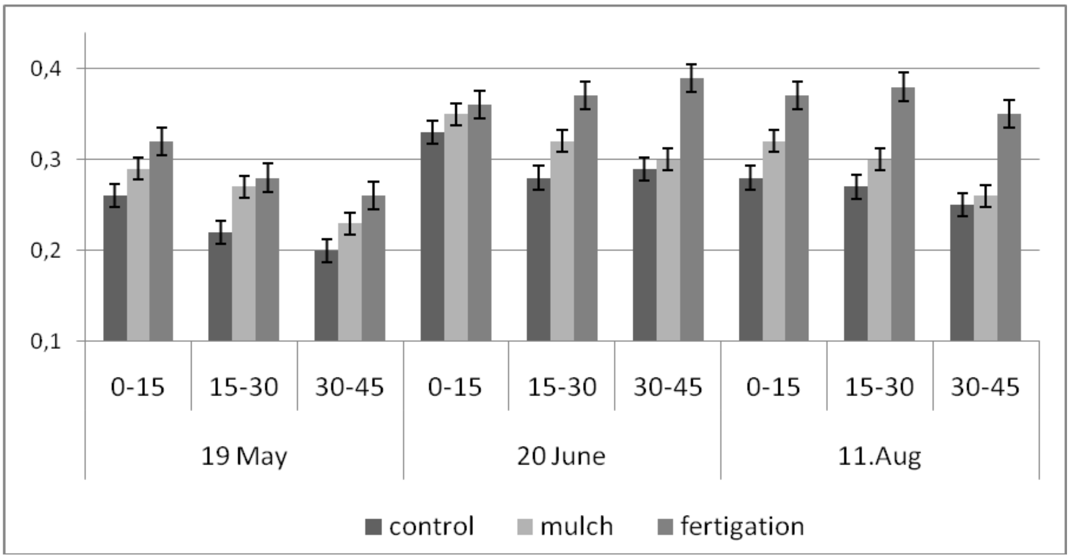


*Fig. 1.* **Height of grass growth at different distances from the tree strip depending of moisture treatment and mowing time, cm**

During the first mowing of grass, the growth at 0 - 15 cm distance from the tree strip was higher in the fertigation treatment and the shortest – in the control treatment, this difference was statistically significant. A similar situation was observed also at 30 - 45 cm distance from the tree strip. At 15 - 30 cm from the tree strip the shortest growth also was in the control treatment, but the growth in mulch and fertigation treatments did not differ significantly. Yet significant influence of fertigation on grass growth in these variants was found during the second and third cutting time. This means that the influence of fertigation may appear later, besides, it must be taken into account that from the beginning of vegetation till the first mowing the precipitation was very low, which can explain the significantly lower grass growth in the control treatment. It is possible that in the control treatment the uptake of nutrients was limited as a result of the drought, as also shown by other investigations [6].

During the second cut, no significant differences between treatments were found at 0 - 15 cm from the tree strip. This may be explained by the fact that fertilizer was applied in the tree strips at the beginning of the growing season. By increase of precipitation, the fertilizer uptake by grass near to the tree strip was facilitated in comparison with the first mowing time. At 15 - 45 cm from the tree strip significantly higher grass growth was found in the fertigation treatment, while in control and mulch treatments the results showed no significant difference.

During the third cut significant differences were found between treatments at 0 - 15 cm from the grass-free tree strip. This can be explained by the positive effect of mulch and fertigation on soil moisture, as well as by the relatively high air temperature during this period. Besides, in all treatments a certain tendency was observed – along with increase of distance from the tree strip, the grass growth decreased. These differences may be the result either of the applied soil moisture treatment or the specifics of fertilization in an orchard. Fertilizer was not applied in the whole area, but only in the tree strips, which means that closer to the tree strips the inter-row grass growth could receive more nutrients along with increased uptake due to higher moisture and temperature.

The results of the investigation showed that the concentration of phosphorus in the grass grown in orchard alleyways was influenced by the applied soil moisture regulation treatments – sawdust mulch and fertigation ($n$ = 54, $p$ < 0.05) (Fig.2).

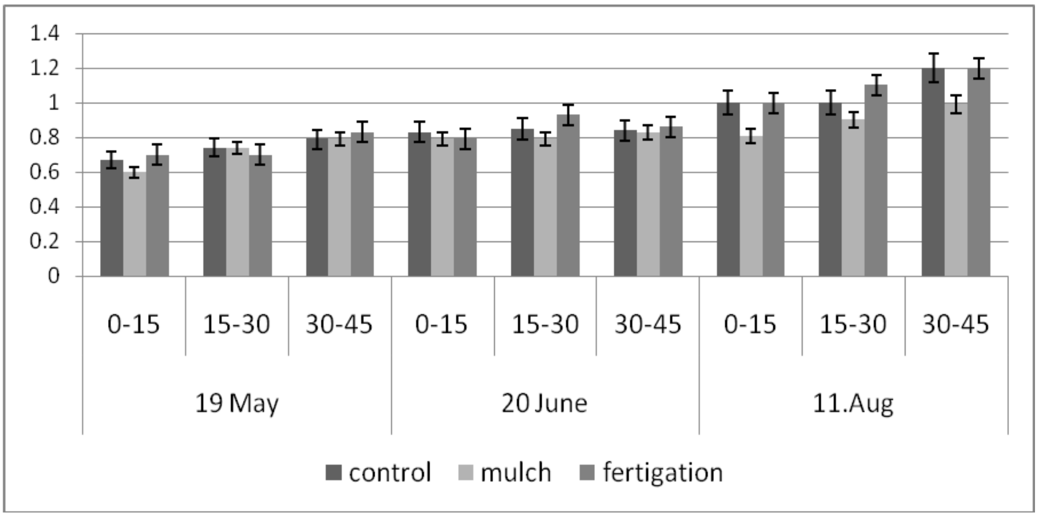


*Fig. 2.* **Content of $P_2O_5$ in grass dry matter at different distances from the tree strip depending on moisture treatment and cut time, mg $kg^{-1}$**

The concentration of phosphorus in grass was the lowest during the first cut. At 0 - 15 cm from the tree strip the lowest phosphorus content was found in the mulch treatment. By increase of the distance from the tree strip, there was a tendency of phosphorus concentration increase in the grass, but significant difference was found only between 0 - 15 cm and 30 - 45 cm zones.

During the second cut, the concentration of phosphorus in grass was higher by 8 - 12%, yet no significant differences were found between the first and third mowing times ($p > 0.05$). The relative increase of phosphorus concentration may be explained by changes in precipitation and temperature during this period. The average air temperature increased for 1.2 °C. Changes in phosphorus concentration did not correlate with changes of precipitation, the latest increased even 10-fold during this period. Insignificant changes may be explained by the relatively slow movement of phosphorus in soil and plants [7, 1], which is witnessed by the content of phosphorus during the third grass cut.

During the third cut the content of phosphorus in grass was by 10% higher than during the first cut and 20% higher than during the second cut. The differences were significant ($p < 0.05$). During the third cut the phosphorus content in grass had a tendency to increase along with the distance from the tree strip. In the mulch treatment the content also increased this way, but it was lower at all distances from the tree strip in comparison with the control and fertigation treatments. It is possible that mulching of the tree strips with sawdust increased soluble aluminium compound content in soil (as this treatment had lower soil pH), while at the same time forming of non-soluble phosphorus compounds increased which are difficult for plant uptake [7, 1]. The results comply with former investigations which founded that for the formation of one ton of grass dry matter about 7.3 kg of phosphorus is needed [8].

Still it is not possible to ascertain that the concentration of phosphorus in the lawn grass was influenced only by the mowing time. Theoretically the concentration of phosphorus in plants should decrease during the growth season [9], but in this study it was an opposite – the concentration increased. These contradictions may be explained by the fact that the grass was cut down several times during the season and so not allowed to go through all development stages, also it was not in the same stage of development during all mowing times. In the grass mown on May 20 the grasses had already reached beginning of flowering, but on August 11 the mown grass was at a much earlier stage. Yet the development stages of grass were not different among moisture regulation treatments.

The concentration of phosphorus could be influenced not only by air temperature and precipitation during the growth of grass, but also other factors. Yet at all mowing times there was observed a tendency of mulch reducing the phosphorus concentration in the lawn.

*Table 1.*

**Grass biomass and phosphorus uptake, kg ha$^{-1}$**

| Time of grass mowing | Treatment | | | | | |
|---|---|---|---|---|---|---|
| | control | | mulch | | fertigation | |
| | biomass, kg ha$^{-1}$ | $P_2O_5$ removal, kg ha$^{-1}$ | biomass, kg ha$^{-1}$ | $P_2O_5$ removal, kg ha$^{-1}$ | biomass, kg ha$^{-1}$ | $P_2O_5$ removal, kg ha$^{-1}$ |
| 1 | 282.40$^{a}$ | 1.98$^{a}$ | 365.50$^{b*}$ | 2.56$^{ab*}$ | 359.33$^{b*}$ | 2.52$^{ab}$ |
| 2 | 443.54$^{b}$ | 3.55$^{b*}$ | 503.39$^{c*}$ | 4.03$^{bc}$ | 542.12$^{c*}$ | 4.88$^{d*}$ |
| 3 | 494.27$^{c}$ | 4.45$^{c*}$ | 503.48$^{c}$ | 3.52$^{b}$ | 567.69$^{c}$ | 3.97$^{c}$ |
| Per season kg ha$^{-1}$. | 1220.21 | 9.98 | 1372.38 | 10.11 | 1469.14 | 11.37 |

a, b, c, d, e, f, – significantly different within columns ($p < 0.05$)

*– significantly different within rows ($p < 0.05$)

Although the phosphorus concentration in the control and fertigation treatments was significantly higher than in the mulch treatment (Figure 1), still the total removal of phosphorus with mown grass was the lowest in the control treatment, besides, it significantly differed from the 13% higher phosphorus removal in the fertigation treatment. In the mulch treatment phosphorus removal was 2% higher than in the control treatment, which was not statistically significant ($p > 0.05$). Such differences were observed because the biomass of the mown grass significantly varied between moisture regulation treatments and mowing times. Till May 20 when the grass was cut for the first time, the precipitation since the start of growth season was only 9.3 mm, therefore in the fertigation and mulch treatments where the soil moisture conditions were presumably better the grass biomass was higher. These results comply with the results of other researchers showing that plant biomass significantly increases when fertigation is used [10].

No similar studies have been done in Latvia, so there are no data about the speed of the decomposition of cut grass and return of phosphorus into the natural turnover, but researchers in other countries [11, 12] have found that phosphorus returns into circulation already 1 – 2 years after grass mowing. Besides it has been investigated [13, 14] that throwing of cut grass onto the tree strips significantly increases the amount of organic matter in soil, which is favourable for the phosphorus turnover and availability to plants.

It should be added that the results of the study could be influenced by weather conditions and other uncontrollable factors, therefore here are only some tendencies discussed. Yet a similar investigation in Latvian conditions was performed for the first time, and the results may become a base for further studies of phosphorus turnover in an orchard as well as for fertilization planning.

## Conclusions

Mulching of tree strips in an apple orchard significantly reduced the concentration of phosphorus in the mown grass, as well as the height of the cut grass growth.

The phosphorus concentration in grass was significantly influenced by the time of cut during the growth season and the height of grass which in turn was determined by air temperature and precipitation, stage of vegetative development and other factors.

Annual removal of phosphorus with the biomass of cut grass in the control treatment was 9.98 kg $ha^{-1}$, in the mulch treatment it was 2% higher and in the fertigation treatment 13% higher ($p < 0.05$).


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## References


1. Neilsen G.H., Neilsen, D., Toivonen P.M. Effective P Fertigation Increases Yield and Quality of Fruit in High Density Apple. Frontiers of Soil Science. Technology and the Information Age. Procceeding of the 18th World Congress of Soil Science, Philadelphia (PA)/USA, 2006, p. 155–132.
2. Nosal K., Poniedzialek W., Kropp K., Porebski S. Effectiveness of Nitrogen and Potassium Fertilization of Apple Trees. Acta Horticulturae, No. 274, 1990, p. 211–214.
3. Fallahi E., Neilsen G. H., Peryea F. J., Neilsen D., Fallahi B. Effect of mineral nutrition on fruit quality and nutritional disirders in apple. Acta Horticulturae, No. 868, 2010, p. 49–59.
4. Raese J. T., Staiff D. C., Visser D. R.. Effect of nitrogen and phosphorus on 'delicious' apple trees grown in caliche soil in the greenhouse. Journal of Plant No. 7, 1984, p. 1433–1442.
5. Līpenīte, I., Kārkliņš, A. Plant Nutrient Balance Studies in Farms of Latvia VI. Farm `Tereni`. Proc. of the Latvia Univ. of Agr. No. 313(18), 2006, p. 9–16 (in Latvian).
6. Nicholas, P. Grape Production. Soil, Irrigation and Nutrition. South Australian Research and Development Institute, Adelaide, No. 2, 2004, p. 201.
7. Haynes J.R., Gog K.M. Distribution and Budget of Nutrients in a Commercial Apple Orchard. Plant and Soil, No.56(3), 1980, p. 445–457.
8. Līpenīte, I., Kārkliņš, A. Calculation of plant nutrient removal for the specification of normatives . Proc. of the Latvia Univ. of Agr. No.4, 2001, p. 35–39 (in Latvian).
9. Nurzinski, J., Kepta, M., Komosa, A., Kozera G. Seasonal changesof N, P, K, Ca and Mg content in apple tree leaves during vegetation period. Acta Horticulturae. No. 274, 1990, p. 365–373.
10. Hornig R., Bünemann G. Fertigation and controlled strip cover by weeds in apple orchrards. Acta Horticulturae, No. 335, 1993, p. 65–72.
11. Shenzuo, F., Huayong, L., Baodong, X. Decomposition and nutrient release of four potential mulching materials for poplar plantations. Agrof. Syst. No. 74, 2008, p. 27–35.
12. Tagliavini, M., Tonon, G., Scandellari, F., Quinones A., Palmieri S., Menarbin G., Gioacchini, P., Masia, A. Nutrient recycling during the decomposition of apple leaves (Malus domestica) and mowed grasses in an orchard. Agr. Ecosyst. & Environ. No. 118, 2008, p. 191-200.
13. Cazzato, E., Anesse, V., Colreto, A. Effects of clipping management on some aspects of tall fescue (Fescue arundinacea) turf. Acta Horticulturae. No. 661, 2004, p. 301–307.
14. Eason W.-R, Newman E.-I., Chuba G.-H., Specificity of interplant cycling of nutrients: the role of mycorrhizas. Plant Soil.V.137, 1991, p. 267–274.

# CASE STUDY ON THE RELATIONSHIPS BETWEEN SOIL CONTENTS OF SOME HARMFUL CHEMICAL ELEMENTS DETERMINED BY DIFFERENT EQUIPMENT

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**Abstract.** *Comparison of total contents of Ba, Cr, Cu, Mn, Mo, Ni, Sn, Pb, V, Zn, Al, Ca, Fe, Mg determined in topsoil of central part of Vilnius by optical atomic emission spectrophotometry (OAES) with respective contents determined by energy-dispersive x-ray fluorescence (EDXRF), analysis of their correlation and linear relationship with and without outliers are the tasks of research. For most elements, except Ca, Sn, Ba, the contents determined by EDXRF are significantly lower and less variable. They can be predicted according to OAES-contents using linear equations. After elimination of outliers for all elements the correlation is significant at p<0.05.*

**Keywords:** *optical atomic emission spectrophotometry, energy-dispersive x-ray fluorescence, urban soil, chemical elements.*

## Introduction

Until 2007 all geochemical investigations at the Institute of Geology and Geography (IGG) were based on the total contents of trace elements determined by optical atomic emission spectrophotometry (OAES) using DFS-13 equipment. This equipment was used both for determination of soil background values [1-4] and for urban geochemical mapping [5-8]. So the results obtained in IGG before 2007 can be compared. In urban topsoil investigations the following potentially toxic trace elements were usually determined: Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn. Since 1997 the laboratory has been participating with OAES in "International Soil-analytical exchange" (ISE) program organised by Wageningen University. In 2007 new energy-dispersive x-ray fluorescence (EDXRF) equipment SPECTRO XEPOS was purchased and IGG started to participate in ISE with EDXRF. Using TURBOQUANT calibration method for pressed pellets the total contents of chemical elements from Na to U can be determined.

Aiming to compare the results obtained by EDXRF and OAES equipment, it is necessary to re-analyse old samples by EDXRF. Case study of the relationships between urban soil contents of Ba, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, Zn, determined by OAES (OAES-contents) and EDXRF (EDXRF contents) is the object of this research. The relationships between OAES-contents and EDXRF-contents of major elements Al, Fe, Ca, Mg are also analysed.

## Materials and methods

Composite topsoil samples were taken in 2006 from 141 site in central part of Vilnius. Each sample was gathered by collecting 20-25 similar mass increments, homogenised and reduced to 1 kg. Then the samples were sieved through 1 mm sieve, ashed at 300-350$^{0}$C and milled. OAES-contents of 13 trace and 4 major elements (Al, Ca, Fe and Mg) were determined by vaporization of 0.5 g of fine-milled soil at 5000-6000$^{O}$C in the electric arc between three graphite nails; determination was done by optical spectrophotometer DFS 13. The results obtained by this type of analysis have been already discussed analysing the distribution of harmful trace elements both in the oldest part of Vilnius [9] and in younger districts [10].

In 2010 real total contents of large group of major or trace elements were determined in the same samples by EDXRF [11]. Sample preparation for this analysis was as follows: the sieved samples were milled with MM 400, homogenised with Licowax (4 g of sample and

0.9 g of wax) and pressed with PP15 press into 32 mm pellets. The primary content of chemical elements in each pellet was determined using SPECTRO XEPOS equipment and TURBOQUANT for pressed pellets calibration method. Total number of measurements was 282, as for each sample two pellets were prepared. The contents of almost all the elements, which are the object of this research, were above their DL in all pellets, the only exception was Mo: in 74.4% of pellets its content was below DL. Great part of undefined measurements of Mo was a serious obstacle for comparison of its results obtained by two methods. In order to have database without missing values, the value 0.1 ppm was inserted for primary measurements of those pressed pellets where Mo content was below DL. Median content of each element in each sample was calculated according to measurements of two pellets. The primary median measurement values in each sample were recalibrated using 44 ISE reference samples, CRM 2709 and CRM 2711. In all cases, except Al, linear regression was used for this aim with coefficient of determination higher than 0.9.
The estimates of relative standard measurement uncertainties for the mean contents of 10 trace elements $U_m$ (%) determined by different equipment are given below. For EDXRF, these values ($U_{m\text{-}EDXRF}$) were estimated according to 56 (for Mo 46) repeated measurements of CRM 2709 during the first quarter of 2010. $U_{m\text{-}EDXRF}$ values of 14 trace and 10 major elements did not exceed 5%, though respective uncertainties for individual measurements ($U_{ind\text{-}EDXRF}$) were higher and for V, Sn, Mo exceeded 5% [11]. As concerns trace elements of this research, $U_{m\text{-}EDXRF}$ values were the following: Zn(0.09), Mn(0.11), Ni(0.15), Pb(0.28), Ba(0.31), Cu(0.50), Cr(0.5), V(0.81), Mo(4.96), Sn(1.66). For OAES, the $U_{m\text{-}OAES}$ values (%) were estimated in 2004 according to 22 repeated measurements of another sample (ISE No.921). All these values were also below 5%. Though element contents in CRM 2709 and ISE No.921 differ and this can influence repeatability, preliminary comparison of $U_m$ values was done. It showed that for most trace elements $U_{m\text{-}OAES}$ values were higher than $U_{m\text{-}EDXRF}$: Zn (11 times), Mn(7.28 times), Ni(6.97 times), Pb(3.69 times), Ba(2.48 times), Cu(2.09 times), Cr(2.01 times), V(1.05 times). Only for 2 elements from 10 they were lower than the values of $U_{m\text{-}EDXRF}$: Mo(4.65 times), Sn(1.63 times). Though in regression models usually more precise variables are taken as independent, namely OAES-content was chosen as independent variable because the number of soil samples in Lithuania analysed by EDXRF is still low, besides, for Mo and Sn the $U_{m\text{-}OAES}$ are lower. The latter 2 elements as well as Cr and V are characterised also by the highest joint uncertainty from trace elements of this research (arising during EDXRF measurement and sample preparation), this uncertainty exceeds 5% [11]. According to increasing joint uncertainty the elements are arranged as follows: Al(0.95) <Fe(1.13) <Zn(1.79) <Mn(1.90) <Mg(2.03) <Ba(2.26) <Ca(2.50) <Ni(3.29) <Cu(3.86) <Pb(4.10) <Sn(6.14) <Cr(10.3) <V(15.0) <Mo(66.7).
To reveal for each chemical element the differences between 2 variables measured in the same samples (OAES-content and EDXRF-content), two non-parametric tests were used: Sign test and Wilcoxon matched pair test. Pearson correlation coefficients were determined between OAES-content and EDXRF-content. Linear regression model (a – coefficient before independent variable, i.e. slope, b – intercept) was used to find out the relationships between these contents. The suitability of this model was checked according to p-value of F-test in ANOVA table. To test the null-hypothesis that regression parameters do not differ from zero, p-values of t-test were checked. The level of significance in all tests was 0.05. If p-values of F-test and t-test are lower than 0.05, the linear equations can be used for prediction of EDXRF-contents according to OAES-contents. When analysing the relationships between different contents, the outliers were revealed and eliminated. There were two consecutive stages of elimination of outliers. The first one was elimination of considerable outliers. The sample measurement (case) was supposed to be considerable outlier, when at least one of 3 criteria was fulfilled: 1) absolute value of standard residual of this case was higher than 3

[12]; 2) Cook's distance exceeded the critical value (as the number of cases was always higher than 120, the $F_{0.5}(2, \infty)=0.693$ was chosen [12]); 3) there was noticeable deviation of this case from the line y=x in the graph "residual versus deleted residual". The second stage (realised after the first stage) was elimination of inconsiderable outliers, i.e. the cases for which the value of standard residual was in the interval [2-3] or which were characterized by less noticeable deviation from the line y=x in the graph "residual versus deleted residual". Higher standard residuals indicate cases with the deviation from regression line. Both Cook's distance and deleted residual are measures of impact of the respective case on the regression equation. Cook's distance indicates the difference between the computed values of slope and the values one would have obtained, had the respective case been excluded. If it exceeds critical value [12], there is reason to believe that the respective case biased the estimation of the regression coefficients. If the deleted residual differs greatly from the respective residual value (this can be seen from the graph), then this case is possibly an outlier because its exclusion changed the regression equation. The minimum and maximum values of OAES-content and EDXRF-content were determined according to all data, according to data after the first stage and after the second stage of elimination.

## Results and discussion

The contents of 11 chemical elements determined by EDXRF are lower than respective contents obtained by OAES. For Al, Fe, Mn and Ni this regularity is observed in all samples (Table 1). For other 7 chemical elements the percentage of samples where the content determined by EDXRF is lower than the content determined by OAES exceeds 50%, according to this percentage the latter elements are arranged as follows: V(99.3)>Mg(95.7)>Cr(95.0)>Pb(91.5)>Cu(90.1)>Mo(88.7)>Zn(85.1). These 11 chemical elements are characterized by higher median OAES-content than median EDXRF-content, all of them, except Pb and Cu, have also higher maximum AOES-content than maximum EDXRF-content.

Only Ca, Sn and Ba are distinguished by the opposite regularity, i.e. higher percentage of samples where OAES-content is lower than EDXRF-content. The opposite tendency is especially characteristic of Ca, which has lower median OAES-content than median EDXRF-content and lower maximum OAES-content than maximum EDXRF-content. For almost all chemical elements there are significant ($p<0.05$) differences between OAES-content and EDXRF-content both according to Sign test and according to Wilcoxon matched-pairs test. For Ba the differences according to both tests are insignificant, for Sn they are insignificant according to Sign test.

For most chemical elements (except Cu, Pb and V) the variation coefficients of OAES-contents are higher than of EDXRF-contents.

For all trace elements Pearson correlation coefficients R between OAES-contents and EDXRF-contents are significant ($p<0.05$) both before and after elimination of outliers though not all coefficients of determination $R^2$ are higher than 0.25 (Table 2). For example, Mn has low $R^2$ both before and after elimination of outliers, Ba and V – after elimination of outliers. Trace elements in Table 2 are arranged according to decreasing $R^2$ (and R) values of linear regression obtained according to data without elimination of outliers.

Linear regression analysis performed according to primary data of trace elements (without any elimination of outliers) as well as after elimination of outliers showed significant p-values of ANOVA F-test (the same as p-values of t-test for slope), also significant p-values for intercept.

In most cases the elimination of outliers according to deviations from line in the graph "residual versus deleted residual" is realised in the first stage, but for Mo, Pb and Cu also in the second stage.

*Table 1.*

**Comparison of chemical element contents obtained by OAES and EDXRF**

| El. | Md1 (ppm) | Md2 (ppm) | Mx1 (ppm) | Mx2 (ppm) | VK1 (%) | VK2 (%) | Md1/ Md2 | Mx1/ Mx2 | VK1/ VK2 | PL (%) | S | W |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ca | 19600 | 20600 | 46800 | 52000 | 34.3 | 32.6 | 0.95 | 0.90 | 1.05 | 36.2 | * | * |
| Mg | 7370 | 4900 | 114000 | 10100 | 115 | 25.3 | 1.50 | 11.29 | 4.54 | 95.7 | * | * |
| Al | 38000 | 20100 | 52300 | 27300 | 13.4 | 11.5 | 1.89 | 1.92 | 1.16 | 100.0 | * | * |
| Fe | 16000 | 8790 | 32800 | 23800 | 21.4 | 20.9 | 1.82 | 1.37 | 1.03 | 100.0 | * | * |
| Ba | 320 | 316 | 908 | 653 | 30.3 | 15.3 | 1.01 | 1.39 | 1.98 | 49.6 | ns | ns |
| Cr | 30.9 | 19.6 | 204 | 95.7 | 60.6 | 50.6 | 1.58 | 2.13 | 1.20 | 95.0 | * | * |
| Cu | 32.6 | 20.9 | 232 | 273 | 72.6 | 107 | 1.56 | 0.85 | 0.68 | 90.1 | * | * |
| Mn | 509 | 300 | 977 | 495 | 24.1 | 16.8 | 1.70 | 1.98 | 1.44 | 100.0 | * | * |
| Mo | 1.06 | 0.61 | 178 | 58.5 | 516 | 385 | 1.75 | 3.04 | 1.34 | 88.7 | * | * |
| Ni | 15.9 | 8.30 | 47.6 | 27.8 | 32.9 | 31.6 | 1.91 | 1.71 | 1.04 | 100.0 | * | * |
| Pb | 60.0 | 43.8 | 914 | 13100 | 108 | 770 | 1.37 | 0.07 | 0.14 | 91.5 | * | * |
| Sn | 5.09 | 6.14 | 49.9 | 38.0 | 81.7 | 58.7 | 0.83 | 1.31 | 1.39 | 41.8 | ns | * |
| V | 35.6 | 14.4 | 137 | 59.7 | 42.7 | 58.0 | 2.48 | 2.30 | 0.74 | 99.3 | * | * |
| Zn | 228 | 133 | 1000 | 530 | 66.7 | 59.3 | 1.71 | 1.90 | 1.13 | 85.1 | * | * |

Explanation: El. – chemical elements, Md1, Mx1, VK1 – median, maximum and coefficient of variation of OAES-content, respectively; Md2, Mx2, VK1 – median, maximum and coefficient of variation of EDXRF-content, respectively; Md1/Md2, Mx1/Mx2, VK1/VK2 – ratios of respective characteristics; PL – percentage of samples where EDXRF-content is lower than OAES-content; S, W – characterization of p values obtained by Sign test or Wilcoxon test (* – significant, i.e. $p<0.05$, ns – not significant). High contents are rounded.

Only for Cu, Sn and Mn consecutive elimination of considerable and inconsiderable outliers increases correlation between their OAES-contents and EDXRF-contents. For most trace elements (Mo, Zn, Pb, Cr, Ni, Ba, V) elimination of outliers leads to the oppose tendency.

This might be explained by fact that single outliers characterized by extremely high OAES-contents or EDXRF-contents can artificially increase the correlation. Obvious decrease of maximum values of both OAES-contents and EDXRF-contents after elimination of considerable outliers confirms this. For Pb, Mo, V, Cr this decrease is especially pronounced.

Elimination of inconsiderable outliers either does not change maximum values of OAES-contents and EDXRF-contents or changes them to a lower extent.

However, the second stage of elimination often leads to some increase of $R^2$ (and R) values, e.g. for Zn, Cr, Ni, Ba, V.

The question arises which linear regression equations should be used. On our opinion, though the correlation between OAES-contents or EDXRF-contents is supposed to exist also at high concentrations of trace elements, there is insufficient data to use the respective linear regression for prediction. Therefore regression equations after elimination of anomalies seem to be more based.

The necessity to eliminate outliers with high contents is confirmed by the fact that for some elements, e.g. Pb, Cu, linear regression parameters without any elimination are greatly different from respective parameters after elimination of outliers (Table 2). On the whole, the estimates of linear regression parameters on different stages are rather similar.

After the elimination of outliers the arrangement of trace elements according to decreasing $R^2$ (and R) values is as follows: Cu>Zn>Pb>Sn>Cr>Ni>Mo>Ba>Mn>V (Fig 1).

*Table 2.*

**Correlation and linear relationship of two different contents of trace elements**

| **$El_i$** | **$R^2$** | **R** | **N** | **Mx(S)\Mx(X); outliers eliminated** | **a** | **b** |
|---|---|---|---|---|---|---|
| $Mo_1$ | 0.9870 | 0.9935 | 141 | **178\58.5;** | 0.3464 | 0.4014 |
| $Mo_2$ | 0.4455 | 0.6675 | 135 | **4.32\3.44;** N21(RDC), N22(RDC), N23(RD), N24(RD), N04(D), Sn13(D) | 0.3869 | 0.2877 |
| $Mo_3$ | 0.4331 | 0.6581 | 136 | **4.32\2.40;** N26(D) | 0.3083 | 0.3683 |
| $Zn_1$ | 0.7777 | 0.8819 | 141 | **1000\530;** | 0.4933 | 33.549 |
| $Zn_2$ | 0.7271 | 0.8527 | 138 | **720\408;** N11(RD), N17(D), Se02(D) | 0.4688 | 37.961 |
| $Zn_3$ | 0.7511 | 0.8667 | 135 | **720\408;** Zr26, Zr28, A09a | 0.4712 | 35.237 |
| $Pb_1$ | 0.7751 | 0.8804 | 141 | **914\13100;** | 11.859 | -751.48 |
| $Pb_2$ | 0.6961 | 0.8343 | 139 | **189\171;** Se04(RDC), Se21(RDC) | 0.6520 | 5.1306 |
| $Pb_3$ | 0.6666 | 0.8165 | 135 | **165\155;** Se05(D), A09(D), Sn17(D), Zv03(D) | 0.6392 | 5.8739 |
| $Cu_1$ | 0.6986 | 0.8358 | 141 | **232\273;** | 0.8147 | -6.1007 |
| $Cu_2$ | 0.7326 | 0.8559 | 139 | **128\111;** A09(RDC), Sn08(RDC) | 0.4971 | 4.6179 |
| $Cu_3$ | 0.7810 | 0.8837 | 136 | **128\111;** Se29, Zr08, A10(D) | 0.5432 | 3.3337 |
| $Cr_1$ | 0.7713 | 0.8782 | 141 | **204\95.7;** | 0.4532 | 5.7101 |
| $Cr_2$ | 0.4238 | 0.6510 | 138 | **70.1\47.3;** N21(D), N22(D), Zr12(R) | 0.4663 | 5.1915 |
| $Cr_3$ | 0.4920 | 0.7014 | 133 | **70.1\47.3;** N09, Se04, Se17, Zr27, A11 | 0.4749 | 4.4621 |
| $Ni_1$ | 0.5309 | 0.7286 | 141 | **47.6\27.8;** | 0.3709 | 2.6565 |
| $Ni_2$ | 0.4450 | 0.6671 | 138 | **39.1\16.7;** Se04(R), Se09(R), Zr12(RDC) | 0.3013 | 3.6589 |
| $Ni_3$ | 0.4744 | 0.6888 | 135 | **39.1\16.7;** N28, Se07, Sn05 | 0.2849 | 3.8154 |
| $Ba_1$ | 0.4701 | 0.6856 | 141 | **908\653;** | 0.3418 | 211.2 |
| $Ba_2$ | 0.2330 | 0.4827 | 139 | **624\462;** N11(RDC), Zv10(D) | 0.2198 | 248.78 |
| $Ba_3$ | 0.2464 | 0.4964 | 134 | **624\413;** N10, N22, Sn2 | 0.2080 | 251.51 |
| $V_1$ | 0.3352 | 0.5790 | 141 | **137\597;** | 0.3125 | 3.2083 |
| $V_2$ | 0.0785 | 0.2802 | 138 | **60.6\33.3;** N21(DC), N22(DC), A10(RDC) | 0.2427 | 5.6373 |
| $V_3$ | 0.0788 | 0.2807 | 136 | **60.6\31.2;** Zr06, Zr16 | 0.2321 | 5.7675 |
| $Sn_1$ | 0.2926 | 0.5409 | 141 | **49.9\38.0;** | 0.3983 | 4.1225 |
| $Sn_2$ | 0.4068 | 0.6378 | 138 | **23.2\17.0;** N28(RDC), Se28(RC), A20(R) | 0.4642 | 3.5344 |
| $Sn_3$ | 0.5233 | 0.7234 | 135 | **23.2\12.3;** Se03, Se26, Zv03 | 0.4473 | 3.4330 |
| $Mn_1$ | 0.1630 | 0.4037 | 141 | **977\495;** | 0.1599 | 216.48 |
| $Mn_2$ | 0.1731 | 0.4161 | 140 | **977\435;** Se09(R) | 0.1559 | 217.28 |
| $Mn_3$ | 0.2132 | 0.4617 | 134 | **977\397;** Se02, Se04, Se19, A02, Sn10, Zv02 | 0.1544 | 215.15 |

Note. $El_i$ – element and information about elimination of outliers: index 1 – without elimination of outliers, index 2 – after elimination of considerable outliers, index 3 – after elimination of inconsiderable outliers; $R^2$ – coefficient of determination; R – Pearson correlation coefficient; N – number of observations in linear regression; **Mx(S)\Mx(X) –** maximum OAES-content and maximum EDXRF-content; estimated values of linear regression parameters: a – coefficient before independent variable, i.e. slope, b – intercept. The outliers are indicated by sample identification numbers with the following additional information given in parentheses: R – absolute value of standard residual exceeds 3; C – Cook's distance exceeds critical value (0.693) [12], D – deleted residual differs from residual.

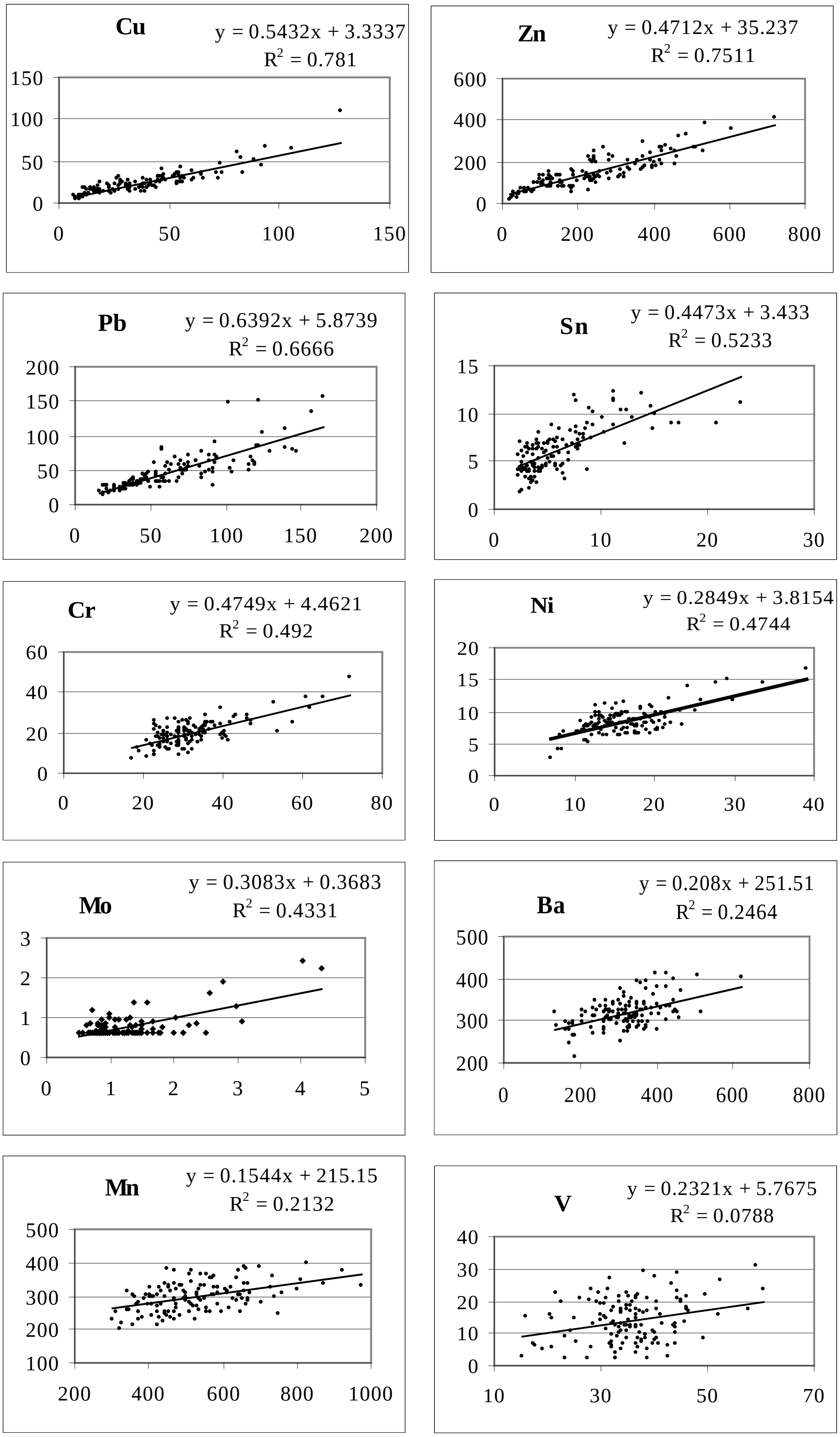


*Fig.1.* **Correlation between trace element contents determined by different equipment**

It is obvious that for chalcophiles (Cu, Zn, Pb, Sn) the correlation between OAES-contents and EDXRF-contents is higher than for siderophiles or lithophiles. The highest slope of linear regression is characteristic of Pb(0.639). It is followed by Cu(0.543), other trace elements are arranged as follows: Cr(0.475), Zn(0.471), Sn(0.447), Mo(0.308), Ni(0.285), V(0.232), Mn(0.213), Ba(0.208). For most siderophile or lithophile trace elements (except Cr) the slope is lower.

As concerns major elements, the coefficients of determination are not always sufficiently high and Pearson correlation coefficients are not always significant, especially for Al, also for Mg before elimination of anomalies (Table 3). Most probably, there were rough mistakes of Mg determination by OAES in 2 samples. Linear regression performed according to primary data of major elements (without any elimination of outliers) showed significant ($p<0.05$) values of ANOVA F-test for Ca, Mg and Fe, both parameters (slope and intercept) being also significant ($p<0.05$). For Al, F-test of ANOVA and t-test for slope being equal to zero resulted in insignificant p-values ($p>0.05$). Elimination of anomalies slightly improved the correlation between OAES-contents and EDXRF-contents of Al and it became significant ($p<0.05$). Still it is hardly possible to predict EDXRF-contents of Al according to its OAES-contents or additional data are necessary. As for most trace elements, for Fe the elimination of outliers lead to decrease of $R^2$ (and R) values as well as considerable decrease of its maximum OAES-contents and EDXRF-contents. For other 3 major elements the tendency was the opposite. According to decreasing values of $R^2$ (and R) after the second stage of elimination of outliers, the major elements are arranged as follows: Ca>Mg>Fe>Al. The same arrangement of major elements is according to regression slope values after the second stage of elimination of outliers.

*Table 3.*

**Correlation and linear relationship of two different contents of major elements**

| $El_i$ | $R^2$ | R | N | Mx(S)\Mx(X); outliers eliminated | a | b |
|---|---|---|---|---|---|---|
| $Ca_1$ | 0.7096 | 0.8424 | 141 | **46800\52000;** | 0.8414 | 4227.7 |
| $Ca_2$ | 0.7124 | 0.8440 | 139 | **36800\35600;** Se03(RDC), Se09(RD) | 0.8670 | 3775.3 |
| $Ca_3$ | 0.7378 | 0.8590 | 137 | **36800\35600;** N22, Se01 | 0.8701 | 3578.7 |
| $Mg_1$ | 0.0522 | 0.2285 | 141 | **114000\10100;** | 0.0314 | 4779 |
| $Mg_2$ | 0.6278 | 0.7923 | 138 | **12300\8010;** Se09(R), A02(R), A07(DC) | 0.4435 | 1779.1 |
| $Mg_3$ | 0.5682 | 0.7538 | 133 | **12300\7510;** A03, A04, A05, Se13, Se15 | 0.3857 | 2235.5 |
| $Fe_1$ | 0.3469 | 0.5890 | 141 | **32800\23800;** | 0.3145 | 3805.4 |
| $Fe_2$ | 0.2684 | 0.5181 | 139 | **24800\13000;** Se09(RDC), A03(RD) | 0.2188 | 5315.1 |
| $Fe_3$ | 0.2503 | 0.5003 | 138 | **24800\13000;** A02 | 0.2031 | 5595.3 |
| $Al_1$ | 0.0267 | 0.1634 | 141 | **52300\27300;** | 0.0763 | 17574 |
| $Al_2$ | 0.0203 | 0.1425 | 139 | **50700\26800;**N25(D), Se17(R) | 0.0656 | 17899 |
| $Al_3$ | 0.0296 | 0.1720 | 132 | **50700\24700;**N08, Se19, Zr05, Zr14, Zr25, Zv03, Zv09 | 0.0658 | 17602 |

Note: explanation is the same as in Table 3.

## Conclusions

Most of chemical elements studied, except Ca, Sn and Ba, are characterised by significantly lower EDXRF-contents than OAES-contents. Unlike most elements, the EDXRF-content of Ca is significantly higher than OAES-content, Sn has also a tendency of higher EDXRF-content. Such differences can be explained by different standard reference materials used for re-calibration of measurements of total element contents obtained by different equipment. Continuous participation of IGG in WEPAL ISE program ensured increase of available ISE samples which can be used as standard reference materials for re-calibration of measurements obtained by EDXRF. Preliminary comparison of relative standard measurement uncertainties of both methods for mean values of two reference materials has shown that most trace elements studied (Ba, Cr, Cu, Ni, Mn, Pb, V, Zn), except Sn and Mo, are characterised by lower uncertainty of EDXRF measurements. Due to these reasons EDXRF-contents are more reliable. However, huge problem of their application in practice arises, when it is necessary to estimate the danger category of contaminated urban soil, because all previous background values for soil were calculated on the basis of OAES measurements. According to the ratio of median EDXRF-content to median OAES-content the arrangement of potentially harmful elements is as follows: V(0.40) <Ni(0.52) <Mo(0.57) <Zn(0.58) <Mn(0.59) <Cr(0.63) <Cu(0.64) <Pb(0.73) <Ba(0.99) <Sn(1.21). It is obvious that the old background values of V, Ni, Mo, Zn, Mn, Cr, Cu, Pb estimated according OAES-content are absolutely unsuitable for calculation of concentration coefficients Kk and additive contamination index Zd (which depends on Kk). If this fact is ignored, theunderestimation of soil contamination categories according to Zd threatens. Therefore the determination of background EDXRF-contents on uncontaminated territories is necessary. Since for all trace elements two contents determined by different equipment are significantly correlated, simple linear regression equations for prediction of EDXRF-content according to OAES-content might be useful. These equations differ before and after the elimination of outliers. The latter relationships indicate that for chalcophiles the correlation between OAES-contents and EDXRF-contents is higher than for siderophiles or lithophiles. Prediction of some major elements (Ca, Mg, Fe) is also possible according to linear regression equations. However, prediction of Al according to available data is problematic.

**References**


1. Lis, J., Pasieczna, A., Taraškevičius R. Total and partial extraction of selected elements in soil of the Poland – Lithuania borderland. Journal of Geochemical Exploration, Vol. 66, Issues 1-2, 1999, p. 211-217.
2. Kadūnas, V., Budavičius, R., Gregorauskienė, V., Katinas, V., Kliaugienė, E., Radzevičius, A., Taraškevičius, R. Geochemical atlas of Lithuania. Vilnius. Institute of Geology, Lithuanian Geological Survey, 1999, 90 p.: 18 tables + 162 maps (in Lithuanian and English).
3. Kadūnas, V., Budavičius, R., Katinas, V., Kliaugienė, E., Radzevičius, A., Zinkutė, R. Geochemical atlas of Mažeikiai district. Municipality of Mažeikiai district, Institute of Geology, Vilnius–Mažeikiai, 2001, 87 p.: 6 tables+29 maps (in Lithuanian and English).
4. Radzevičius, A., Gregorauskienė, V., Kadūnas, V., Putys, P. 2004. Geochemical atlas of Panevėžys county. Administration of Panevėžys county, Institute of Geology and Geography, Lithuanian Geological Survey, Vilnius-Panevėžys, 2004, 123 p.: 10 tables + 54 maps (in Lithuanian and English).
5. Radzevičius, A., Budavičius, R., Kadūnas, V., Katinas, V., Zinkutė, R., Tverkutė, Z. Geochemical atlas of Panevėžys. M 1:25000. Institute of Geology, Ecological department of Panevėžys municipality, Vilnius–Panevėžys, 1997, 18 p.: 7 tables + 25 maps (in Lithuanian and English).
6. Taraškevičius, R. 2000. Sunkieji metalai Vilniaus miesto Naujamiesčio, Senamiesčio, Šnipiškių, Žirmūnų, Žvėryno ir Antakalnio seniūnijų dirvožemiuose. Aplinkos inžinerija, T. 8. Nr. 3, 2000, p. 137-145 (in Lithuanian).
7. Jankauskaitė, M., Taraškevičius, R., Zinkutė, R., Veteikis, D. Relationship between landscape self-regulation potential and topsoil additive contamination by trace elements in Vilnius city. Journal of environmental engineering and landscape management, Vol.16. No. 1, 2008, p. 5-14.
8. Taraškevičius, R. Klaipėdos prieuosčio dirvožemio ir grunto geohigieninis vertinimas. Jūros ir krantų tyrimai – 2008. Konferencijos medžiaga. 2008 balandžio 09-11 Palanga. Klaipėda, 2008, p. 143-147 (in Lithuanian).
9. Zinkutė, R., Taraškevičius, R., Jankauskaitė, M. 2009. Variation of accumulating associations in topsoil of the oldest part of Vilnius. Vide. Tehnoloģija. Resursi. VII starptautiskās zinātniski praktiskās konferences materiāli, 2009. gada 25.-27. jūnijs. Rēzekne, 2009, p. 241-248.
10. Taraškevičius, R., Zinkutė, R., Jankauskaitė, M. Differences of Vilnius topsoil contamination in the Neris River valley due to anthropogenic factors. Geologija, Vol. 50, No. 3(63), 2008, p. 135–142.
11. Zinkutė, R. Taraškevičius, R., Želvys, T. Major elements as possible factors of trace element urban pedochemical anomalies. Central European Journal of Chemistry, Vol. 9, Issue 2, 2011, p. 337-347. Doi: 10.2478/s11532-011-0012-z.
12. Čekanavičius, V., Murauskas, V. Statistika ir jos taikymai. II. Vilnius: TEV, 2004, 272 p. (in Lithuanian).

# NANO SCALE METHODS FOR WATER POLLUTION MONITORING

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**Abstract.** *The article deals with issues related to the textiles coated with metal nanoparticles and detection of the concentrations of released particles in water. The main risks associated with the use of metal covered textiles are detaching of metal nanoparticles from the material during use and care and thus polluting the environment, or inhaled to get in a human or animal body. Nanoparticles can be detached from the textile during washing also, thus polluting the water body and making detriment to the living beings in them. This article aims to look at equipment for nanoparticle size and concentration detection in liquids. Described the world's most popular methods (Microscopy techniques, Photon Correlation Spectroscopy, Nanoparticle Tracking Analysis) and compared to new, alternative method - Gas Discharge Visualization (GDV) electrography. Within the framework of the article analyzed the advantages and disadvantages of each method and estimated the perspective of GDV electrography for detection of metal nanoparticles in water.*

**Keywords:** *GDV electrography, metal covered textile, nanoparticles, testing methods.*

## Introduction

The article deals with issues related to the textile coated with metal nanoparticles, the persistence of the metal coverings and detection of the concentrations of released particles in water. The main risks associated with the use of metal covered textiles are detaching of metal nanoparticles from the material during use and care. Friction resulting nanoparticles can be detached from the product and thus end up in the air, resulting in polluting of the environment, or inhaled to get in a human or animal body. Nanoparticles can be detached from the textile during washing also, thus polluting the water body and to the detriment of the living beings in them.

Quantitative assessment of the impact of nanoparticles and an adequate characterization is still a serious problem for scientists, industrial hygienists and toxicologists. Nanoparticle detection methods and their specific parameters measuring is necessary for two reasons: first, to detect nanoparticles in environments in which people and ecosystems are exposed to their influences such as water, air, soil, nanocomposites and consumer products. The second reason is the need to measure the physical and chemical properties of nanoparticles in these environments. Nanoparticles dimensions are outside the visible light diffraction limit, so that in the optical microscope they are not visible, it creates a need for highly sensitive testing method.

The most common nanoparticle detection equipment is allocated according to environment in which the particles are disposed - fluid, air or solids. Nanoparticle detection methods and equipment can be divided also according to the parameters which they calculate - the mass concentration, particle number (numerical concentration), surface specific (surface concentration) or granulometric structure. In literature is found the following breakdown - devices attached to a computer (on-line) and equipment that are not connected to the computer (off-line).

The article deals with certain equipment and methods for detecting of nanoparticles in fluids, as well as analysis of relatively new method (Gas Discharge Visualization (GDV) electrography) possible use for metal nanoparticles level monitoring in water.

## Materials and methods

Quantitative determination of nanoparticles is problematic, because virtually in every environment is the presence of natural origin nanoparticles. Of the total suspension, which is a complex mixture of different composition and granulometry nanoparticles, must isolate interested objects. So the first must find all the nanoparticle composition, to select necessary components and determine their parameters.

Analised devices vary with the required sample number for measurements, preparation techniques and the resulting parameter range. For several equipment necessary special preparation of the sample, but can meet such devices which permit the measurement of raw substance. The required pre-treatment is problematic because the sample may react or decompose during the preparation. The required quantity of material for testing may limit the choice of equipment, because, according to the apparatus, the sample requires up to 300µl. Some equipment needs of additional measurements in order to calculate any of the indicators.

Most of the equipment cannot distinguish agglomerates from individual nanoparticles, which limits their use, because the toxicity of nanoparticles depends on their size - the size reduction increases toxicity. So toxicity of nanoparticles agglomerate will be higher than the same size bulk substance toxicity. If device nanoparticle agglomerates considered as a single element, the wrong suspension toxicity is calculated.

This section deals with three main methods for the analysis of nanoparticles in liquids - Microscopy techniques, Photon Correlation Spectroscopy and Nanoparticle Tracking Analysis. The article gives the general characteristics of the equipment. Instrument sensitivity, use and accuracy can vary depending on the manufacturer.

**Microscopy methods.** In Transmission Electron Microscopy (TEM) is used an electron beam, which by interacting with the sample, form an image on photographic plate or in a specialized camera. The sample must be able to withstand the electron beam and the high vacuum chamber, where it is placed. The sample must be made in the form of thin film, which in turn can cause problems. The method is also time consuming and therefore increase the costs [1].

In High-Resolution Transmission Electron Microscopy (HRTEM) can observe the sample crystallographic structure in the atomic level. HRTEM maximum resolution is 0.08 nm. Method is used in semiconductor and metal properties nano scale study. In High-Resolution Transmission Electron Microscopy is used phase contrast or high resolution imaging technique. Phase contrast imaging analyzes through the sample atoms going electron beam diffraction contrast in comparison with the transmitted beam contrast. HRTEM use limits complexity of image interpretation, which includes a variety of mathematical calculations, such as a determination of microscope lens aperture and aberrations caused image distortions [1].

Environmental Transmission Electron Microscopy (ETEM) compared with conventional TEM is a significant advantage - the sample must not be placed in a vacuum chamber, the process may be carried out in situ [1].

In the Scanning Electron Microscopy (SEM) is also used electron beam, only in this case the sample surface is scanned, and the image forms the back scattered electrons. SEM disadvantage is that the sample is placed in a vacuum chamber and surface of the sample must be electro conductive. On the samples with low electrical conductivity is sprayed metal coating, as a result Scanning Electron Microscope application is limited, and sample preparation process is time consuming and expensive [2].

One of the Scanning Electron Microscope modification is Environmental Scanning Electron Microscope (ESEM), which, like a ETEM, suitable for operation in low pressure gaseous environment [2].

Scanning Transmission Electron Microscope (STEM) combines the scanning and transmission electron microscopy features - can be obtained images of the sample surface and the internal structure [2].
Atomic Force Microscope (AFM) is a Scanning Probe Microscopy (SPM) type, which uses a mechanical probe to palpate the sample surface. Atomic Force Microscope is one of the most commonly used equipment in nano scale substances measuring and displaying.
Console with nano scale probe moves over the sample surface, vibrations of the console and therefore the sample surface is fixed with the reflected laser beam, which is received in photodiodes matrix. In this way can obtain three-dimensional image. AFM are several test modes - contact mode, non-contact mode, and intermittent contact mode. To see the nanoparticles with the Atomic Force Microscope, they must be dispersed in the air or liquid, and the substrate must be less rough than the particles to be measured. This method is less time-consuming and lower-cost [3].
The benefits of Microscopy methods include the high resolution - up to 1 nm.
The main disadvantages of Microscopy methods in measuring nanoparticles are referred to the complex sample preparation. Another problem is sample selection, because the picture in the microscope is a small fraction of the total sample, therefore difficult to determine whether the findings of the research relate to whole object.
**Photon Correlation Spectroscopy.** In Photon Correlation Spectroscopy (PCS) analyses from the nanoparticles reflected laser beam created curve. By combining this method with the Brownian motion caused diffusion calculations by Einstein - Stokes equation acquires the average particle size and size distribution in the sample. The sample must be liquid, solution or suspension in a low concentration, otherwise the light scattering is not clear. Measuring equipment is sensitive to impurities, and must be given sample viscosity. Particle size range that can be detected by Photon Correlation Spectroscopy ranges from 1 nm to 10 µm **[4]**.
For application of Photon Correlation Spectroscopy in higher concentrations or opaque samples testing, was created Photon Cross Correlation Spectroscopy (PCCS), which can be applied even in emulsion analysis [5].
**Nanoparticle Tracking Analysis.** Nanoparticle Tracking Analysis (NTA) provides information on particle size, size distribution and observation of nanoparticles in the sample in real time (Fig.1).

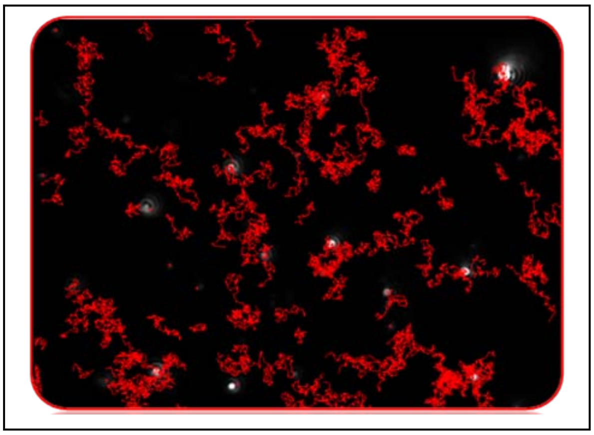

*Fig.1.* **Monitoring of the nanoparticle movements in NTA equipment [6]**

The sample must be a suspension; it is placed on an opaque background and using a laser, observes the movements of nanoparticles in the optical microscope. In the device is also a digital camera to record the movement of particles. By a computer program is created nanoparticle size distribution frequency chart. NTA equipment may be used together with

Photon Correlation Spectroscopy, thus increasing the amount and the accuracy of the obtained information [7].

**Gas Discharge Visualization Electrography (GDV EG)** working principle is based on Kirlian effect. High-frequency high-voltage current produced discharge or radiation around an object (human, animal body parts, plant, inanimate object or liquid) is detected by a digital camera in separate shots or video format. The resulting images are analyzed by specialized software. Radiation shape and size reflect the object properties.

GDV camera is the most widely used in medical studies - allergy diagnosis [8], the diagnosis of autism [9], various fluids (for example, blood, energetic preparations, homeopathic preparations) properties determination by influence of different factors [10]. GDV camera is widely used in sports medicine - sportsman's training and health status estimation [11]. GDV equipment may be used in powerful, geo-active places surveys, as well as the impact of such locations exploration [12].

In view of the GDV electrography broad spectrum of use, proposed the task to adapt the method for nano scale metal particles detection in water. In order to clarify the method outlook of reaching the target carried out pilotexperiment with four cotton fabric samples coated with copper particles (size 180-210 nm) layer in a thermal evaporation process. Thermal evaporation process duration - 3 seconds.

Samples washed in cold water by hand for about 5 minutes, in resulting the copper coating diverged from the textile, shown by the water color changes and easily reddish precipitate at the bottom of the container. The sample size - 75x85 mm; washing water for one sample - 60 ml. For comparison used uncontaminated cold water (designation- *control*). Water stored in enclosed glass container.

Before the GDV electrography session, the container with water is thoroughly shaked to disperse the sludge. Prepared water (1 - 2 ml) embroiled into a syringe and a syringe fixed on a stand above the GDV camera lens. From one sample get 5 static GDV electrogramms. The experiment is repeated 8 times, resulting in a 40 pictures of the same time interval between electrogramm fixing moments. Time intervals, used in experiment (3, 5 and 7 seconds), and number of images (5 electrogramms) is entered into the program "GDV Capture" settings.

GDV electrogramms fixed with gas discharge visualization camera "GDV Camera" using toolkit "GDV Mini-Lab" for liquid analysis. The data recorded in a computer program "GDV Capture" and processed in the program "GDV Scientific Laboratory". The resulting parametric analysis was conducted in "Microsoft Excel" software.

## Results and discussion

A computer program "GDV Scientific Laboratory" calculates 12 parameters for each electrogramm. The most important parameters of the radiation are area, intensity, form coefficient and entropy. This paper presents two leading indicators- the area and intensity; they both describe the object energy potential. Area of GDV electrogramms is number of pixels in the picture or electrogramm, but the intensity is brightness of the picture elements (pixels).

During the analysis of the experiments calculated various statistical indicators - the arithmetic mean, variance, range, standard deviation, average standard error and relative average standard error. The measurements obtained from four samples, pooled into two groups (designation Group 1A and Group 1B) for better obviousness.

Figure 2 represents the water samples mean values at three different electrogramms exposure intervals (3, 5 and 7 seconds). Each of the indicators calculated as the arithmetic mean of 40 values. The relative average standard error don't exceed 3% limit for anyone of the data packages, so calculus have sufficient reliability.

Figure 2 illustrates the area differences in pixels for the washing water of Group1A samples and fresh water (control), receiving GDV electrogramms with different time intervals between the fixing moments (3, 5 and 7 seconds). In this case, 3-second pause between the image fixing moments show the smallest differences between polluted and unpolluted water.

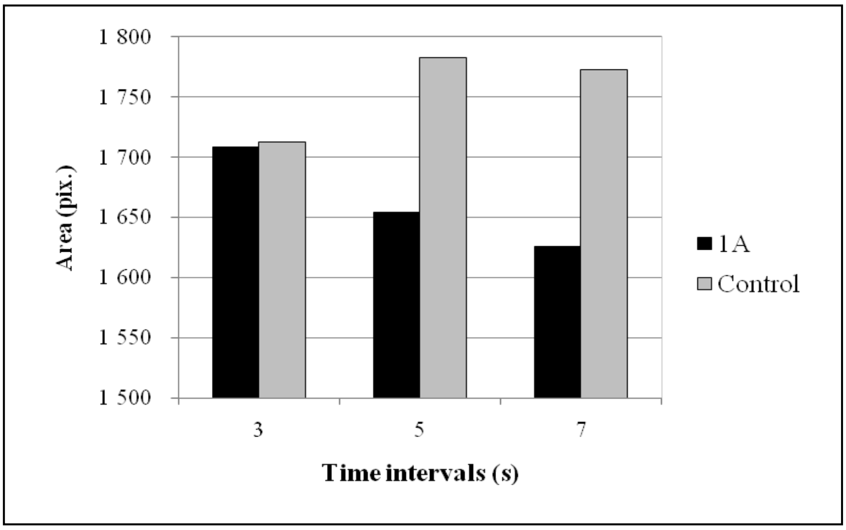


*Fig.2*. **Indicators of area for 1A samples washing water and uncontaminated water**

As shown in Figure 3, for Group 1B samples all of the time intervals present enough significant differences between polluted and unpolluted water.

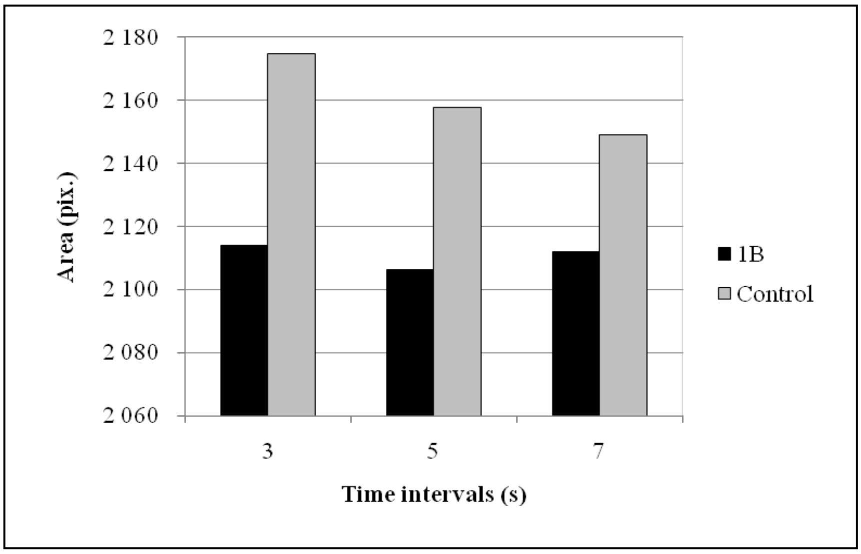


*Fig.3*. **Indicators of area for 1B samples washing water and uncontaminated water**

Figure 4 represents the GDV electrogramms intensity results obtained from samples 1A washing water and clean water. In this variant smallest difference between polluted and unpolluted water show electrogramms taken with 7-second intervals.

In Figure 5 represented intensity indices for Group 1B samples washing water and control water radiation, show the smallest difference between electrogramms, taken with 5-second intervals.

Summarizing results of pilotexperiment, it appears that the GDV electrography method show differences between polluted and unpolluted water samples at all measurement points, and unpolluted water radiation area and intensity are higher than the contaminated water. This means that the method is usable for detection of metal nanoparticles pollution in water. However, the results must be stabilized, it can be achieved taking a video file instead of detached electrogramms and analyzing the resulting set of shots.

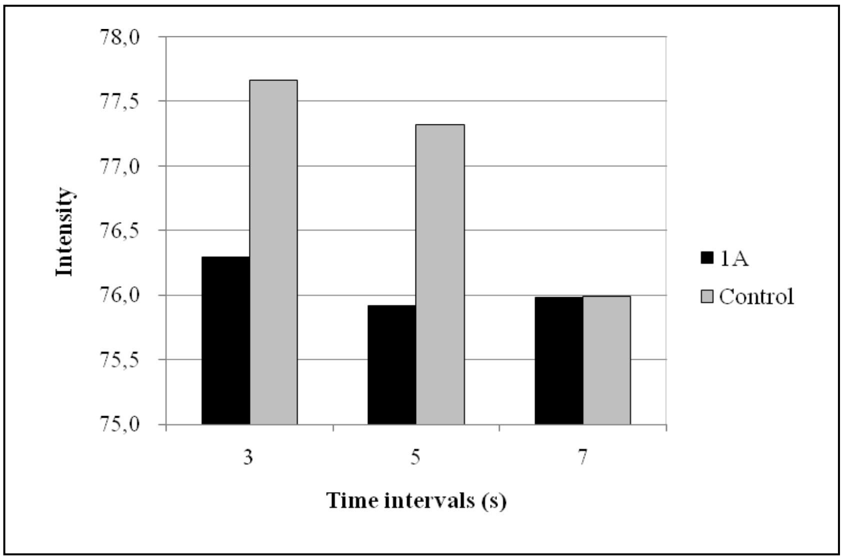


*Fig.4*. **Indicators of intensity for 1A samples washing water and uncontaminated water**

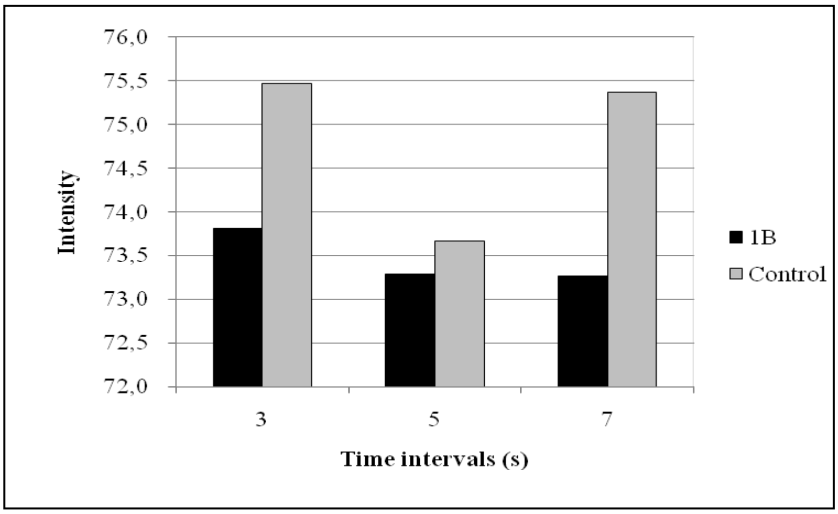


*Fig.5*. **Indicators of intensity for 1B samples washing water and uncontaminated water**

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**Conclusions**

In the paper presented methods for nanoparticle detection in liquids differ with parameters they calculate - Photon Correlation Spectroscopy and Nanoparticle Tracking Analysis estimate particle size and size distribution, with Microscopy techniques can detect particle size and surface properties, while the GDV electrography characterizes energetic characteristics of the liquid's radiation.

Each method has also disadvantages - Photon Correlation Spectroscopy is necessary to know the viscosity of the sample, while Microscopy methods require prior sample preparation, which is expensive and time-consuming process. In addition, all methods have nanoparticle size limits imposed by its ability to capture. Recognition of nanoparticle agglomerates is quite problematic also. Such problems have not GDV electrography, because it analyzes the radiation of fluid, whose properties depend on its composition. Nanoparticle size or the agglomerates does not change capture capabilities of the equipment. However, GDV camera also has drawbacks - it cannot be used in detection of nanoparticles of unknown origin, when is needed to know the chemical composition of particles. Respectively, developing an appropriate measurement methodology, GDV camera can be used in detecting a known source of nanoparticles in water.

**References**


1. Williams, D.B. Transmission Electron Microscopy. A Textbook for Materials Science. Second Edition. Heidelberg: Springer-Verlag, 2009, p. 757.
2. Reimer, L. Scanning Electron Microscopy. Physics of Image Formation and Microanalysis. Second Edition. Heidelberg: Springer-Verlag, 1998, p. 515.
3. Eaton, P., West, P. Atomic Force Microscopy. Oxford: Oxford University Press, 2010, p. 241.
4. Berne, B.J., Pecora R. Dynamic Light Scattering: with Applications in Chemistry, Biology, Physics. Ontario: General Publishing Company, 2000, p. 371.
5. Photon Cross Correlation Spectroscopy. Sympatec GmbH. System–Partikel-Technik. *Available from*: http://www.sympatec.com/PCCS/PCCS.html *Accessed:* 2010-12-29
6. Comparative Technologies. NanoSight. *Available from*: http://www.nanosight.com/technology/comparative-technologies *Accessed:* 2011-01-14
7. Elsersawi, A. World of Nanobioengineering. Potential Big Ideas for the Future. Bloomington: AuthorHouse, 2010. p. 196.
8. Степанов, А.В., Свиридов, Л.П., Ахметели, Г.Г., Коротков, К.Г., Юсубов, Р.Р. Метод этиологической диагностики аллергии путем анализа параметров стимулированного свечения крови // Materials of Internetional Scientific Congress “Science. Information. Spirit.”, Russia, St.Petersburg, 4.-5. July, 2009. – p. 52-61.
9. Kostyuk, N., Rajnarayanan, R., Isokpehi, R., Korotkov, K., Howcroft, S., Yeager, M., Mann, H., Cohly, H. Bio-electrographic Method in Detecting Heterogeneity and Unique Features in Autism // Materials of Internetional Scientific Congress “Science. Information. Spirit.”, Russia, St.Petersburg, 4.-5. July, 2009.
10. Bell, I., Lewis, D., Brooks, A., Lewis, S., Schwartz, G. Gas Discharge Visualization Evaluation of Ultramolecular Doses of Homeopathic Medicines Under Blinded, Controlled Conditions // Journal of Alternative and Complementary Medicine, 2003, Feb., p. 25-38.
11. Rodina, J. D., Ovcharenko, S.V., Malojvan, J.V. Psychological Aspects of Disabled Sportsmen Training and the Usage of Gas Discharge Visualization Technique // Materials of Internetional Scientific Congress “Science. Information. Spirit.”, Russia, St.Petersburg, 4.-5. July, 2009.
12. Velichko, E.N., Sochevanov, V.N., Brunov, V.V. Influence of “Places of Power” of Vologodskaya Area on Human State // Materials of Internetional Scientific Congress “Science. Information. Spirit.”, Russia, St.Petersburg, 4.-5. July, 2009.



**Anotācija.** *Rakstā apskatīti jautājumi, kas saistīti ar tekstilmateriālu metāla nanodaļiņu pārklājuma noturību un atbrīvoto daļiņu koncentrācijas noteikšanu ūdenī. Galvenie riski, kas saistīti ar metālpārklātu tekstilmateriālu lietošanu, ir metāla nanodaļiņu atdalīšanās no materiāla lietošanas un kopšanas laikā. Berzes rezultātā nanodaļiņas var atdalīties no izstrādājuma un tādējādi nonākt gaisā, rezultātā piesārņojot vidi, vai arī ieelpojot nokļūt cilvēka vai dzīvnieka organismā. Nanodaļiņas var atdalīties no tekstilmateriāla arī mazgāšanas laikā, tādējādi piesārņojot ūdens tilpnes un kaitējot tajās esošajām dzīvajām būtnēm. Šī raksta mērķis ir apskatīt iekārtas, kas paredzētas šķidrumos esošo nanodaļiņu izmēru un koncentrācijas noteikšanai. Raksturotas pasaulē pazīstamākās metodes (mikroskopijas metodes, fotonu korelācijas spektroskopija, nanodaļiņu trases analizators) un salīdzinātas ar jaunu, alternatīvu metodi – gāzizlādes vizualizācijas (GDV) elektrogrāfiju, kas piemērojama dažādām vajadzībām, bet līdz šim visbiežāk lietota medicīnsika rakstura pētījumiem. Raksta ietvaros analizētas katras metodes priekšrocības un trūkumi, kā arī novērtētas GDV elektrogrāfijas perspektīvas metāla nanodaļiņu noteikšanā ūdenī.*

# OPTIMIZATION OF SORBENT SYSTEM FROM PAPER MILL WASTE SHORT FIBERS FOR BIOREMEDIATION OF HEAVY HYDROCARBONS IN SOIL

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**Abstract.** *The aim was to develop a new improved Sorbent system (S-S) from organic sorbent material, nutrients, biosurfactant and microbial cell producing it for bioremediation of heavy oil hydrocarbons in various soil types. New sorbent material (S-M) was developed from paper mill short waste fibers because it requires very low energy to manufacture and the production costs of this S-M is extremely low compared to similar products in the market. S-M has good sorption characteristics for various oil products, is fully biodegradable, can be applied at sensitive environmental areas. S-M can be combined with microorganisms producing biosurfactant. The goal of investigations was to optimize S-S composition to minimize the leakage of heavy hydrocarbons to deeper soil layers or ground water. The optimal composition of S-S for all types of soil was determined: S-M 86.3-89.3%, microorganisms producing biosurfactant* $\geq 10^7$ *CFU/g, biosurfactant solution – 3%, nutrients (nitrogen and phosphorous) 0.5 and 0.2%. Recommended optimal S-S moisture is 7%.*

**Keywords:** *sorbent system, oil bioremediation, heavy oil hydrocarbons, biosurfactant, optimization,.*

## Introduction

Environmental pollution with oil is very large problem all around the world, because oil is used in many industries. In fact, production and consumption of oil and petroleum products are increasing worldwide, and the risk of oil pollution is increasing accordingly. Most spills take place on land, and this accounts for a high volume of oil spilled. However, the cleanup is more difficult on land since soil has a tendency to absorb the oil leakage and only some biodegradation techniques are available for the clean up of oil from ground.

Therefore, the aim of this work is to develop and optimize novel cost-efficient Sorbent system (S-S) for soil remediation. S-S has be applied in-situ for heavy hydrocarbons treatment to reduce contaminant concentration to an acceptable level for starting up biodegradation process. This system is targeted to collection of oil products after spillage and for control of the hydrocarbons level in soil. So this integrated S-S effectively combines different soil remediation techniques for bringing the site back to acceptable environmental standards. Current sorbent market is very fragmented with different targeted applications and many products. Innovations are mainly related to development or selection of novel sorbent materials and targeted to make green and environmentally friendly products having sufficient functionalities. Common approaches are improvement of sorbent structure or adaptation of package for the more efficient oil degradation processes.

Although, it is not common practice to compose sorbent materials into systems, several types of sorbent systems are currently available consisting of different elements: sorbtic material and specific microbial strain [1, 2], sorbtic material and specific microbial strain and fertilizers [3, 4], sorbtic materials and microbial cells producing bio-surfactants [5], sorbtic materials and the biosurfactant itself [6].

The great majorities of these sorbent systems are targeted to oil remediation in water environment [1, 3, 4, 6] and are not applicable in non-aqueous media. Although, combining different elements, some of them were investigated for oil remediation in non-aqueous media [2, 6], but commercially reliable results still have not been reported.

Whereas, the new developed S-S is based on low-cost natural organic sorbent material (S-M) developed from paper mill short fiber wastes and embedded with specific biosurfactant acting as activating agent for microorganisms producing more biosurfactant for further cleaning. Microorganisms are responsible for producing biosurfactant capable to separate the migration fraction of oil.

Surface active compounds embedded into S-M improve bioavailability of highly hydrophobic pollutants thus reducing surface tension and therefore enhancing both: solubility of heavy hydrocarbons in water and effect of sorption. Microorganisms start to produce biosurfactant, which begins to separate non-migration fraction of oil (which is strongly tied to soil), from soil binding it to S-M. The initial amount of biosurfactant acts as activating agent for removal soaked oil both from soil and from S-M, thus increasing bioavailability of hydrophobic compounds. Biosurfactant is also environmentally friendly, thus, does not cause any secondary contamination. Therefore, S-S presents unique and novel way of fast and effective reduction of pollution concentrations to required level for starting up enhanced bioremediation process. Nitrogen and phosphorus are added to the S-S in order to stabilize and preserve microorganisms producing biosurfactant.

The goal of experimental investigation was to optimize the composition of S-S elements in order to minimize the leakage of heavy hydrocarbons to deeper soil layers or ground water. For S-S development, optimal composition of soil treatment system had to be identified by defining the exact required amount of S-S elements. Since analysis of research results requiring large amounts of samples and equipment would have been comparatively expensive, computer modelling of the environmental processes has been selected as the best option. Computer modelling allows simulating physical and chemical processes in selected environment using selected parameters, being cost and time efficient as well as offering more flexibility of research that could be performed in comparison to other methods.

## Materials and methods

### 1) Materials

*Sorbent system components* were used in the investigations: S-M, biosurfactant producing microbial culture, nutrients (nitrogen and phosphorus) and biosurfactant. Crude oil was used as heavy hydrocarbon pollutant in the experiments.

*Sorbent material* developed from paper mill short fiber wastes was used. Hydrocarbon sorption capacity of S-M was 4.3 g oil/g S-M.

*Biosurfactant producing microbial culture and biosurfactant*. Crude preparation of the biosurfactant was prepared by centrifugation of *Arthrobacter sp* N3 strain culture liquid at 12000 rpm for 20 min. *Arthrobacter sp* N3 strain viable cell count of $8.4 \cdot 10^8$ CFU/mL was also measured in biosurfactant preparation.

*Nutrients (Nitrogen and Phosphorus).* Ammonium nitrate ($NH_4NO_3$) was a source of nitrogen and dicalohydrogen phosphate ($K_2HPO_4$) was source for phosphorus.

### 2) Methods for optimization of SORBENT system composition

The goal of optimization was to get the most effective S-S while changing its composition for two reasons: 1) that S-S could stop migration of oil contaminants in soil, and 2) to improve bio-accessibility of S-S to oil-oxidizing microorganisms that are used in decontamination technique of soil contaminated with heavy hydrocarbons.

The set of methods and procedures used for optimization of S-S composition is listed below.

*Soil research and reaction surface methodology*

These procedures were applied to define optimal S-S composition for different types of soil. Soil texture was taken as a core soil property for investigations, as it affects the nature and extent of physical, chemical, and biological reactions. Investigations were based on the

following assumptions: a) contaminants diffuse in soil from its top to the bottom; b) water sources are localized and protected, so the heavy hydrocarbons do not diffuse to these deep areas; c) biosurfactant initially embedded into S-M improves separation of heavy oil fractions from soil particles, and upgrades binding of this contaminant to oil-oxidizing microorganisms. Experiments were carried out in 10 L flowerpots, in which samples were taken from 3 cm, 8 cm, 13 cm and 18 cm depth. In this model, length units are measured in centimeters, weight in milligrams, and time in days.
The optimization procedure refers to the reaction surface methodology. Six factorial experiment series were realized using close to D-optimal experimental design. Extra flowerpot was used for realization of repeated experiment to evaluate the reproducibility of experiments results (Table 1). The experiments were carried out for three different types of soil: loam, clay and sand.

*Table 1.*

**Experimental design matrix with code ($x_i$) and real ($X_i$) variables for S-S elements**

| No | $X_1$ biosurfactant producing strain N3 and biosurfactant [%] | | $X_2$ N : P [%] | | Depth [cm] |
|---|---|---|---|---|---|
| | $x_1$ | X1 | $x_2$ | X2 | |
| 1 | +1 | 5 | +1 | 0.5:0.2 | 3/8/13/18 |
| 2 | -1 | 1 | +1 | 0.5:0.2 | 3/8/13/18 |
| 3 | +1 | 5 | -1 | 0.1:0.04 | 3/8/13/18 |
| 4 | -1 | 1 | -1 | 0.1:0.04 | 3/8/13/18 |
| 5 | 0 | 3 | +1 | 0.5:0.2 | 3/8/13/18 |
| 6 | 0 | 3 | -1 | 0.1:0.04 | 3/8/13/18 |
| 7 | +1 | 5 | 0 | 0.3:0.12 | 3/8/13/18 |
| 8 | -1 | 1 | 0 | 0.3:0.12 | 3/8/13/18 |
| 9 | 0 | 3 | 0 | 0.3:0.12 | 3/8/13/18 |

Dried and riddled through sieve with 5 mm diameter holes, the clean soil was poured into the flowerpots up to the 0 cm line as compact as possible. To stimulate the interaction of pollutant with S-S, 1 kg of the same soil contaminated with crude oil (200 g/kg) and the 5 % or 10 % S-S added, was poured on the top of soil in flowerpots. The required amount of S-S was calculated according to concentration of pollution. Laboratory investigation results were used for identification of statistical models designed for prediction of migration of oil contaminants in the investigated types of soil at different amounts of S-S.
Biosurfactant producing microbial cell N3 and initial investigation range of the biosurfactant amount was 1-5 % of amount of heavy hydrocarbons. Investigation range of the nitrogen amount was $0.1 \le C_N \le 0.5$ % of amount of heavy hydrocarbons concentration, whereas phosphorus amount investigation range was $0.04 \le C_N \le 0.2$ % of amount of heavy hydrocarbons contaminants concentration. Experiments were carried out at room temperature (25±2 °C). Vertical migration of oil was evaluated after 1 and 5 days.
Calculations related to the process model identification and model-based optimization experiments were performed using Matlab/Simulink tools. Experimental data were used to identify parameter values of the statistical model (1), which was used to calculate the predicted responses corresponding to the results of six consecutive factorial experiments. The response surfaces are illustrated by isoresponse contour plots in Fig. 1.
Residual hydrocarbon mixtures in soil samples were determined by IR-spectrophotometry.
*Evaluation of initial moisture content in Sorbent system*. Investigations were carried out to evaluate values of S-S optimal moisture content, when system does not lose its sorbtic

characteristics. Also S-S moisture had to be suitable for biosurfactant producing microorganisms' immobilization and had to be prepared easily and cost-effectively. During the investigations, sorbtic ability of S-S with different initial moisture content was evaluated.

*Preparation of S-S with different initial moisture.* Dried S-S was sprayed with analytical water that S-S moisture would be 5 %; 10 %; 15 %; 20 %; 25 % and 30 %.

*Sorption capacity* tests under different S-S moisture levels were carried out. Method developed for the measurement of hydrocarbons sorption capacity by the S-S was based on ASTM F726-99: Standard Test Method for Sorbent Performance of Adsorbents.

*Process optimization procedure*

In this investigation, 4 steps experimental optimization procedure was applied. Detailed description of this procedure is presented below.

*Step 1.* Selection of initial composition of S-S using *a priori* knowledge about S-S components under optimization.

*Step 2.* Design and realization of statistical experiment in the selected area of S-S components concentration variations.

*Step 3.* Identification of statistical model for the response surface estimation. A second order polynomial model, which includes interaction term, was used to calculate the predicted response:

$$Y = a_0 + a_1 \cdot x_i + a_2 \cdot x_j + a_{11} \cdot x_i^2 + a_{22} \cdot x_j^2 + a_{12} \cdot x_i \cdot x_j \quad (1)$$

Where Y – predicted response (hydrocarbons concentration); xi – independent variables (S-S components subjected to optimization); n – number of independent variables.

Parameters of the polynomial model (1) were identified using the least-squares method:

$$A = [F^T F]^{-1} F^T Y \quad (2)$$

Where A – model (3) parameter vector, $A = [a_0 \ldots a_i \ldots a_{ii} \ldots a_{ij}]^T$; F is matrix of model independent parameter values at factorial experiment.

Standard statistic tests were applied to evaluate adequacy of model and significance of model parameters.

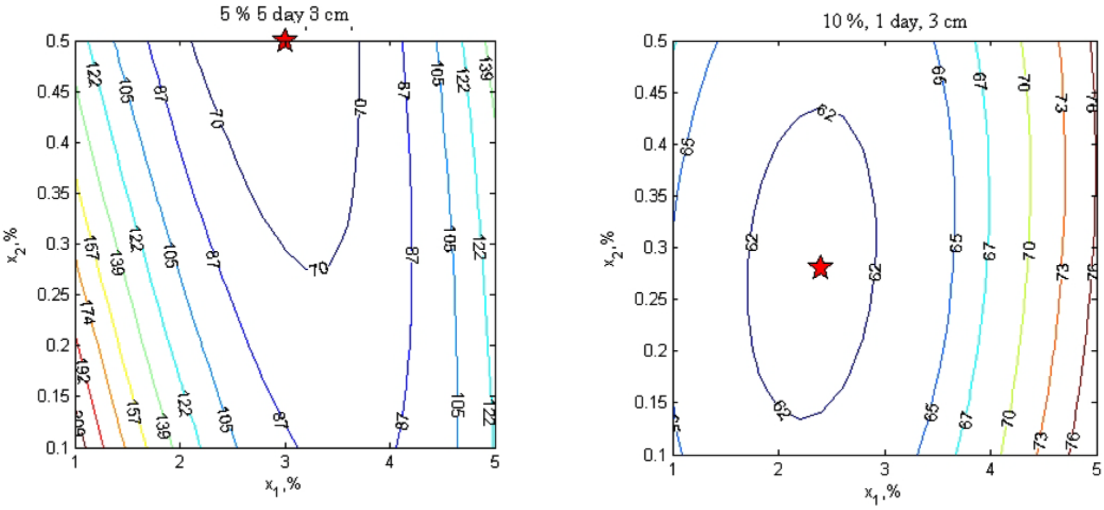
*Step 4.* Model-based prediction of S-S composition point $x^* = [x_1^* \ldots x_n^*]^T$, at which the minimum yield of hydrocarbon leakage with the particular S-S composition was obtained, and determination of optimal point location [7, 8; 9].

## Results and Discussion

*Sorbent system composition optimization in loam.* Seven statistical models for S-S optimization with respect to detention of oil contaminants were identified. Experimental data were used to identify parameter values of the statistical model (1), which was used to calculate the predicted responses corresponding to the results of the factorial experiments. From the modeled response surfaces, it can be stated that to stop heavy hydrocarbons vertical migration, when 5 % S-S was used, optimal S-S components concentrations were: $X_1 \approx 3$ % and $X_2 \approx 0.5$. The same results of modeled response surfaces were, when 10 % Sorbent was used, as optimal S-S components concentrations were $X_1 \approx 2.6$ (2.2÷3.0) % and $X_2 \approx 0.5$.

Soil as not homogenous substrate determines wider dispersion of results when measuring the oil concentration in deeper layers. The calculated response surfaces, based on identified statistical models, demonstrated that predicted optimal value of $X_1$ concentration was about $X_1$opt ~ 3 %, the predicted optimal value of $X_2$ for ground was outside the experimental design area, i.e., exceeds the value 0.5 %. However, taking into account that the soil is not homogenous substrate, it can be stated that $X_2$opt is 0.5 %, i.e. S-S consisted of 3 % of biosurfactant producing microorganisms' culture and biosurfactant (where amount of microorganisms was $\geq 10^7$ CFU/g), 0.5 % of ammonium and 0.2 % of phosphorous.

Test experiments using 5 % and 10 % of S-S at the predicted optimal concentrations ($X_1$ = 3 %, $X_2$ = 0.5) confirmed the expected decrease of crude oil vertical migration (Fig. 1a). The oil concentration measurements were made after 5 days in 3 cm depth (5 % S-S) and after 1 day in 3 cm depth (10 % S-S, Fig. 1b). The results revealed that in the first case the predicted oil leakage was set at 56.9 mg/kg, whereas experimentally achieved at 55.1 mg/kg, so it can be stated that the model prediction well coincides with the experimental result. The same results were achieved in the second case, i.e. predicted by model minimal leakage was 61.2 mg/kg, and 63.4 mg/kg was obtained in the control experiment.




a) b)

*Fig. 1.* **Comparison of experiments results (a) 5 % S-S, 5th day, 3 cm; b) 10 % S-S, 1st day, 3 cm)**

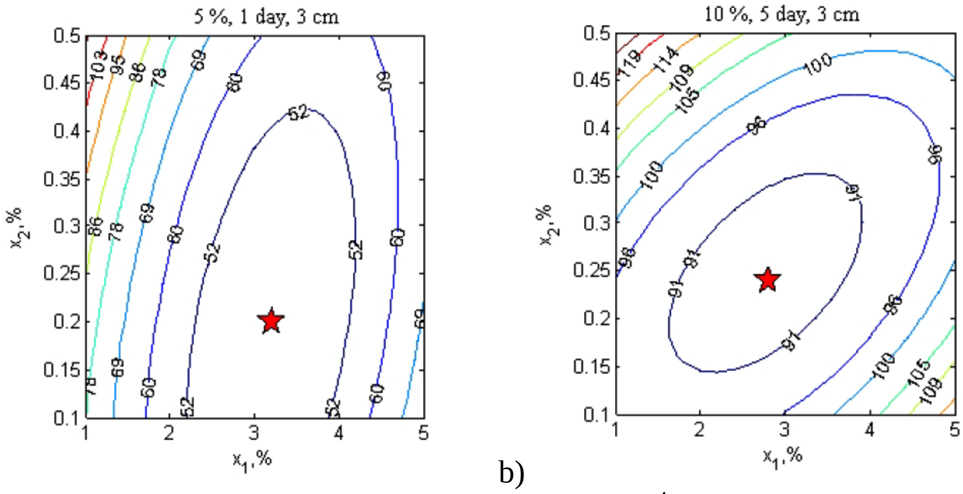
*Sorbent system composition optimization in clay.* In clay for S-S optimization according to oil contaminants detention possibilities, ten statistically reliable models were made by the same procedure as previous.

The modeled response surfaces showed that after measurement of concentrations of vertically migrating oil contaminants in various depths, it can be concluded that with 5 % S-S the optimal component concentrations were $X_1 \approx 3$ % and $X_2 = 0.2 \div 0.3$ ($\approx 0.25$ %) after 1 day and $X_1 \approx 3$ %, $X_2 = 0.25 \div 0.35$ ($\approx 0.3$ %) after 5 days.

The experiments results with 5 % S-S in deeper layers are more corrupted by random factors however the determined concentrations of S-S elements $X_1$ and $X_2$ are close to optimal (Fig. 2a). Even more, for both type substrates – loam or clay, the optimal concentrations are very close.

The calculated response surfaces show that the predicted optimal value of $X_1$ concentration is $X_1opt$ = 3 %, the predicted optimal value of $X_2$ for clay is $X_2opt$ = 0.3 %, i.e. S-S consist of 3 % biosurfactant producing microorganisms culture and biosurfactant (where amount of microorganisms was $\geq 10^7$ CFU/g), 0.3 % of ammonium and 0.12 % of phosphorous.

Test experiments using 5 % and 10 % of S-S at the predicted optimum ($X_1$ = 3 %, $X_2$ = 0.3) confirmed the expected decrease of vertical crude oil migration (Fig. 2b). Oil concentration measurements were performed after 1 and 5 days in 3 cm depth and in 8 cm depth when 10 % S-S was used. The results showed that in the first case, forecasted oil leakage was 45.7 mg/kg after 1 day and 64.2 mg/kg after 5 days, whereas experimentally calculated results were also very close – 43.7 and 67.2 mg/kg. In the second case, analogues results were achieved. Minimal leakage was 5.76 mg/kg and 23.5 mg/k (after 1 and 5 days), and during the repeated experiment vertically leaked oil concentration in 8 cm depth was 5.94 mg/kg and 21.3 mg/kg, respectively.



a) b)

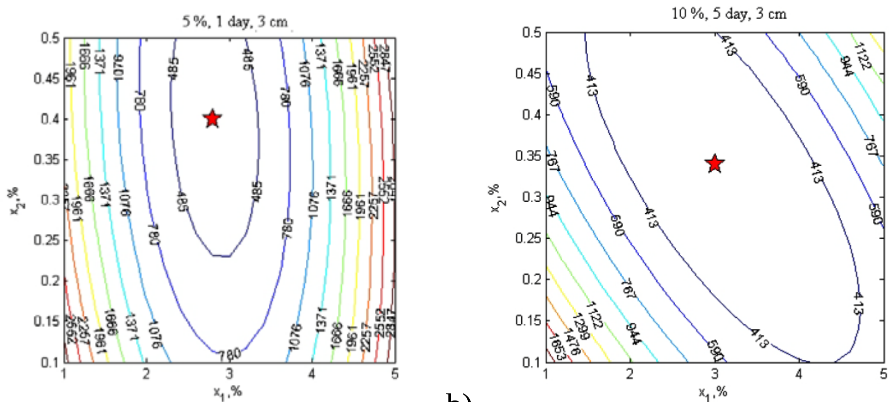
*Fig. 2.* **Comparison of experiments results (a) 5 % S-S, 1st day, 3 cm; b) 10 % S-S, 5th day, 3 cm)**

*Sorbent system composition optimization in sand.* In sand for S-S optimization according to oil contaminants detention possibilities, five statistically reliable models were made by the same procedure as previous. When oil concentration was measured in deeper layers wider data scatter was observed, which was caused by not homogenous substrate – sand.

Test experiments with 5 % and 10 % of S-S at the predicted optimal conditions ($X_1$ = 3 %, $X_2$ = 0.4 %) confirmed the expected decrease of the vertical crude oil migration (Fig. 3a, Fig. 3b). The crude oil vertical flow rate decreased 3.8 times in 3 cm depth using 5 % and 4.8 times using 10 % of S-S at the same depth, compared to that obtained at conditions corresponding to the center point of factorial experiments.

The calculated response surface, demonstrate, that the predicted optimal value of the $X_1$ concentration is $X_1$opt = 3 %, and the predicted optimal value of $X_2$ for clay is $X_2$opt = 0.4 %, i.e. S-S consisted of 3 % biosurfactant producing microorganisms culture and biosurfactant (where amount of microorganisms was $\geq 10^7$ CFU/g), 0.3 % of ammonium and 0.16 % of phosphorous.

The results show that the predicted oil leakage is 330 mg/kg (after 1 day in 3 cm depth with 5 % S-S) and 229 mg/kg (after 5 days in 3 cm depth with 10 % S-S), during the repeated experiment vertically leaked crude oil concentration results were also very close – 224 and 234 mg/kg respectively. These results showed that forecasted model results coincided with experimental.



a) b)

*Fig. 3.* **Comparison of experiments results (a) 5 % S-S, 1st day, 3 cm; b) 10 % S-S, 5th day, 3 cm)**

*Evaluation of initial moisture content in Sorbent system*

Too wet or too dry sorbtic material makes unfavorable medium for biosurfactant producing microorganisms' culture. That is why optimal level of moisture is required to keep stable amount of vital microbial cells producing biosurfactant. Therefore, it was necessary to determine the optimal initial S-S moisture. Investigations showed that with 5 % of initial S-S moisture S-S loses 5.20 % of sorbtic capability, whereas with initial 10 % of S-S moisture – up to 16 % (Fig. 4).

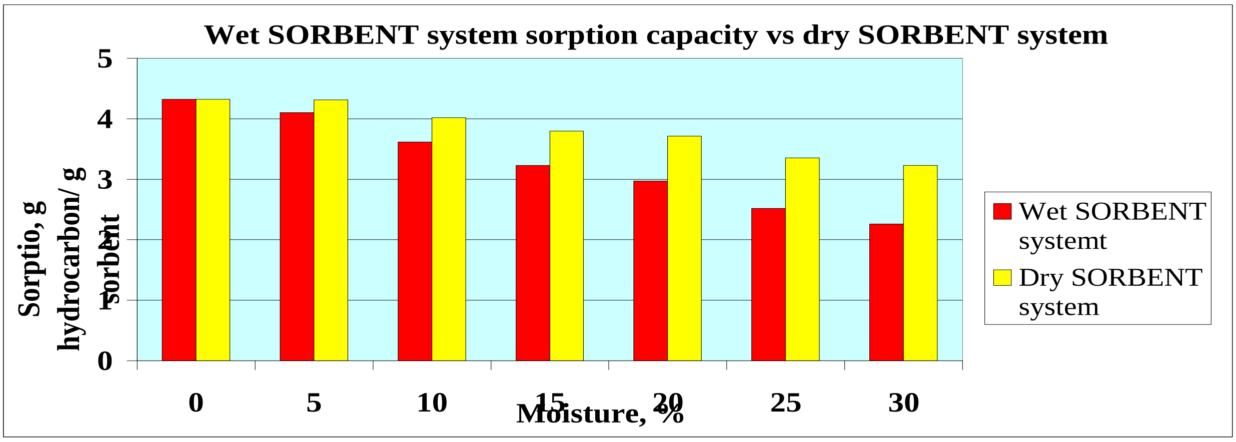



***Fig. 4.*** **Dependence of S-S sorbtic capability from initial moisture content in S-S**

As it is shown in Fig. 4, when the initial S-S moisture increased, its sorbtic capabilities decreased. According the research results, recommended optimal S-S moisture is 7 %, and it should not exceed 10 %.

*Optimum Sorbent system composition*

In loam and clay systems optimal composition of S-S reduced vertical oil contaminants migration in 8 cm depth up to 3-5 times, whereas in sand – approximately 10 times compared to when only S-M alone was used. Compared to when no S-M was used to stop vertical oil contaminants migration, S-S reduced vertical oil migration up to 10 times in loam and clay, whereas in sand – up to 30 times, when initial oil contaminants concentration was the same – 200 g/kg.

Identical experimental design procedure was used to optimize the amounts of S-S components. In all types of soil (loam, clay and sand) modeled reaction surfaces and concentrations of oil that migrated vertically in various depths showed that with 5% and with 10% of S-S used for heavy hydrocarbons degradation, optimal concentrations of its components were very similar.

Repeated experiment system composition and achieved results were approved – following optimum composition for all types of soil was determined: S-M 86.3-89.3 %, microorganisms producing biosurfactant $\geq 10^{7}$ CFU/g, initial amount of biosurfactant – 3 %, nutrients, such as nitrogen and phosphorous 0.5 and 0.2 %, additionally.

## Conclusions

Four components required in the sorbent system are indentified: sorbent material, biosurfactant producing microbial culture, nutrients (N and P) and biosurfactant.

In various depths of vertically migrated oil concentrations treated with 5 % and 10 % of Sorbent system used for heavy hydrocarbons degradation, optimal concentrations of Sorbent system components were very similar in all types of soil (loam, clay and sand). Using computer modeling it was determined that the initial amount of biosurfactant and

microorganisms' producing it has to be 3 % (where amount of microorganisms was $\geq 10^7$ CFU/g).
Optimal amount of nutrients in S-S after computer modeling was determined at 0.5 % of nitrogen and 0.2 % of phosphorous.
Also it was determined that it is necessary to keep enough amount of biosurfactant producing microorganisms' vital cells immobilized on S-M with required moisture level. Therefore, recommended optimal S-S moisture is 7 %, and it should not exceed 10 %.
Therefore, very novel and optimized S-S was developed, combining different elements that allow S-S to solve environmental problems of heavy oil pollution, especially in soil, by being both: very efficient and made from inexpensive natural components. As investigations revealed that depending on type of soil, S-S can reduce vertical oil migration up to 30 times with initial 200 g/kg oil concentration.


## Acknowledgments

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## Summary

Novel Sorbent system was developed and optimized for application *in-situ* for heavy hydrocarbons treatment in various soil types. Sorbent system is based on low-cost natural organic sorbent material developed from paper mill short fiber wastes and embedded with specific biosurfactant acting as activating agent for microorganisms producing more biosurfactant for further cleaning. During the investigations composition of S-S elements was optimized in order to minimize the leakage of heavy hydrocarbons to deeper soil layers or ground water.


### References


1. Setti, L., Mazzieri, S., Pifferi, P. G. 1999. Enhanced degradation of heavy oil in an aqueous system by a Pseudomonas sp. in the presence of natural and synthetic sorbents. Bioresource Technology, 67(2), 191-199.
2. Suni, S., Kosunen, A. L., Romantschuk M. Microbially Treated Peat-Cellulose Fabric as a Biodegradable Oil-Collection Cloth. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering, 1532-4117, Volume 41, Issue 6, 2006, Pages 999 – 1007.
3. Gertler, C., Gerdts, G., Timmis, K.N., Golyshin, P.N. Microbial consortia in mesocosm bioremediation trial using oil sorbents, slow-release fertilizer and bioaugmentation. FEMS microbiology ecology, Vol. 69, No. 2, Aug 2009, pp. 288-300.
4. Gertler, C., Gerdts, G., Timmis, K.N., Yakimov, M.M., Golyshin, P.N. Populations of heavy fuel oil-degrading marine microbial community in presence of oil sorbent materials. Journal of applied microbiology, Vol. 107, No. 2, Aug 2009, pp. 590-605.
5. Biswas S., Chaudhari S. K., Mukherji S. (2005). Microbial uptake of diesel oil sorbed on soil and oil spill clean-up sorbents. Chem Technol Biotechnol 80:587–593.
6. Martha, D., Mulligan C.N. Rhamnolipid Biosurfactant Assisted Dispersion and Biodegradation of Spilled Oil on Surface Waters. Paper presented at the 2005 Proceedings, Annual Conference - Canadian Society for Civil Engineering, 10 p. 2005.
7. Montgomery, D.C. 2008. Design and Analysis of Experiments. John Wiley&Sons. P. 680.
8. Myers, R.H, Montgomery, D.C. 2002. Response Surface Methodology, Process and Product optimization Using Designed Experiments. John Wiley & Sons, 798 p.
9. Theodore, R., Panda, T. 1995. Application of response surface methodology to evaluate the influence of temperature and initial pH on the production of beta -1,3 glucanase and carboxymetyl cellulose from Trichoderma harzianum. Enzyme Microb. Technol, 17, 1043-1049.

# WATER QUALITY MODEL DESCRIPTION

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**Abstract.** *Water wise use and conservation is one of the key prerequisites for economic sustainable development. Accession to the European Union, Latvia is committed to meeting the EU environmental requirements. Water Framework Directive (Directive 2000/60/EC, 2000) is a legal act, which provides water protection and sustainable management principles and tasks of the European Union. It provides uniform protection and management system for all waters: rivers, lakes, coastal waters and groundwater, providing that they must also achieve good water quality by 2015. year. The Directive provides for the identification of the current water situation and to obtain additional information by following the water monitoring and for basic background information to establish an action program to improve water quality. Therefore, the Latvian conditions are important to assess the flow of nutrients, their sources and amounts of Latvian detention basins using existing models and innovations in methods and model systems for the retention of part of the calculation. Therefore, in this publication are offered in various countries of the world models will be useful in Latvian processing of data.*

**Keywords:** *monitoring of water, nutrients flow, retention, calculation, mathematical modeling opportunities.*

## Introduction

Geological structure, hydrogeological conditions, climate, land use character and intensity, as well as anthropogenic pollution levels Latvian significantly different from the situation in other countries. Latvian has been quite extensive and long-term studies of water chemistry and water structure analysis, however, these studies have been summarized and critically reviewed. Similarly, until now relatively little Latvian is used in mathematical modeling capabilities that allow analysis of the flow basin sub-basin level, and to identify human activity is causing pressure on surface water quality. In general, the concentration of nutrients in Latvian waters characterized by high turnover, which provides natural and anthropogenic factors interact. Of natural factors have significant effects of climatic conditions and hydrological regime variability, and biotic conditions in the development of a water body. Therefore, the Latvian conditions are important to assess the flow of nutrients, their sources and amounts of Latvian detention basins using existing models and innovations in methods and models of systems and nutrient retention of part of the calculation. To do this, it is necessary to study in Europe and the world of the models offered.

## Materials and methods

Global assessment of nutrients loads are widely used modeling techniques which reflect existing knowledge about the emissions, flows and transformation processes in the catchment and water body. [1, 2, 8, 10] the large number of models provides a growing range of problems, and the fact that models typically are created for a particular catchment area or the region, where other models have not yet been applied. It should be noted that the models are diverse in their capabilities and limitations, so they must be carefully chosen. So far, Latvian diffuse or diffuse modeļing calculations used only a few studies (projects) to a defined catchment area or any part in the effective use of limited available data and the lack of research (especially in the last ten years), the model could be adapted to Latvian conditions. Therefore, in order to make calculations for the diffuse distribution of river basin districts, is used in the Helsinki Commission "loads to the Baltic Sea (HELCOM PLC) program following recommended methodology. [6; 7] It is worth noting - if not available the necessary data and calculations are make certain assumptions, the calculation result obtained approximate figures for the diffuse (mostly forest and farmland-related) and point source pollution in the percentage distribution of river basins. Since the currently lacks the necessary information and the lack of a separate study of the Latvian river basin and the resulting diffuse the results of calculations can be considered as estimates. Water quality models are powerful tools for effective water management and planning. Large number of models provides a growing range of problems, and the fact that conventional models are created for a particular catchment area or the region, where other models have not yet been applied.

*Table 1.*

**Water quality models in Europe**

| **Model name** | **Origin** | **European applications (Nation)** | **Purpose / Substances modelled** | **Process description** |
|---|---|---|---|---|
| AGNPS | USDA; 1987 | AUT, BE, CH, CZ, DE, DK, ESP, FI, FR, HU, IRL, IT, LTU, NL, POL, PRT, RUS, SVK, UK | nutrients, pesticides | conceptual |
| HBV-N | SMHI; 1994 | SE, EST | eutrophication control / nitrogen transport | conceptual |
| INCA | Univ. of Reading; 1998 | UK, FI, NO, DE, DK, NL, FR, ESP | eutrophication control / nitrogen transport | conceptual / mechanistic |
| MAGIC | Univ. of Virginia; 1985 | UK, NO, DE, ESP, FI | acidification control / nitrogen transport | conceptual / mechanistic |
| MERLIN | Univ. of Virginia; 1997 | UK, SE, NL, NO | acidification control / nitrogen transport | conceptual |
| MIKE SHE | DHI; 1993 | BE, CH, DE, DK, CZ, ESP, FR, GR, HRV, HU, IT, LTH, NL, NO, POL, SVK, SLO, SE, UK, YU | eutrophication control / pollutant transport, nitrogen transport | mechanistic |
| SHETRAN | Univ. of Newcastle; 1996 | UK, ESP, FR, IT, PRT | pollutant control / sediment and nitrogen transport | mechanistic |
| SMART | Wageningen UR; 1989 | FI, NL, CZ, TUR, RUS, ESP, AUT | acidification control | mechanistic |
| SWAT | USDA; 1993 | 13 European countries e.g., IT, DE, UK, BE | eutrophication and pesticide control /sediment, nutrients, | conceptual |

AGNPS (Agricultural Non-Point Source pollution model) - a model developed to examine the water quality as affected by soil erosion from agricultural and urban areas. AGNPS has three major components: hydrology, soil erosion and nutrient pollution.
HBV-N - simulate nitrogen leaching and transport through the groundwater, river and lake systems.
INCA (Integrated Nitrogen in Catchments) - Using the mass balance and reaction kinetics, INCA model composed of several sources of N and N of the principle of mechanism, including mineralization, immobilization, nitrification and denitrification.
MAGIC (Model of Acidification of Groundwater in Catchments) - a dynamic model of soil and water acidification can reconstruct and predict the catchment scale.
MERLIN (Model of Ecosystem Retention and Loss of Inorganic Nitrogen) - C and N cycle in ecosystems.

SHE (Système européen Hydrologique) - modeling system, which describes the main land hydrological cycle-flow processes. With regard to water quality modeling, SHE was first used in the modeling of nitrogen.
MIKE SHE - a dynamic simulation tool for analysis, planning and management, large water resources and environmental problems associated with surface water and groundwater, particularly where there is human intervention.
SMART (Simulation Model for Acidification's Regional Trends) - It is a simple soil acidification and nutrient cycle model that includes the main hydrological and biogeochemical processes.
SWAT (Soil and Water Assessment Tool) - There is a complex conceptual model. It is a continuous-time model, which operates daily during the period, the model is designed to control the impact of decisions on water, sediment, nutrient and pesticide yields with reasonable accuracy river basins. [4, 12, 13, 14, 15]

*Table 2.*

**Water quality models for soil water and field scale in Europe**

| **Model name** | **Origin** | **European applications (Nation)** | **Purpose / Substances modelled** | **Process description** |
|---|---|---|---|---|
| ANIMO | Wageningen UR; 1991 | BE, CH, DE, DK, CZ, FR, IT, NL, NO, POL, RUS, SLO, UK | nitrogen leaching to groundwater | mechanistic |
| EPIC | USDA; 1984 | FR, DE, UK | soil erosion, nutrient cycling, pesticide fate, agricultural economics | conceptual |
| GLEAMS | USDA; 1987 | FI, POL, DE, SE, RUS, UK, CZ | agricultural pollutants | conceptual |
| HYDRUS / SWMS | USDA; 1996 | AUT, BE, DK, FR, DE, IT, NL, POR, ESP, SE, CH, UK | solute transport in porous media | mechanistic |
| MACRO | Swe. Univ. Agric.Scien.; 1994 | SE, SP, DE, UK | solute transport in arable soils | mechanistic |
| PEARL | Alterra, NL; 2000 | NL, SE, IT | pesticide leaching | conceptual / mechanistic |
| PRZM | US EPA; 1984 | pesticide movement | | mechanistic |
| SOILN | Swe. Univ. Agric.Scien.; 1987 | SE, NO, FI, DK, EST | nitrogen leaching from arable soils | mechanistic |
| WAVE | Univ. Leuven; 1995 | BE, NL, TUR | soil chemical transport | mechanistic |

ANIMO (Agricultural Nitrogen Model) - dynamic model of carbon, nitrogen and phosphorus cycles, and saturated and unsaturated soil systems. This model has been developed for the analysis of nitrogen leaching from the soil surface, groundwater and surface water.
EPIC (Erosion- Productivity Impact Calculator) - This model has been developed to assess the impact of soil erosion on soil productivity.
Gleams (Groundwater Loading Effects of Agricultural Management Systems) - It has four major components: hydrology, erosion, sediment yield, pesticide transport, and nutrients.
HYDRO / SWMS - environmental modeling water flow analysis, and solute transport porous.
MACRO - The mathematical model of water flow and reactive solute transport in soil
PEARL (Pesticide Emission Assessment at Regional and Local scales) - have been used for pesticide registration procedure.

PRZM (Pesticide Root Zone Model) - This model consists of the hydrological (flow) and chemical components of transport channels to simulate the erosion, leaching, decay, etc.
SOILN (or Coupe Model) - Model description of nitrogen dynamics and losses in the soil profile of agricultural lands.
WAVE (Water and Agrochemicals in the Soil, Crop and Environment Lead) - describes a substance transport and energy transformations in the soil and the soil. [4, 5, 6, 9, 11]

*Table 3.*

**Water quality models to groundwater in Europe**

| Model name | Origin | European applications (Nation) | Purpose / Substances modelled | Process description |
|---|---|---|---|---|
| ASM/ASMWIN | ETH; 1986 | CH | pollution dispersion | mechanistic |
| MODFLOW/MT3D/RT3D | USGS; 1988 | e.g. NL, DE, FR, IT, SE, UK | groundwater flow, solute transport | mechanistic |

ASM / ASMWIN (Aquifer Simulation Model / for Windows) - is a horizontal or vertical, two-dimensional groundwater flow and transport model.
MODFLOW/MT3D/RT3D - is used to simulate the water supply system. [9, 13, 14, 15, 16, 17]

*Table 4.*

**Water quality models for lakes in Europe**

| Model name | Origin | European applications (Nation) | Purpose / Substances modelled | Process description |
|---|---|---|---|---|
| DELWAQ-BLOOM-SWITCH (DBS) | RIZA; 1994 | NL, Danube countries | eutrophication management | mechanistic |
| DYRESM | Centre for Water Research, University of Western Australia; 1980 | BIH, FI, FR, DE, GR, IT, NL, NO, POL, PRT, ESP, SE, CH, TUR, UK | hydrodynamics and water quality in lakes and reservoirs | mechanistic |
| LIMNOD | Eldgenössische Technische Hochschule, Zürich, Switzerland; 1992 | CH | lake management and scenario modelling | mechanistic |
| PC-LAKE (PCLOOS) | LWD; 1992 | NL | eutrophication management | mechanistic |
| PH-ALA | Univ. of Rome, Italy; 1996 (?). | IT | eutrophication trend analysis | mechanistic |

*Table 5.*

**Water-quality samples of urban rainwater in Europe**

| Model name | Origin | European applications (Nation) | Purpose / Substances modelled | Process description |
|---|---|---|---|---|
| MOUSE | DHI; 1980's | distributed to all European countries, but unclear if used for water quality modelling | water quality and sediment transport modelling package for urban drainage systems, storm water sewers and sanitary sewers | mechanistic |
| SWMM | US EPA; 1970's | CZ, DK, FR, IT, ROM, ESP, SE, but unclear if used for water-quality modelling | all aspects of the urban hydrologic and quality cycles, including rainfall, snowmelt, surface and subsurface runoff, flow routing through drainage network, storage and treatment | mechanistic |

*Hydrology Models*

MIKE model families. These are the Danish Hydraulic Institute (DHI) has developed physically reasonable models (MIKE 11, MIKE FLOOD, MIKE 21, MIKE Basin. Model operation requires a comprehensive and detailed information about the river basin.

*HBV model*

HBV model developed in the Swedish Meteorology and hydrology Institute (SMHI), 20th century 70 years old at the beginning, it was created by Professor S. Bergstrom. The model has many different variations. The advantage for the Nordic countries - it is believed that this pattern is best developed in the snow melting / formation scheme. Rain, snow, air temperature is used as raw data for calculating the water flow rate.

Channel general water can be described as follows:

$$P - E - Q = \frac{d}{dt}\left[SP + SM + UZ + LZ + lakes\right] \qquad (1)$$

The various versions of the HBV model has been applied in over 40 countries worldwide. It is suitable for countries with so different climatic conditions, such as Sweden, Zimbabwe, India and Colombia. HBV can be used as a semi-distributed model. Each area is divided into zones according to altitude, lake area and vegetation. The model is usually open every day for rainfall and temperature calculation, as well as daily and monthly estimates of potential evaporation. Model is used for flood forecasting in the Nordic countries, and many other purposes such as flood modeling, water resources assessment collection, nutrient load calculation.

Input data are observations of precipitation, air temperature and estimates of potential evapotranspiration. For example, proposed in the literature: [5, 13]

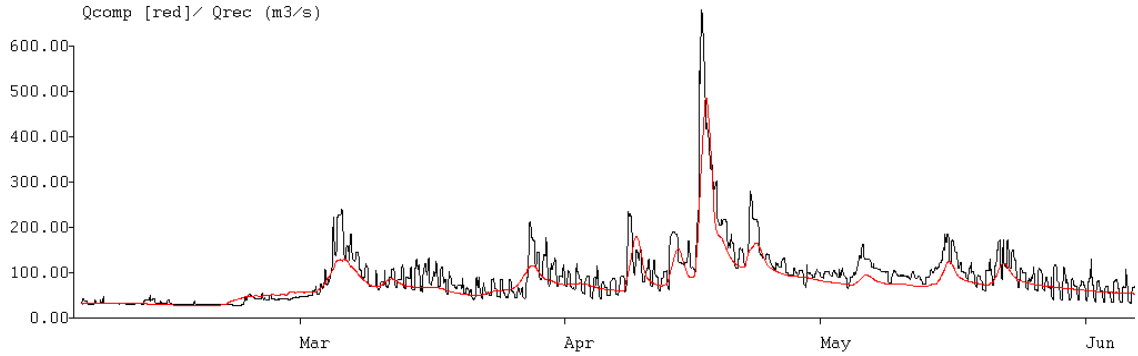


*Figure 1*. **Obtained (Qrec) and calculated (Ocomp) A comparison of data at 1 hour of inundation model**

*SWAT model*
The model aims to: provide for and determine the impact of economic activities on water quality, provide for the consequences of various business-to-water, sediment, certain nutrients, pesticides and large quantities of N in closed basins. In studies using data on weather conditions, surface runoff, flow, infiltration, ET, transmission losses, pond and reservoir location, grain yield and irrigation, groundwater flow, nutrient and pesticide use, water movement. [17]
Fyris model
There was the 1996th in Sweden to determine the characteristic of river nutrients (nitrogen and phosphorus) pollution load distribution, and retention (retention) factor FRYS river in central Sweden. Since the case of river basins divided into homogeneous fractional basins, which represent the hydrochemical monitoring of water quality measurement points.

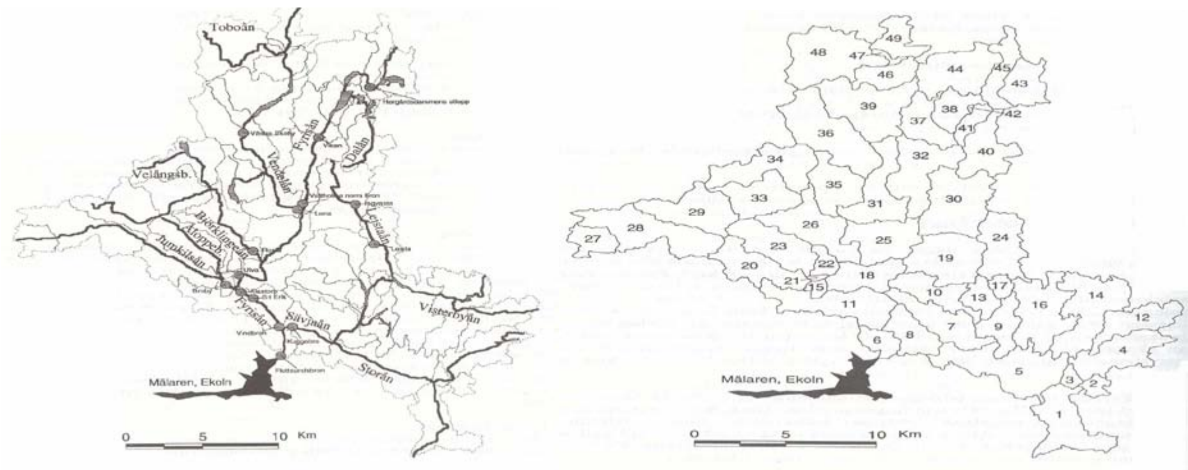


*Figure 2*. **River basin fractional basins** [15]

## Results and analysis

Loads of biogenic elements and flow of the assessment can be used for statistical and dynamic models. Statistical models based on regression analysis, for example, between the observed concentrations of nutrients and water flow rate, or between the observed nutrients loads and catchment characteristics. Dynamic model conceptually describes the physical, chemical and biological processes in the catchment and water and nutrients simulate load and water flow rate. Dynamic models can be used for water quality forecasting purposes. [3] From the HELCOM PLC guidelines, for a given river basin in diffuse or diffuse pollution discharged to surface waters from the mainland, Latvian at the expense of two ways: (1) where it is monitored in all diffuse and point source pollution load of the river basin, the result can be calculated by the river load (2) if the monitored river and separate the diffuse and point sources of pollution of the river basin. In my opinion, would be applicable in Latvia HBV model for nutrient load calculation [6].

*METQ model*

Latvian since the late 80th years of groundwater regime and runoff mathematical modeling is used in conceptual models and METUL METQ family. On the input data used in daily meteorological observations. So far, the model is successfully calibrated for both large (the Daugava, Salaca), although some small river basins. Develops over time METQ model, it has been several versions (METQ96, METQ98, METQ2005, METQ2006). Model is the latest version of METQ2007BDOPT with semi-automatic calibration feature. It is possible to calibrate a conceptual model METQ2007BDOPT with different values describing the pool surface climatic and geomorphologic conditions Latvian river basins, which have been terminated or will continue to hydrologic comments Model METQ a conceptual mathematical model with the use of variable sites (distributed) parameters. METQ conceptual model has the following user options: ground and surface water runoff (including runoff transformation) estimates of snow accumulation and melt modeling. Using this model, it is possible to calculate hydrological variables - the average daily flow rate. Of the simulated and observed flow rate reproducibility indices have been adopted by the statistical criterion R2, correlation coefficient r and the average permanent drainage basin. River District runoff process model representing the four main calculations: snow formation and ablation, the active soil layer balance, ground water and the inside layer of the balance sheet as well as runoff transformation parts of the basin drainage network. River basin or parts of the basin a space less than 2000 km2, which is not large lake or broad flood plain with a large pop-regulating capacity, can be considered as linear hydrological system and the relationship between the output can be described by linear differential equations with concentrated or fixed parameters. Conversely, if the lake basin, the drainage basin of such a transformation is calculated with the hydraulic methods. In Mode total runoff is characterized by the following components - surface runoff (Q1) and groundwater runoff, which in turn divided into the upper layer of groundwater runoff (Q2) and the lower layer groundwater runoff (Q3). Surface runoff can be divided into two groups depending on the underlying frameworks: infiltration excess runoff, or Horton runoff: soil saturation runoff, which occurs when the soil is saturated with water to land surface. In Model METQ2007BDOPT is divided up into three different types of water collections: collections of moisture in the snow, Stocks soil moisture on the active layer moisture and groundwater stocks capillary-off layer. [6 7]

## Summary

Latvian circumstances, it is important to assess the flow of nutrients, their sources and amounts of detention basins, using existing models and innovations in methods and model systems for the retention of part of the calculation. Therefore, in this publication are offered in various countries of the world models will be useful in Latvian processing of data and approbation.

### References

1. Arheimer B., Brandt M. (1998) Modelling nitrogen transport and retention in the catchments of southern Sweden. *Ambio* 27(6), 471-480.
2. Clark M.J., Cresser M.S., Smart R., Chapman P.J., Edwards A.C. (2004) The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland. *Biogeochemistry* 68, 1-19.
3. Grimvall A., Stalnacke P. (1996) Statistical methods for source apportionment of riverine loads of pollutants. *Environmetrics* 7, 201-213.

4. Helsel D.R., Hirsch R.M. (1992) Statistical methods in water resources. Amsterdam: Elsevier Science Publ. B.V.
5. Iital A., Stalnacke P., Deelstra J., Loigu E., Pihlak M. (2005) Effects on large-scale changes in emissions on nutrient concentrations in Estonian rivers in the Lake Peipsi drainage basin. *J. Hydro*l. 304, 261-273.
6. Jansons V. (2005) Lauksaimniecības noteču monitorings. LLU tēma Nr.13/04 L-105.
7. Kļaviņš M., Rodinovs V., Kokorīte I. (2002) Chemistry of Surface Waters in Latvia. Rīga:LU, 286 pp.
8. Petersen W., Bertino L., Callies U., Zorita E. (2001) Process identification by principal component analysis of river water-quality data. *Ecol.Model.* 138, 193-213 26
9. Rantakari M., Kortelainen P., Vuorenmaa J., Mannio J., Forsius M. (2004) Finnish lake survey: the role of catchment attributes in determining nitrogen, phosphorus, and organic carbon concentrations. *Water, Air, Soil Pollut.: Focus* 4, 683-699.
10. Shrestha S., Kazama F. (2006) Assessment of surface water quality using mulitivariate statistical techniques: A case study of the Fuji river basin, Japan. *Environ.Modell.Softw. (in press)*
11. Stalnacke P., Vandsemb S.M., Vassiljev A., Grimvall A., Jolankai G. (2004) Changes in nutrient levels in some Eastern European rivers in response to large-scale changes in agriculture. *Water, Sci. Technol.* 49, 30-36.
12. Vassiljev A., Stalnacke P. 2003. Statistical modelling of riverine nutrient sources in the Lake Peipsi drainage basin. Diffuse pollution conference proceedings, Dublin, 41-46.
13. http://iopscience.iop.org/1755-1315/4/1/012004/pdf/ees8_4_012004.pdf
14. http://www.meteo.lv/upload_file/Udens%20kvalitates%20modelesanas%20sistema%20Lielupes%20upju%20baseina%20apgabalam.pdf
15. http://kalme.daba.lv/faili/materiali/LU_Zin_konference/Prezentacijas%20LU65KONF/AbramenkoK_LegzdinsA.pdf
16. www2.llu.lv/homepg/lif/konf/kagm.ppt
17. www2.llu.lv/homepg/lif/konf/vj.pdf

# SYSTEM ANALYSIS IN THE ENVIRONMENTAL SCIENCE

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**Abstract.** *The paper discusses the essence, structure, research objects, methods and aims of the environmental science.*
*Due to interdisciplinary character of the environmental science, large scale term and vague boundaries with other sciences there are various definitions of environmental science and different concepts, sometime delusions in research fields and methods .*
*Author analysed the current location of research objects in environmental science and their connection with other sciences and came to conclusion that up to nowadays there are not developed essential part of every independent science yet – general theoretical base of environmental science.*
*It is necessary to find out perfect proper research fields and objects of environmental science, which differ from other natural , and technical sciencies.*
*Analysis showed that the objects of environmental science must be neither nature nor technology itself but only contact zones between technosphere and biosphere –namely, between systems – technosystems and ecosystems .*
*Exactly in these contact zones arises most environmental problems , conflicts and stresses between human activities and nature.*
*The properties and processes in these zones obey to laws which must be determined, interpreted and used for mankind wealth.*
*It is the aim of environmental science and the complex system analysis must be essential research methodology and accordingly system engineering as instrument for solving practical environmental problems.*

**Keywords:** *Environmental science, ecology; complex environment systems; environmental education; technosphere; biosphere.*

## Introduction

Specificity of the environmental science is related to its complex multifactorial structure. Literally the term “environmental science” is very broad.
Generally a title of any science derives from multiple, sometimes subjective, considerations and it is not essential per se.
Usually the title has no reflect on the essence and the content of particular science.
It is different when the content, structure and methodology of the science are not fully formed yet. Then the title can become the reason for various and ambiguous interpretations of the content of the science and the source for misunderstandings.
Environmental science is a relatively new field of science. Therefore it is important to clarify terminology and define its content and essence.
The term “environment” has meaning only if a central object exists which has surrounding – living organisms and objects, energy and information fluxes, space, social interactions etc constituting an environment.
Any kind of science research area also is environment in its different aspects. It examines an object surrounded by a particular environment.
In this regard the term “environmental science” is not entirely accurate – “environment” is not linked to an object and therefore becomes too broad in comparison with the complex of problems this science deals with. It creates an impression that environmental science is not a completely autonomous science, but conglomerate, artificially comprised with components from other sciences. This view is further enforced by the fact that research areas of environmental science continuously broaden and new sub-sectors of environmental science emerge.

The problem is not new. Issues related to the essence and content of environmental science, its place between other sciences is discussed constantly due to its various definitions. Currently used definitions [1, 2, 3, 4] see environmental science as

- Synonymous to ecology,
- Same as ecology, but including humans in its biota,
- Science of interaction processes between humans and the environment,
- Science of physical and chemical pollution processes,
- Science of problems of pollution, overpopulation, depletion of resources etc.

Components included within the scope of environmental science also vary. Different sources show atmospheric sciences, ecology, environmental chemistry, environmental biology, geological sciences etc. being included.

Therefore views about the place of the environmental science among other sciences vary.

Environmental science is seen as a part of ecology and vice versa – includes ecology, is separated or put on the same level as environmental management, environmental protection, included in the block of Earth sciences or left out of it etc.

Often the definitions of environmental science are formulated following principle of additivity – first they state interdisciplinary nature of the science, which gives a justification for adding the array of problems from other, related scientific fields. Finally, they conclude with comprehensive global aim. [5, 6, 7, 8].

Such constructions cannot distinguish the field of environmental science clearly and unambiguously.

Current voluntary distribution of environmental science research areas across other scientific fields without one nucleus may be illustrated with Fig. 1.

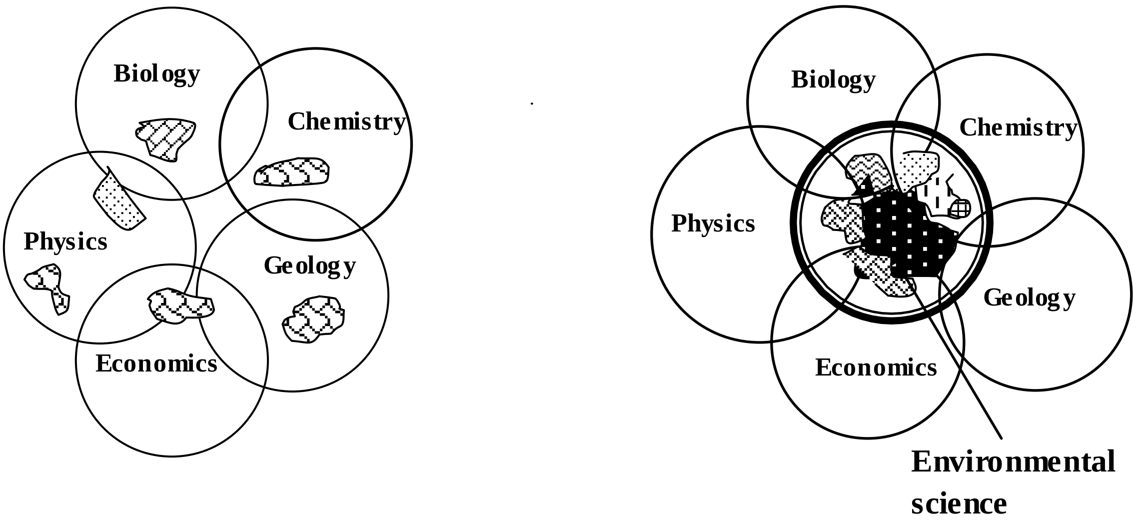


*Fig.1.* **The current (a) and optimal (b) - centred by nucleus of the theory - environmental science research objects in relation to other branches of science**

- problems related to environment science

In Latvia a de-centralized approach prevails not only in environmental education (in schools environmental issues are distributed across different subjects) but also in official nomenclature of scientific degrees. In Latvia, a doctor's degree in environmental science (Dr. env.) as such does not exist. Only doctor's degrees in biology (Dr.biol.), economy (Dr.oec.), physics (Dr.phys.), geography (Dr.geogr.), chemistry (Dr.chem.) with an extension to environmental science are obtainable. [9]

In addition to that in the Latvian Education Classification environmental protection is included in the thematic group of service industries. [10]
All the above proves that despite large and growing number of researches, problem solving projects and publications, which with different level of concessions can be associated with environmental science, the science itself in its classical meaning has not yet materialized.
At first, any science cannot exist without its nucleus – theory.
Research shows that currently environmental science lacks a theoretical basis forming this science. Environmental science cannot be only a collection of methods of environmental protection, preservation of resources, pollution prevention etc.
Environmental science just as any other science must have developed, researched, proved theory, laws, regularities and methodology that would serve as a base for applied solutions of environmental problems. However, currently in environmental science practical problem solving prevails and development of theory is slow.
Any autonomous science has clearly defined research objects (including processes), research methodology (and methods) that are founded on a common theoretical basis of this scientific field. Let's examine the essence of these parameters in environmental science.

**Research objects in the environmental science**

The term "environmental science" was created at a time when ecology already existed; furthermore, it was actually a derivation of ecology. This lead to the definitions of "ecology" and "environmental science" being identical and at present they are often perceived as one science. [11]
The term "ecology" in its classical meaning was introduced in 1866 by German scientist Ernst Haeckel [12] but only 10 years later when Danish botanist Johannes Eugenius Warming wrote the first monograph stating theoretical fundamentals of ecology, did it become a science [13].
System analysis were implemented in ecology by H.G. Andrewartha, L.C. Birch, [14], E.P Odum, [15], Kelly, Evelyn B. [16].
Ecology as a scientific field gradually expanded its research scope including almost all areas of human activity (int. al. social ecology, human ecology, even ecology of ecosystems). Currently, the original concept of ecology as the science that deals with organisms and their relations with surrounding environment, does not comply with the actual scope of its research. Consequently the definition of ecology is changed.
The number of directions of scientific research that has "ecology" (or "eco") in their title already exceeds 30 and continues to grow.
Research directions such as "environmental ecology", 'industrial ecology" and "agroecology" have emerged.
The main research object of ecology is ecosystem. Unity of biotic and abiotic environment creates a system. Subsequently principles of system analysis can be applied to it. [17]. At the same time these ecological research objects are components of the greater system – natural formation - the biosphere.
Articifial systems made by humans belong to other formation – the technogenic sphere or the technosphere. The technosphere and the biosphere exist in the same space. (Fig. 2)
The biosphere and technosphere are linked to each other and together form a complex system (super system) [18].
Characteristic properties of complex systems are:
- No centralized control,
- Many autonomous heterogeneous components,
- Each subsystem has its own operational purpose,
- Processes are characterized by nonlinear dynamics,
- They mainly are indeterministic, capable of destroying stability and even create chaos.

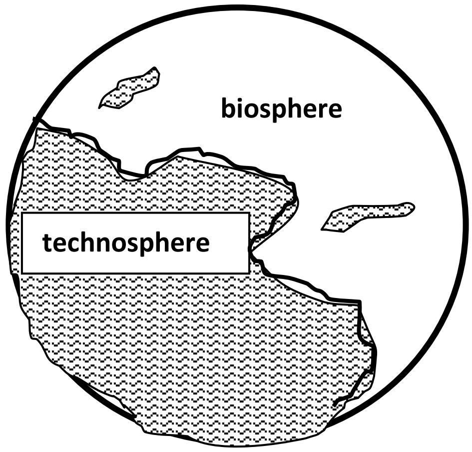


*Fig.2.* **Interaction fields of the technosphere and biosphere**

The subsystems of these complex systems develop by constantly interacting, exchanging energy, matter and information and trying to gain positive results according to their own operational purpose. [19,20]

Let’s examine the technosphere in this context.

The key structural element of the biosphere is ecosystem, but the key element of technosphere is technogenic system (technosystem, anthroposystem). The technosystems just as ecosystems are controlled by respective laws but they are different.

Ecosystems are natural systems and are controlled by laws of nature whereas technosystems are constructed by humans and controlled by laws set by humans.

Technosystems and the whole technosphere is part of the biosphere – they occupy space within it, gradually force natural systems out and replace them with artificial ones (see Fig. 2).

The main conflict is that laws set by humans do not comply with the laws of nature. As rules of nature are primary, absolute and cannot be altered, technogenic systems have to be secondary to the laws of nature.

Contact zones between the technosphere and biosphere (or more precisely technosystems and ecosystems) are dynamic, variable and become zones of conflicts where tension and conflicts arise and environmental protection problems emerge.

There are direct and indirect contact zones. Technosystems are mostly separated from natural systems by a transitional buffer zone – the environment altered and adapted by humans – infrastructure that assures quality of level of human life.

This zone is the interaction zone of natural laws and human laws (Fig. 3)

As its conditions and efficacy are controlled by human intellect and knowledge conditionally it can be identified as the noosphere in its narrowest meaning according to Theilard de Chardin [21] and V.Vernadsky [22].

These zones are the object of research of environmental science.

The research object of environmental science is the contact zone of structural elements of two common systems, the links between the technosphere and biosphere and their interaction processes.

The driving forces of environmental research are: the elimination of internal conflicts in the development of the biosphere and technosphere as a common complex supersystem, harmonization of natural and anthropogenic laws with improvement of the latter according to the former.

**Research methods in the environmental science**

The research area of environmental science is systems. Therefore the cornerstone of an environmental research methodology is systems theory and environmental system analysis.

Criteria of systemic approach (thinking) were developed by biologist Ludwig von Bertalanffy in the third and the forth decades of $20^{th}$ century released initially in his publications in biology and later in psychology, ecology [23].

A fundamental contribution to the theory of open systems was given in 1970-ties by Ilya Prigogine who developed the theory of self-organization of dissipative structures. [24]

Systems analysis includes flux of energy and materials, structural analysis of components and their optimization. But the main research tool of systems analysis and therefore environmental science is systems modeling and a whole complex of methods of physical, chemical and biological environmental research.

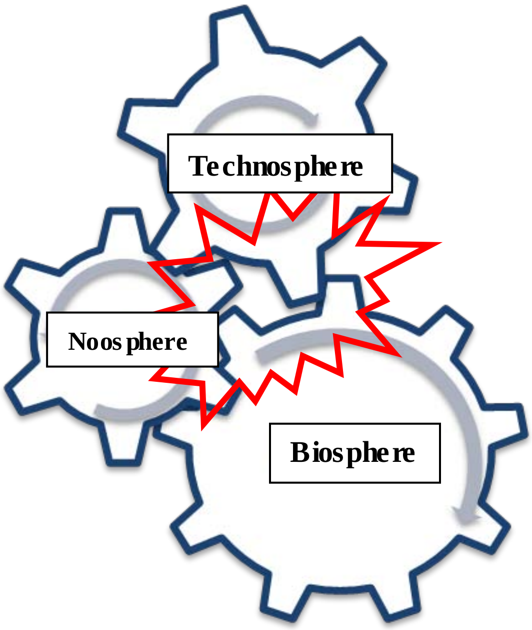


*Fig. 3.* **The scheme of interaction between the biosphere, technosphere and noosfere**

 **-** Interaction zones with high potencial of conflicts

System analysis provides an opportunity to find exact zones of interacting entities where conflicts emerge. Thus it becomes possible to express conflict mathematically and also to perform analogue and mathematical modeling. As a result, the problem transfers to the category of engineering exercises and can be solved using methods of engineering, including creative engineering problem solving methodology TRIZ [25], which is rooted in system analysis.

The process of analysis and the relationship between the spheres can be illustrated using example of the interaction model where the biosphere, technosphere and noosphere are depicted as gearwheels (Fig. 3). It shows numerous zones of conflicts and risk (speed of gearwheels, shape, size, number of gears etc). If in the model gearwheels are changed to round reels (Fig. 4), the number of potential conflict points and level of risk reduces by 86%.

According to systems theory, complex systems analyse on different levels of hierarchy, separating an individual group of interactive components for each level. For environmental system analysis it is important to determine the correlation between intensity parameters of technology T (basic structural element of technosphere), environmental quality V (conditions of natural systems) and resources consumption (the strongest link between nature and technology – input flux) as well as the dynamics of their change.

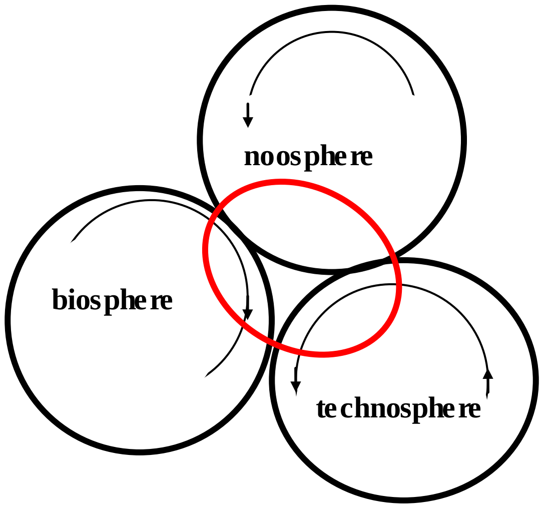


*Fig. 4.* **Interaction between spheres with reduced potential of conflicts**

These links can be examined by constructing a structural triangle "Environment – Technology – Resources" (ETR) diagram (Fig.5). The ETR diagram allows comparing different technologies and areas of industry in terms of resources (input of energy and materials) and environmental capacity (acceptable environmental damage) depleting dynamics regardless of particular type of industry. The diagram allows examination of interaction between separate variable parameters and gives the option to make decisions based on it.

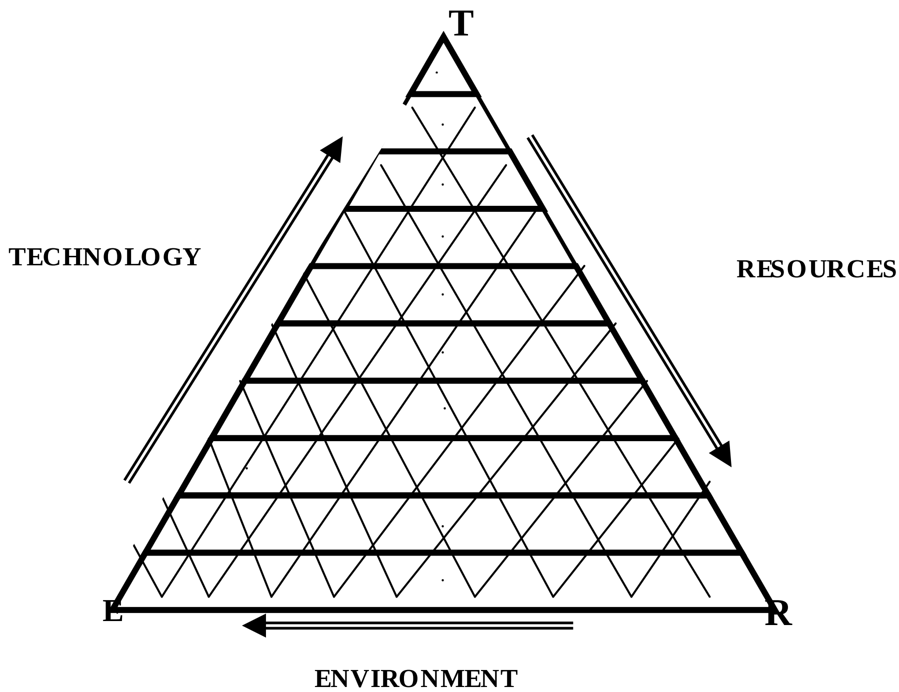


*Fig.5.* **Structural diagram „Environment - Technology – Resources"**

The similar triangle diagram with coordinates "Ecosystem quality – Resources – Human health" was applied in the development of a methodology for life cycle assessment [26, 27] and development of eco-indicators for models of the technosphere, ecosphere and valuesphere.

As the main objective of environmental science is to ensure human wellbeing, the system analysis has to be applied to assess correlation between quality of life integral parameter $C_k$, intensity of loss of environmental quality $V_L$ and technological capacity T.

Regularity between these parameters mathematically can be expressed as the equation [28]:

$$C_k = a_0 + QTt - V_L t_2 + T_2 ,$$

where Q – environmental capacity, $a_0$ – minimum level of quality of living (starting point), t – time.

Analysis and modeling of this equation shows that an increase in technological capacity (that sometimes is considered guaranteed solution for all problems) really can provide an increase in quality of living, however, if loss of environmental quality (e.g. pollution) is not reduced at the same time, development of technologies can only delay point of collapse of human wellbeing $t_{cr}$ (Fig. 6, curves 1, 2, 3). Only if, with increasing technological capacity, parameters of loss of environmental quality at the least stay the same, it is possible to provide sustainable development for humans (Fig. 6, curves A, B).

Consequently, it is necessary to modernize technologies and transform them into ecotechnologies but it requires performing successive system analysis of all technological processes and firstly establishing principal opportunities to implement physical effects in constructions according to the equation $C_k = f(Q, T, V_L)$ if $t_{cr} = \infty$.

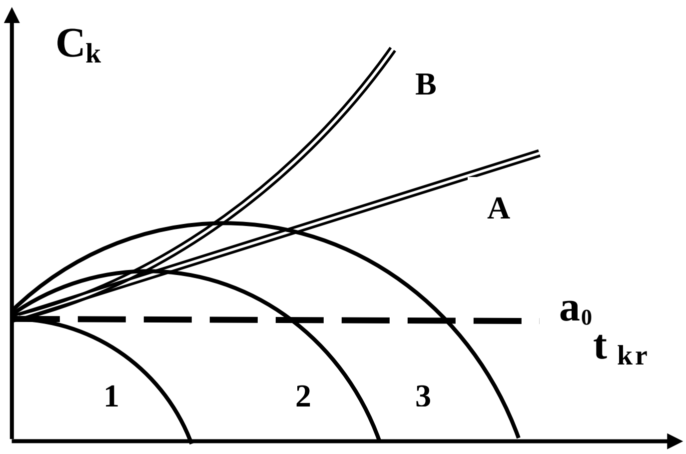


*Fig.6*. **The changes in the quality of human living Ck in the course of time depending on technological growth E and losses of environment quality $V_L$**

The methodology of the complex theoretical analysis of ecotechnology [29] has two stages:

- determination of implementation probability areas of ecotechnology that consists of determination of boundaries for areas of technical possibility, social and economical effectiveness and environmental warranty;
- construction of a model of input and output fluxes of energy and matter and its application in evaluation of every technological process and whole technological line, including calculations of effectiveness of resources utilization at successive stages of production and calculations of pollution generation and effectiveness of its treatment at the different stages of production and whole process.

The probability areas of ecotechnologies are shown graphically with coordinates “Effectiveness – Stability” (Fig. 7) and analytically using their equations.

For any concrete technology problem can be solved if use theoretical equations that limits o technical possibility $S_t$, social and economical effectiveness $S_s$ and environmental warranty $S_e$ areas.
A complex solution of all three equations gives area $S_0$ and its optimal limits confining the best parameters of efficiency, economical and environmental warranty and operational span [29].

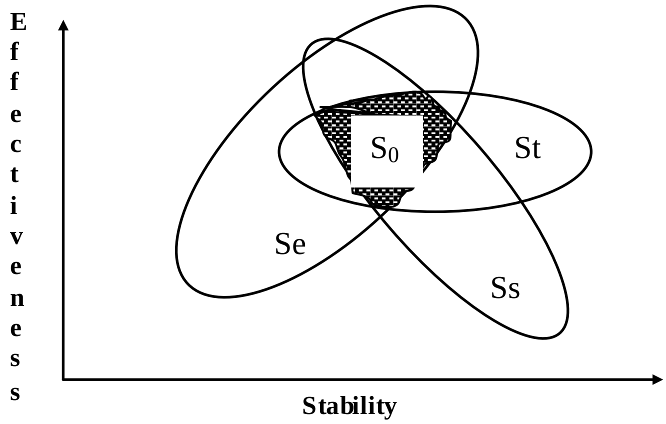


*Fig. 7.* **The technological possibility T, environment warranty V and economical effectiveness E harmonization areas**

The technological, economical and environmental quality areas can overlap in following ways: fully harmonized, non-conflict, conflict but solvable and fully un-harmonized. [30]
Replacing abstract parameters with parameters of a particular technological process we can determine optimal regimes for a real technology. [31]

**The aim of environmental science**

It is usually perceived that the aim of environmental science is environmental protection. The first question emerging from analysis of this perception is "what is environmental protection?" The Latvian classification of the scientific fields offers a broader explanation of the aim: "protection of biological and genetic diversity of natural resources, possibility of sustainable existence…" followed by the main point of this definition "protection of humans from negative consequences of their actions".
The rest is only tasks and methods how to achieve this aim. If in distant times protection from environment was understandably crucial for human survival then now the essence of the problem is not changed in principle. Only at some point in time it was inverted and protection of environment from humans became primary.
Essentially environmental protection is protection of humans, provision of successful existence of all civilization and development processes. The adverse effect of the nature on humans is not changed and is still the same.
Any action taken by humans in the environment has counteraction. The response from the environment is not adequate, it is multiplicative and the greater load humans put on the environment, the stronger it becomes with less predictable consequences. This relation mathematically can be described as the equation

$$R= - t^a . I^b / C . \rho,$$

where R – counteraction of the biosphere – a fundamental property of the nature; t – time of humans affecting environment; I – intensity of impact; C- environmental capacity – equilibrium of input and output fluxes of energy and matter; ρ – factor of environmental resistance to external impact; a,b – coefficients of reaction intensity (average a = 2 -2,5, b= 2,5- 4).

Studies of the mechanisms and laws of the co-existence process of these two systems in a unified super system, regularities determining this interaction and development of methods to apply findings in solutions of cardinal environmental problems – that is the aim of environmental science.

Calls to protect environment alone will not deliver results. It is not an easy task – to harmonize human activities and development with preservation of natural environment. It does not depend on good will and willingness only, the essence is deeper – it is necessary to learn and apply fundamental regularities of interactions in the system "biosphere – technosphere – noosphere".

## The place of environmental science among other scientific fields

Based on that established above:

- the object of environmental science – interaction zones between technosphere and biosphere,
- research methodology of environmental science – principles of system analysis, physical and chemical methods, modeling,
- the aim of environmental science – studies and application of interaction laws between elements of complex systems,

It can be concluded that environmental science fully complies with the criteria for autonomous science, it is not part of any other science and does not have other science as its part.

## Conclusions

Analysis of the subject and structure of environmental science provides a short and concise definition of it:

Environmental science is the science that deals with structure, interaction laws and processes of multifactorial complex systems "technosphere – ecosphere" in order to ensure human existence that is viable and sustainable.

The rest of the information included in existing definitions of environmental science is the extended explanation of tasks and actions.

According to the author's view, they are the origin and structure of biogeophysical and technogenic systems and their components, functioning, energy and dynamics in interaction zones, the principles of rational utilization and reproduction of natural resources, the preservation and improvement of biological equilibrium and environmental quality, the principles and methods for development of environmentally friendly technological systems.

The last task directly relates to the sub-science "environmental engineering" that is determinative for the aim of environmental science.

Environmental engineering is the sub-science of environmental science that deals with technosystems, their operational processes affecting the environment and their regularities in engineering and technological applications that are based on principles of systems engineering and aimed at preservation of environmental quality.

### References


1. http://www.biology-online.org/dictionary/Environmental_Science
2. http://www.thefreedictionary.com/environmental_science
3. http://en.wikipedia.org/wiki/Glossary_of_environmental_science
4. http://www.newagepublishers.com/samplechapter/001281.pdf
5. Keller Edward,A., Essential Environmental Science, 2008.
6. Anger ,E.D.,Smith B.F.,Environmental Science: A Study of interrelationships, 1995.
7. Jorgensen, S. E.,I.Johnson.,Principles of Environmental Science and Technology 1989.
8. Annotations of Latvia science sectors and subsectors ,1999., Latvia Council of Science act. (in Latvian).

9. Nomenclature of doctors'of science degrees ,1998.,Latvia Council of Science act. (in Latvian).
10. Latvia education classification Regulations issued by the Cabinet of Ministers Nr 2675.
11. Cunningham, W. P.,Cunningham,M., Environmental Global Concern, 2008.
12. Haeckel, E., Art Form of Nature ,1866.
13. Warming, E.,Vahl,M., Oecology of Plants –an Introduction to the Study of Plant-communities, 1925.
14. Andrewartha ,H.G., Birch ,L.C., The Ecological Web, 1984.
15. Odum,E.P., The strategy of Ecosystems Development. *Science* 164, 1961,pp.262-270.
16. Kelly, Evelyn B., The Rise of Environmental Science, 2005
17. Walonic,D.S., General Systems Theory, 1993
18. Mitchell, M., Complexity. A Guided Tour , 2009.
19. Rihani, S., Complex Systems Theory and Development Practice, 2002
20. Mitchell,M.,Newman, M., Complex Systems Theory and Evolution, 2002
21. Theilard de Chardin, The Phenomenon of Man, 1965
22. Vernadsky ,V.V., Some Words about Noosphere, *Uspehi sovremenoi biologii*, 1944, pp.113-120.
23. Bertalanffy,K.L. General System Theory. Foundations, Development, Applications, 1968
24. Prigogine, I., Self- Organization in Non-Equilibrium Systems, 1977
25. Altshuller,G., To Find Idea. Introduction in Solving Innovation Problem, 2003, (in Russian).
26. Hofstetter, P., Perspectives in Life Cycle Impact Assessment; A Structured Approach to Combine Models of the Technosphere, Ecosphere and Valuesphere, 1998
27. Hofstetter, P., Braunschweig A., Mettier M., Müller-Wenk R., Tietje O., Dominance Analysis in the Mixing Triangle, A Graphical Decision Support Tool for Product Comparisons. *The Journal of Industrial Ecology*, 1999
28. Noviks,G., Environmentally Sustainable Technologies and Environmental quality indicators. *International conference" City Environment Proceedings*. 2000, pp. 4-12.
29. Noviks, G., Development of Ecotechnology Complex Analysis System, *Rēzeknes augstskolas zinātniskie raksti*, 2003, pp.97-111,(in Latvian).
30. Noviks, G., Motivation of waste treatment technology optimization. *Environment. Technology .Resources. VI International scientific conference proceedings*, 2007, pp.87-101., (in Latvian).
31. Noviks,G., Ecotechnology- Physical and Technical Substantation of Pyrolysis . *Environment. Technology .Resources. IV International scientific conference proceedings*, 2003, pp.191-201, (in Latvian).

**Kopsavilkums**

*Trīs faktori – vides zinātnes interdisciplinārais raksturs, plašais nosaukums un neprecīzas robežas starp vides zinātni un citu zinātņu pētījumu jomām – ir iemesls daudzveidīgiem un dažkārt pretrunīgiem priekšstatiem par šīs zinātnes nozares darbības jomām.*

*Rakstā izanalizēts pašreizējais stāvoklis vides zinātnes definējumos, tās attiecības ar citām zinātnēm un ekoloģiju. Izdalītas vides zinātnes galvenās darbības sfēras – kontakta zonas starp tehnosfēru un biosfēru, tehnogēnām sistēmām un ekosistēmām. Konstatēts, ka tieši šīs divu sistēmu saskarsmes zonas, savstarpējās saites un mijiedarbības procesu likumsakarības tajās ir vides zinātnes pētījumu objekts.*

*Tā kā šīs sistēmas darbojas kopējā telpā – veidojas kompleksā virssistēma. Tātad vides zinātnes pētījumu metožu teorētiskā bāze ir sarežģīto sistēmu teorija, sistēmanalīze un sistēminženierija praktisko uzdevumu risināšanai.*

*Parādīta metodiskā pieeja atsevišķo vides zinātnes uzdevumu risināšanai ar sistēmanalīzes metodēm.*

*Definēts vides zinātnes pamatmērķis – cilvēka dzīves eksistencei labvēlīgās ilgtspējīgās vides nodrošināšana.*

# URBAN DEVELOPMENT TRENDS IN THE LATGALE REGION AT THE BEGINNING OF THE 21ST CENTURY

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***Abstract.*** *The paper provides a comprehensive analysis of urban development trends in the Latgale region, observed at the beginning of the 21st century and to a large extent also outlines the direction of future development. The paper is based on the evaluation of spatial development planning documents,the analysis of the available statistical data and the review of the urban development projects subject to implementation, supplemented by some results of field studies on the urban environment quality. Though the urban environment and partly also the landscape quality has been improved during the last period, as well as in many areas with support of the EU programmes major urban environment development projects are being implemented, however the economic growth is stalling, depopulation processes are not contained, and the regional urban development index is expressly negative. In the course of the administrative and territorial reform the status of the majority of towns and cities of the Latgale region has significantly changed, and sustainable urban development in the region is still under real threat.*

**Key words:** *depopulation, Latgale region, urban development, urban environment quality.*

## Introduction

Urban development process is continuous in time and space and is closely related to the overall social development trends. Structural changes in the economy and increasing population mobility have modified the urban development perspectives. Urban development of the Latgale region nowadays is actually determined by the same processes that commenced in the 90-ties of the past century, along with Latvia regaining its national independence and with transition from the planned centralized economy to spontaneous development based on the free market principles. Exactly during the periods of economic boom or recession, the urban economic potential and demographic situation change significantly, considerable changes occur to the shape of urban landscape and the socio-psychological space [1].

Activities based on the new knowledge are concentrated in large agglomerations, but some remote regions, including Latgale, with less competitive urban centres are considerably lagging behind in their development. In these areas strengthening of the urban functions is required, which to a great extent would allow to restrict the population decline, since this process greatly reduces the functionality of areas and makes provision of services to citizens difficult [2].

Currently, on both the European Union and the Latvian scale there has been a significant change from the previous views to the spatial development issues and the integrated view to urban and regional development is increasingly used. The Territorial Agenda for the European Union sets a priority task of the need to facilitate polycentric development and innovations, via extensive use of urban cooperation networks [3]. Emphasis is placed also on searching for new forms of territorial governance and cooperation between urban and rural areas. The Latvian National Development Plan 2007 to 2013 is also highlighting polycentric national development, with application of the urban development potential and capacity to affect the development of wider areas, as well as to create urban networks as a precondition for sustainable national development [4].

In Latvia during 2007 a priority of "Polycentric Development" co-funded by the ERDF was developed, in order to promote urban competitiveness. It is intended for each city to highlight and to strengthen their specific development potential, which would complement activity

profiles selected by other cities, as well as would support processes having a beneficial impact on the development of neighbouring territories [5]. Within the priority framework, provision of support to regional development centres is planned, among which in Latgale are listed Daugavpils, Rezekne and Līvāni. In determination of beneficiaries also the urban socio-economic development indicators are taken into account, by assessing the concentration of resources required for maximum return on investment and amount of investment, which will be available for the cities from other support activities of the EU funds from 2007 to 2013.
It should be noted that the towns and cities of the Latgale region are exactly among the first ones in the country having developed programmes appropriate for the EU criteria. For example, emphasis of the Daugavpils City Development Programme (2008-2014) is laid on cultural and ethnic diversity of the city as well as its multifunctionality, positioning the city as an important cross-border economic development and service centre [6]. While the Rēzekne City Integrated Development Programme (2007-2013) highlights importance of the city as major cultural and educational centre for the Eastern Latvia [7]. Medium-term development programmes are elaborated in Balvi, Krāslava, Līvāni, Ludza and Preiļi, and are also in the making in Dagda, Ilūkste and Kārsava. These programmes provide for integrated development of the cities and newly established regions as well.

## Materials and methods

Urban development is a complex multidimensional process; hence the analysis of its trends requires an integrated approach, involving use of various types of information sources.
First, these are normative and planning documents, which determine development of areas at different scales, i.a., also urban development programmes and plans.
Second, comprehensive statistical information that defines processes and trends of the urban spatial, socio-economic and demographic development.
Third, data obtained during the urban environment quality field research, such as traffic intensity measurements and air quality assessment.
For situation analysis in urban areas of the Latgale region, information summarized by the Central Statistical Bureau of Latvia, as well as publicly available data of other public bodies and results of individual studies are mainly used. Objective assessment of the existing situation is significantly encumbered by insufficient availability of information, because in Latvia statistical data on the administrative territories at the level of local municipalities (cities, towns, civil parishes and municipalities) has not been published since 1998 [8]. Only in demographic yearbooks figures for all cities and towns in the region are found, but in other areas detailed information is available only for the cities of republican subordination Daugavpils and Rezekne, while liquidation of districts and creation of municipalities, which took place in the course of implementation of the administrative-territorial reform, has brought about problems in mutual comparability of statistical data.
For urban development evaluation in Latvian the territorial development index (TDI) is used, the methodology for calculating this was developed by the Latvian Statistical Institute in 2000. TDI and the territorial development rank are generalized or composite indicators of the territorial development level and assessment of the development trends. It is recognized that elaboration of professionally convincing development indices for cities and towns is much more difficult than for the rural areas. Experts have set out key development factors and scales for their importance, which are used to calculate some Latvian urban development indices as follows: unemployment rate (0.30), individual income tax per 1 person (0.30), demographic burden (0.20) and changes in permanent population during five-year period (0.20) [9].
In this study, the following urban development indicators were mainly used: 1) demographic data, placing emphasis on the importance of population dynamics in evaluation of the

development potential of settlements, 2) environmental ecological quality parameters as indicators by using the volume of air pollution from stationary sources and intensity of traffic flows, 3) implementation of projects relevant for improvement of the urban environment quality. Less attention this time was paid to the economic development indicators and analysis of the urban environment attraction factors.

## Results and discussion

### *General information*

The Latgale region covers the area of 14,547.2 km$^2$ or 22.5 % of the state territory and at the beginning of 2010 the population of the region was 339,783 people or 15.2 % of the total Latvian population. There were 191,035 people living in urban areas and the urbanization rate in Latgale reached 56.2 %, while more than 40 % of the regional population was concentrated in Daugavpils and Rezekne. Since 1990 the urban population of Latgale has decreased by approximately 22 %, while the degree of urbanization in the region has not significantly changed.

Still disputable is the question of number of cities and towns in the Latgale region. Thus, for example, the Latgale Urban Development Strategy developed in 2001 identifies 17 cities and towns in the region [10], including Jēkabpils, Aknīste, Viesīte, Ilūkste and Subate which historically and geographically have never belonged to Latgale, while clearly Latgalian Varakļāni is not mentioned in this strategy. The author believes that, with certain reservations, not only Ilūkste and Subate - as existing components of the Latgale planning region, can be counted in Latgale but culturally and historically - also Krustpils (the part of the city of Jēkabpils situated on the right bank of the Daugava river).

Thus, today there are 15 cities and towns in the Latgale region (see Table 1), which are significantly different according to their geographical location and natural environment conditions, area and spatial structure, demo-geographical and socio-economic indicators, as well as the administrative status.

Cities and towns in Latgale are forming several functional urban networks exceeding boundaries of the region. Support frame of the central urban network is constituted by the urban triangle - Daugavpils, Rēzekne and Jēkabpils, which is a major focal point in the direction from Latgale to the capital. These cities are directly linked to the major transport corridors and are building up polycentric structure of the Latgale region and in the future will provide the widest choice of various functions and high quality services [11].

### *Territorial Development Index (TDI)*

TDI is a generalized indicator that shows the area development above or below the average national level of socio-economic development during the current year. For all the towns and cities in Latgale this index is consistently negative purporting that urban development in the region is below the national average. There are considerable variations in the index and the rank of the towns and cities can experience both a fall and a rise year by year.

According to the most recent data [12] it is evident that uppermost in ranking of the Latvian cities is Daugavpils (rank 22), Balvi (35) and Rēzekne (39), while Subate (70), Dagda (72), Viļaka (73), Varakļāni (74), Viļāni (75), Kārsava (76) and Zilupe (77) are traditionally at the bottom of the list of Latvian cities. It should be noted that positive trends in recent years have been witnessed in development of Daugavpils, Balvi, Krāslava, Ludza, Preiļi and Ilūkste [12, 13].

### *Impact of administrative-territorial reform*

Administrative-territorial reform (2009) implemented in the Latvian state will inevitably affect the distribution of population, including urban structures of the Latgale region. All the towns and cities of the Latgale region have had realistic and geographically reasonable opportunities to become centres of the newly created regions, in which they have succeeded. Debatable is the question how the former district centres will develop further, since in the course of the reform process their status changed and the impact area became narrower, and whether small towns – centres of the newly created municipalities, currently has sufficient potential for development in order to fully perform the new functions.

Cities are interested in strengthening their impact areas and already existing social infrastructure base, as well as in attracting additional investments, which would promote creation of new businesses and facilitate more regular development of the state territory, reducing the existing regional disparities. Complex development programmes of municipalities are currently being elaborated to achieve this goal.

In assessing the potential of newly formed municipalities, first of all number of population and territory, it is possible to classify cities and towns of Latgale as follows:

• Daugavpils and Rēzekne - keeping their status of republican subordination cities, are strengthened also as centres of the largest municipalities in the region;

• Balvi, Ludza, Preiļi, Krāslava - former district centres, - to a greater or lesser extent narrowing down their impact area, reducing their development potential;

• Dagda, Ilūkste, Līvāni - the biggest winners of the administrative-territorial reform, since by raising their status and significantly expanding the impact area, these are developing as centres of strong and viable municipalities;

• Kārsava, Viļāni, Varakļāni, Viļaka, Zilupe - becoming centres of relatively small municipalities, failing to significantly increase their development potential and continue to languish;

• Subate - without becoming even a centre of small municipality, limits its development potential and is under threat of losing a town status.

***Depopulation threat***

Demographic situation in the Latgale region during the post-Soviet period vividly describes decline in population numbers or depopulation, as well as population ageing caused both by the negative population migration balance and the negative natural growth rate. If in Latvia the number of population has decreased by 5.6 % since the beginning of the 21st century, then in Latgale it has shrunk by as much as 11.9 % [14]. Almost all the Latgale demographic indices are less favourable than in other regions of our country, for example, the natural growth is -8.0 % (average Latvian figure is -3.7 %), while infant mortality is twice as high as in Riga. Proportion of the retirement age population even in big cities of the Latgale region is approximately half as much again exceeds the number of children under the age of 14. Emigration is one of the factors that have significant impact on number of population in Latgale, which has particularly intensified since opening of the labour market in the old EU member states, putting socio-demographic and economic development of the region under threat. A very significant number of population has left cities and towns of the Latgale region within the last 5 years searching for employment, however, calculations of the emigration volumes are performed implicitly, hence they cannot be accurate – hopefully, the results of the 2011 Census will show the real situation.

Urban population dynamics in Latgale during the post-Soviet period is presented in Table 1, being set up on the basis of the information provided by annual reports of the Central Statistical Bureau.

Population has consistently decreased in all the cities and towns of the region, but differences have been observed in the dynamics of this process. At the beginning of the 21st century depopulation intensified in most cities and towns of Latgale, including both regional cities and all the former district centres, while depopulation rate slowed down considerably in Līvāni, Dagda, Ilūkste and Zilupe.

*Table 1.*

**Resident population dynamics of the Latgale cities and towns in the post - Soviet period (1990–2010)**
(calculated according to [15])

| City, town | 1990 | 2000 | 2010 | Depopulation (2000 to 1990, %) | Depopulation (2010 to 2000, %) |
|---|---|---|---|---|---|
| Daugavpils | 126 575 | 115 574 | 103 922 | 91,3 | 89,9 |
| Rēzekne | 42 832 | 39 430 | 35 074 | 92,1 | 89,0 |
| Ludza | 11 853 | 10 857 | 9 616 | 91,8 | 88,6 |
| Krāslava | 12 434 | 11 414 | 10 194 | 91,8 | 89,3 |
| Līvāni | 12 263 | 10 379 | 9 016 | 84,6 | 86,9 |
| Balvi | 9 340 | 8 693 | 7 903 | 93,1 | 90,9 |
| Preiļi | 9 421 | 8 902 | 7 988 | 94,5 | 89,7 |
| Viļāni | 4 608 | 4 058 | 3 483 | 88,1 | 85,8 |
| Varakļāni | 2 798 | 2 421 | 2 103 | 86,5 | 86,9 |
| Kārsava | 3 110 | 2 726 | 2 424 | 87,7 | 88,9 |
| Zilupe | 2 441 | 1 951 | 1 774 | 79,9 | 90,9 |
| Viļaka | 2 152 | 1 848 | 1 536 | 85,9 | 83,1 |
| Dagda | 3 325 | 2 814 | 2 512 | 84,6 | 89,3 |
| Ilūkste | 3 275 | 2 969 | 2 829 | 90,7 | 95,3 |
| Subate | 1 041 | 952 | 752 | 91,5 | 79,0 |

Particularly worrying trend is observed in small towns of the Latgale region, within 20 years of independence having lost a quarter of the population on average, with the result that in Subate, Viļaka and Zilupe number of population is already inadequate for maintenance of the town status, since, according to existing legislation in Latvia, "the town status may be granted to settlements, which are cultural and business centres with developed engineering - infrastructure and street network and which have not less than 2000 permanent residents "[16]. Indeed, the law also provides for exceptions.

***Environmental indicators***

A large number of pollution sources are concentrated in towns and cities; therefore the urban environment is characterized by high atmospheric pollution related to high intensity of traffic, industrial production and production of thermal energy. In accordance with existing procedures, the emission data from stationary pollution sources are defined according to methodological rules approved by the Ministry of Environment and Regional Development, while for assessment of urban transport pollution the data is required on the traffic flow intensity and dynamics, or variability in the space of weeks, days and hours [17].

The summarized information on air pollution caused by stationary sources demonstrates (see Table 2) that at the beginning of the 21st century in most cities of the Latgale region, in particular, Daugavpils and Rēzekne, air pollution significantly reduced. This is attributable to decline of industrial production (proportion of factories in emissions from stationary sources in Rēzekne accounts for only 13 % and in Daugavpils – 42 %), as well as replacement of oil and coal with environmentally more friendly natural gas and local resources of wood, woodchips and peat used for the urban heating supplies.

The $SO_2$ pollution being particularly hazardous to environment and health in most cities of Latgale now accounts for only a few percent and only in big cities of the region it varies within range of 10 – 20 %, moreover, amount of sulphur-containing emissions in Daugavpils is approximately 5 times higher than in Rezekne.

*Table 2.*

**Emissions from stationary air pollution sources in cities of Latgale region (tons) [18, 19]**

| City | 1998 | 2003 | 2005 | 2009 |
|---|---|---|---|---|
| Daugavpils | 8044 | 1340 | 911 | 719 |
| Rēzekne | 2669 | 1368 | 1317 | 219 |
| Krāslava | … | 576 | 472 | 359 |
| Ludza | … | 215 | 226 | 210 |
| Preiļi | … | 355 | 137 | 129 |
| Balvi | … | 315 | 38 | 100 |

If volumes of emissions from stationary sources in the atmosphere in cities and towns of the Latgale region are gradually decreasing, as much as persistent is the increase in environmental pollution caused by vehicle-produced exhaust gases and a variety of harmful by-products from operation of machinery. It is thought that road transport generates more than half of air pollution in urban areas and the highest atmospheric pollution is usually observed in the centre of a city and in industrial areas [20]. Impact of transport on the urban environment quality is displayed by the dynamics of amount of cars (see Table 3), the technical condition of vehicles and the traffic flow intensity on streets of cities.

*Table 3.*

**Number of vehicles registered by the Road Traffic Safety Directorate in largest cities of the Latgale region [21]**

| Area | 1998 | | | 2011 | | |
|---|---|---|---|---|---|---|
| | Trucks | Busses | Cars | Trucks | Busses | Cars |
| Daugavpils | 2 841 | 469 | 17 790 | 2 421 | 233 | 22 401 |
| Rēzekne | 1 613 | 363 | 7 154 | 1 211 | 152 | 9 148 |

Level of automobilization in urban Latgale is significantly lower than in the country as a whole, for example, number of the registered cars per 1000 inhabitants in Rezekne in 2011 constituted 261, Daugavpils - 217, but in Latvia on average - 415 units. At the beginning of the 21st century the number of cars in urban areas of the Latgale region increased approximately by a quarter, while the number of trucks and busses decreased by approximately the same amount. We can unequivocally declare that the maintenance condition of vehicles has significantly improved within the last 5 years, and hence the decline in the pollution of the environment caused by them, however concerns are due to considerable consumption in Latgale of the semi-legal fuel imported from Russia and being less environmentally friendly.

Annual traffic intensity measurements carried out by students of the Rezekne Higher Education Institution at intersections of the main city streets suggest that the intensity of the vehicle movements in Rezekne during the period 2000 - 2007 increased by 35 %, but the growth has come to an end recently. More than 1,000 vehicles, mainly cars and vans, cross the busiest city streets intersections within one hour on weekdays, while the most environmentally friendly mean of conveyance – bicycle, in the streets of Rezekne is making only about 1 % of the enumerated amounts of vehicles. It is observed that the frequency of bicycle use is significantly higher in small towns of the Latgale region. Air quality

lichenoindication research does not present particularly high atmospheric pollution in cities and towns of the Latgale region, however significantly worse air quality is found in urban areas adjacent to railways.
Within framework of the study “Trends of the Latvian Urban Socio-economic Development" in seven cities of Latgale region in 2007 - 2008 the survey was carried out to ascertain public opinion with regard to satisfaction with the city where they live. The survey results show that the population of Balvi, Preiļi and Krāslava has most appreciated their place of residence (more than 2/3 affirmative responses). In Ludza, Rēzekne and Līvāni the number of residents being satisfied with their place of residence was just over 50 %. However in Daugavpils, despite the lowest unemployment rate in the region, only 40.5 % of respondents were satisfied with their city, and even then only ~ 20 % were satisfied with the ecological situation at their place of residence. In other towns of Latgale the population has also evaluated the environment quality more critically than the overall standard of living [22].

***Projects for Development of Urban Environment***

After Latvia acceded to the EU (2004) in towns and cities of the Latgale region had been commenced implementation of important and financially large-scale projects for improvement of urban environment, in which an average 85 % of the project costs are covered by the EU ERDF and the Cohesion Fund. This has contributed to increased volumes of construction, urban landscape transformation, as well as increased intensity of land use. In cities large-scale reconstruction operations of the main streets are taking place, traffic overpasses and bridges are being built or reconstructed, municipal heating system is brought into order. For example, in Daugavpils only for implementation of the street infrastructure development projects in 2010 funds amounting to LVL 38.3 million were allocated [23].
In cities and towns of the Latgale region construction of major tourist, cultural and sports facilities has been initiated or completed. In Daugavpils have been discussed such ambitious projects as the complex development of the fortress and foundation of the M. Rothko Art Centre, as well as the idea of the international airport on the former Lociki military aerodrome site. While Rēzekne since the end of 2009 has turned into a huge construction site, as at the same time in the city was initiated construction of the creative service centre for Eastern Latvia and of the Eastern Latvia regional multi-functional centre (Concert Hall), as well as a pedestrian street joining these objects and reconstruction of Atbrīvošanas alley. It should be noted that efficiency of implementation of these projects for various reasons has not received straightforwardly positive evaluation among the urban population.
Practically in all the cities and towns of the Latgale region complex water management development projects are implemented, which include renovation and expansion of the water and sewerage systems, as well as construction of drinking water and iron removal plants and new sewage treatment plants. For example, in Krāslava centralized water supply is now available for 97 % of the urban population (previously – 81 %), and centralized wastewater collection is provided for 81 % of the population (previously – 59 %), while the overall cost of the project was LVL 12.3 million [24]. We can affirm that the quality of drinking water in towns and cities of the region now complies with all the EU regulations.
Important measures have been taken for improving the municipal waste management systems: near Daugavpils and Rezekne up-to-date regional municipal waste management landfills have been built, separate waste collection has been introduced in the cities. For improvement of the tourism infrastructure several cross-border cooperation projects are being implemented in cooperation with Lithuanian, Belarusian, Russian and Estonian local governments. At the beginning of the 21st century in Latgale scientific research potential significantly increased, by means of the regional universities, involved in major international research projects and modernization of material and technical facilities for research work.

## Conclusion

1. The beginning of the 21st century has marked a new milestone in urban development of the Latgale region, conditioned, to a decisive extent, by Latvia's accession to the European Union (2004), which has contributed to attraction of substantial international investments for implementation of various development projects of urban environment.
2. Urban environmental quality in the Latgale region has significantly improved, which is mainly associated with transition to environmentally friendly fuels and implementation of many, environmental projects, basically the EU-funded, as well as with a decline in industrial production.
3. After several years of dynamic development, the economic crisis, which began at the end of 2008, has affected Latgale harder than other regions of the country, to which has contributed slow pace of industrial restructuring, insufficient funding, considerable distance from the national capital Riga and unsettled inter-state relations with Russia and Belarus.
4. The regional cities Daugavpils and Rēzekne are characterized by more dynamic development pace and less explicit depopulation, while in the small towns of the region positive development processes have been considerably more difficult, and they have already lost about a quarter of the population.
5. Serious concerns are created by the steady decline in the number of population in all the Latgale region's towns and cities, the rapid ageing of the society, persistently high unemployment rate, social exclusion and apathy dominant in the region, as well as deepening of regional inequalities.
6. In order to prevent threats to the sustainable development of Latgale, strengthening of urban functions in the entire region is required, which would allow to increase the viability of the peripheral territories and to smooth out regional disparities. This is particularly important since exactly the direct implementation of the principles of cohesion has been declared as one of the cornerstones of the EU regional policy.

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### References

1. Matisovs, I. Quality of the Urban Environment Landscape and its Influencing Factors in Latgale.//V International scientific and practical conference „Environment. Technology. Resources." Collected articles.- Rēzekne: Rezekne Higher Education Institution, 2005 /in Latvian: *Matisovs, I. Pilsētvides ainavas kvalitāte un to ietekmējošie faktori Latgalē.//V Starptautiskās zinātniski praktiskās konference „Vide. Tehnoloģija. Resursi." Rakstu krājums.- Rēzekne: RA, 2005*/.
2. VASAB 2010+. Spatial Development Action Programme: Vision and Strategies around the Baltic Sea 2010. Wismar, 2001.
3. *The Territorial Agenda* of the *European Union*. http://www.eu-territorial-agenda.eu/ *(viewed 25.02.2011)*
4. *Latvian National Development Plan* /in Latvian: Latvijas Nacionālais attīstības plāns/ *2007-2013*. http://www.nap.lv/in site/tools/download.php. *(viewed 26.02.2011)*
5. Priority "Polycentric development" /in Latvian: *Prioritāte „Policentriska attīstība"*/ http://www.raplm.gov.lv/pub/index.php?id=2469 (*viewed* 27.02.2011)
6. http://www.daugavpils.lv/upload/2010_dok/departamenti_un_nodalas/attistibas_departaments/ievads_un_situacijas_analize2010.pdf (*viewed* 28.02.2011.)
7. http://www.rezekne.lv/uploads/media/I_Esosas_situacijas_raksturojums_14_01.pdf (*viewed* 28.02.2011)
8. Vanags, E., Vilka, I. *Activities and Development of Local Governments.* /in Latvian: *Pašvaldību darbība un attīstība/.* Rīga: LU Akadēmiskais apgāds, 2005.
9. Survive though changes, Latvia diverse. Riga, Central Statistical Bureau of Latvia, 2008 /in Latvian: *Mainoties saglabājies, dažādā Latvija.Rīga, LR Centrālā statistikas pārvalde, 2008*/.

10. Latgale urban development strategy /in Latvian: *Latgales pilsētu attīstības stratēģija*/ (2001). http://www.latgale.lv/lv/files/download3 (*viewed* 20.12.2010)
11. Valdmane, I. Spatial plan of the Latgale region /in Latvian: *Latgales reģiona teritorijas plānojums*/. *Latvijas architektūra. #3 (65)/2006*.112.-116.
12. Regional development in Latvia 2009. Riga: State Regional Development Agency, 2010. /in Latvian: *Reģionu attīstība Latvijā 2009. Rīga: Valsts reģionālās attīstības aģentūra, 2010*/. http://www.vraa.gov.lv/uploads/Regionu_attistiba_Latvija_2009.pdf (*viewed* 20.02.2011)
13. Diversity of Latvia in numbers and visions. Rīga, Central Statistical Bureau of Latvia, 2009 /in Latvian: *Latvijas dažādība skaitļos un vīzijās. Rīga, LR Centrālā statistikas pārvalde, 2009*/.
14. Depopulation in Latvia. Managing editor Zvidriņš, P. Riga: LU Academic Publishing House, 2010 /in Latvian: *Depopulācija Latvijā. Atb. red. Zvidriņš, P. Rīga: LU Akadēmiskais apgāds, 2010*/.
15. Demography 2010. Statistical data collection. Riga: Central Statistical Bureau of Latvia, 2010 /in Latvian: *Demogrāfija 2010. Statistisko datu krājums. Rīga: LR Centrālā statistikas pārvalde, 2010*/.
16. Law On Administrative Territories and Populated Areas (2008). http://www.likumi.lv/doc.php?id=185993 &from=off (*viewed* 25.12.2010)
17. Environmental Impact Assessment. Riga: Environmental Impact Assessment State Bureau, 2002 /in Latvian: *Ietekmes uz vidi novērtējums. Rīga: Ietekmes uz vidi novērtējuma Valsts birojs, 2002*/.
18. Environmental indicators in Latvia. Collection of statistical data. 2004-2010. Riga: Central Statistical Bureau of Latvia, 2004-2010.
19. Regions of Latvia in numbers 2001.- Riga: Central Statistical Bureau of Latvia, 2001 /in Latvian: *Latvijas reģioni skaitļos 2001.- Rīga: LR Centrālā statistikas pārvalde, 2001*/.
20. Environmental Science. Ed. Kļaviņš, M. Riga: LU Academic Publishing House, 2008. p. /in Latvian: *Vides zinātne. Red. Kļaviņš, M. Rīga: LU Akadēmiskais apgāds, 2008.*
21. Distribution of Vehicles in Towns and Municipalities /in Latvian: *Transporta līdzekļu sadalījums pilsētās un novados*/. http://www.csdd.lv/?pageID=1296470925. (*viewed* 01.02.2011)
22. http://www.raplm.gov.lv/uploads/filedir/Nozares/Petijums_Lv_pils_soc_ek_att_tend.pdf (*viewed* 04.03. 2011.)
23. Minova, I. Attīstības departaments piesaistīs pilsētai papildus 25 miljonus latu /in Latvian: *Departament of Development will attract extra 25 million lati for the city*/. *Latgales Laiks, 18.02.2011.*
24. Krāslava city is not contaminating the Daugava any more /in Latvian: *Krāslavas pilsēta vairs nepiesārņo Daugavu*/ *Neatkarīgā Rīta Avīze, 03.03.2011.*

# USING OF INDICATORS FOR ENVIRONMENTAL IMPACT ASSESSMENT IN LATVIA AND NECESSITY FOR INDICATORS VALIDATION

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**Abstract.** *The EIA procedure in Latvia as it`s known today was implemented by the law „On environmental impact assessment" in 1998. The quantity assessment of expected environmental impact is provided by indicators giving the highest impartiality in this process. The choice of indicators and their approval in EIA projects in Latvia have not received the right attention, the issue is left upon the EIA performers. The problematic issues on necessity of indicator selection and validation are dealt with in the article. 39 environmental indicators were selected for EIA of motor road projects, with the evaluation of their significance and essence, as well as the analysis f application of these indicators in 14 reports concerning EIA of motor road projects. The results revealed the existing problems of indicator application and proved the assumption that there is no common indicator system for the assessment of impact of similar economic projects, proving the necessity of indicator validation to ensure good quality of assessment.*

**Keywords:** *environmental impact assessment, indicators, validation.*

## Introduction

Environmental impact assessment includes several generally approved good practice elements, for example, application of legislative acts, several alternatives [1] and credible forecasting models [2], which can be used as quality indicators in environmental impact assessment. While accumulating experience in EIA, several EIA methods have been worked and adopted, such as data matrix, control lists, networking methods, method of hierarchical analysis, rapid impact assessment matrix (RIAM), expert methodology and others [3,4]. Irrespective of methods chosen for particular case of EIA, different indicators or the experience of experts are used in assessment. As pointed out by Van der Werf H.M.G. and Petit J. [5], if only it is possible, the indicators must define the limit values, which in ideal case would be based scientific grounds.

According to formulation of Garrido J. and Requenavides I. [6], the environmental indicator is an element which provides information on condition of environment or close to it. The definition of environmental indicator is incorporated into Latvian legislation and it states that environmental indicators or indices are established reference system into which the environmental condition is assessed. Environmental indicators must be understandable, easily measurable, must clearly reflect the changes in environmental setting [7]. These allow forecast the planned impacts of the project, the environmental quality changes and resource consumption. Still, the indicators are only one of the generally approved sources of assessment of particular theme or problem [8]. The characteristics of indicators have been defined in many research works and literature sources [9, 10,11] and these are following:

- quantity values, credible and available,
- easily understandable and politically significant [important],
- showing whether progress has been achieved,
- these are to be verified, comparable, expressed by concrete and standard measurements,
- allow forecasting processes,
- without mutual duplication,
- necessary for users,
- sensitive to changes,

- in future forecasts, easily combined with socio-economic scenarios,
- allow comparing the results among countries, are scientifically correct (or precise).

Environmental indicators are chosen for each goal or problem in particular sphere. The few most characteristic indicators are selected from the wider scope of indicators which describe the concrete sphere or situation in the best way. For one sphere of environment, for instance, biological diversity, it is recommended to select not more than 2 - 4 indicators [12].

Environmental indicators are important source for policy makers and are helpful in decision making, as well as in the process of monitoring and assessment since they can provide information on complicated issues in quite comprehensible manner [13]. However, it is big challenge to determine which of the indicators of particular sphere are simple enough to be effectively examined and modeled.

According to Cloquell-Ballester V.A. a.o. [14], the quantity assessment of environmental impact is generally carried out which is based on 2 different strategies. The first one is based on the direct quantification of experts' evaluation by using the figure scales. The assessments arising from this approach which are expressed by figures are weighted and summarized and the experts' opinions are the only reference. Therefore, the assessment result is completely Dependant on experts' knowledge, experience and objectivity. Such strategy of environmental impact assessment is also used in Latvia. As the EIA is carried out mainly on contractual basis, the result of EIA is based on independence of experts in the process of EIA. Such assessment strategy is actually in compliance with quality assessment, based on experts' evaluation. Still, as pointed out by Joa˜o E. [15], the inclusion of qualified EIA expert evaluation is important, since the experts' opinion is one of the most common methods of EIA. In Latvia, the initiator of planned activity is responsible for the preparation of EIA report which allows for carrying out EIA by the initiators of planned activity themselves therefore, in some cases, it can still theoretically present the risk of impartiality or complete lack of assessment. In fact, the indicator selection for EIA is left upon the choice of assessment performer (not always being the experts in particular sphere). The fact that such contractual relations can have adverse effect on credibility of research results are likewise approved by other authors [14].

The other assessment strategy, according to Cloquell-Ballester V.A. a.o. authors [14] is to quantify the impacts by using indicators, considering the difference in environmental quality between „project implementation" and „discontinuation of project or zero-alternative" situations. This strategy is attractive because it allows carrying out verifiable assessment. Therefore, considering the EIA performers and interested parties, in the process of assessment of social and environmental impact, these indicators are validated and approved.

Still, as it is pointed out by Cloquell-Ballester V.A. [14], it is hard to create universal and detailed list of validated indicators, because: a) there can be difference in project land area characteristics, b) lack of data about particular area, c) previously approved indicators might be outdated. The environmental impact assessment must be of multi-disciplinary approach [16]. It means that EIA working party must be represented by experts of different branches, because no person can be expert in all of the areas, including technical ones. In order to carry out the impact assessment of particular activity, EIA working team must select the required and characteristic indicators [14]. The easiest way is to select such indicators that are accepted by scientific and professional circles, examining the possibility of their application, to improve or define the new indicators. The values of indicators must be comparable to real data but as their modes are determined by experts, the assessment is more impartial. The lack of indicator validation or approval can cause adverse reference on the quality of assessment of social and environmental impact, usefulness and credibility, i.e., discredit or question the results of EIA. The necessity of approved indicator system is greater in those countries where the EIA related costs are covered by initiator of planned activity [14], as it is also in Latvia.

## Materials and methods

The aim of this research is to select environmental indicators for particular object group - i.e., motorway projects and to assess their significance in the context of Latvia. The results obtained will serve as the basis for further research by choosing and adopting into practice indicator validation methods. The hypothesis has been brought forward that the environmental impact assessment of similar projects of economic activities (ex. motorway projects) carried out according to common system of environmental indicators improve the quality of EIA report and reduces influence of subjectivity.

The expert methodology has been used in research, the selecting of indicators due to experience and assumptions. The authors of research summarized indicators that are important for motorway projects, based on the reports of EIA for motorways, their experience and environmental indicators prescribed in literature sources. Not more than 6 indicators were selected for each concrete factor of environmental sphere (air, water, nature, etc.) which characterize the possible impact from motorways. The value in the scale of their significance from 0 to 5 was assigned to each indicator. The description of value significance is presented in Table 1. The assessment of significance of the selected indicators is carried out based on the experience of experts and evaluation of EIA reports of 14 motorway projects, including publications about foreign experience with respect to motorway impact on environment.

*Table 1.*

**The evaluation scale of indicator significance**

| Numerical valuation | Mutual valuation |
|---|---|
| 0 | insignificant |
| 1 | negligible significant |
| 2 | low significant |
| 3 | Enough significant |
| 4 | significant |
| 5 | very important |

After that the significance of each indicator was determined according to the value scale from -2 till +2, where “-2” - means insignificant and “+2” – is significant. Other significant values were not singled out at this stage of research, following the assumption that if the indicator is not included in the assessment process or is not regulated by the law, then, on the national level it can be considered insignificant. At this stage of research, the significance is not valued according to whether or not the particular indicator is included in EIA reports, but following the principal approach.

Analyzing EIA reports, the task was set to determine the application of selected indicators in numerical way, to find out unanimity of experts’ opinions in selection of indicators and whether or not there is a need for validation.

The comparison of importance and significance of indicators provides the possibility to evaluate the weakest points in practical phase of EIA, so that the outcome would not be formal but helpful for decision makers and those bringing the project into effect, as well as for supervising institutions and definitely for public interest on the whole.

## Results and discussion

The environmental impact of linear infrastructure such as motorways, must be assessed carefully and in responsible manner since motorway is long-lasting object whose building and reconstruction cause irreversible changes in environment, upon affected territories, causing the barrier effect in environment, as well as promoting the economic development of particular region, which, in turn, can result again in additional load on environment. On the whole, 39 environmental indicators were evaluated, as being the most characteristic for impact of motorways on environment (Fig.1.).

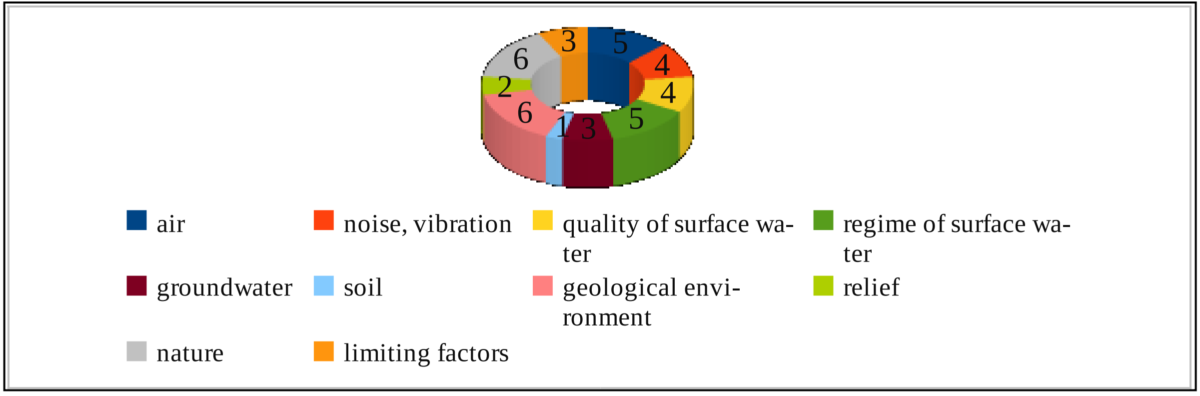


*Fig.1.* **The selection of environmental indicators EIA of motorway projects (number of indicators for each of the environmental factors)**

The results of indicator significance are presented in Fig.2. and they show that many of indicators (13 out 39) which have received high evaluation grades (4 and 5 points) are not now significant on the national level.

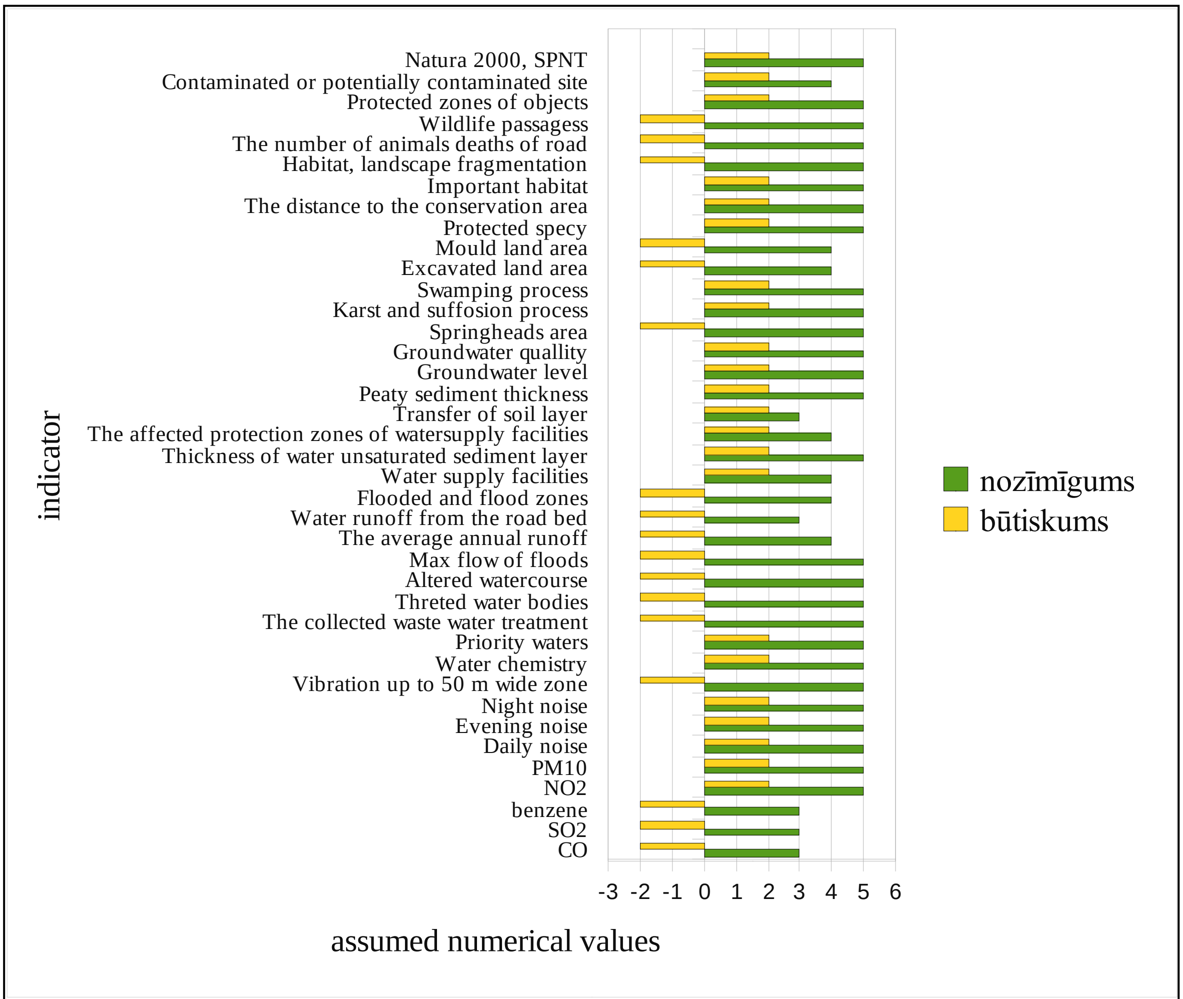


*Fig.2.* **Environmental indicator assessment according to experts' methodology**

The significance in this case was evaluated according to the content of EIA report, the requirements for the issued programs of carrying out EIA of motorway projects and the indicators and limit values stipulated by the legislative acts, as well as following concrete criteria- whether or not the concrete answer and numerical evaluation is given for the indicator in question. For example, the indicator called "natural wildlife passages" (measured in numbers) is mentioned in largest part of EIA reports, but actually there is no concrete data where and how many such crossing (transfer) places exist on a planned motorway route and what kind of animals use them. Therefore, the significance of this indicator at the present context of EIA in this research was considered as being undervalued or insignificant (-2) on the national level.

During the course of research, the practical application of 39 environmental indicators in EIA reports concerning motorway projects was analyzed in greater detail. Indicators can be divided into 2 groups: a) those, whose limit values are determined by legislative documents of Republic of Latvia, b) which are not determined by the law and are put forward by experts. Besides, the application of concrete indicators also from the first group is chosen by experts (for example, PM10 and $NO_2$ are mainly chosen for the forecast of changes in air quality).

The analysis of indicator application within the framework of research was encumbered by several factors: a) the analyzable indicators are not formulated in large number of cases, b) quite often no numerical values, expressed in measuring units are provided, assessment is given in wording (is, isn't and etc.), c) indicators are not compared before (the current status) and after the project implementation (anticipated condition), as well as d) indicators are not compared among different project alternatives. The above mentioned problems are more particularly evident in EIA reports during the last years.

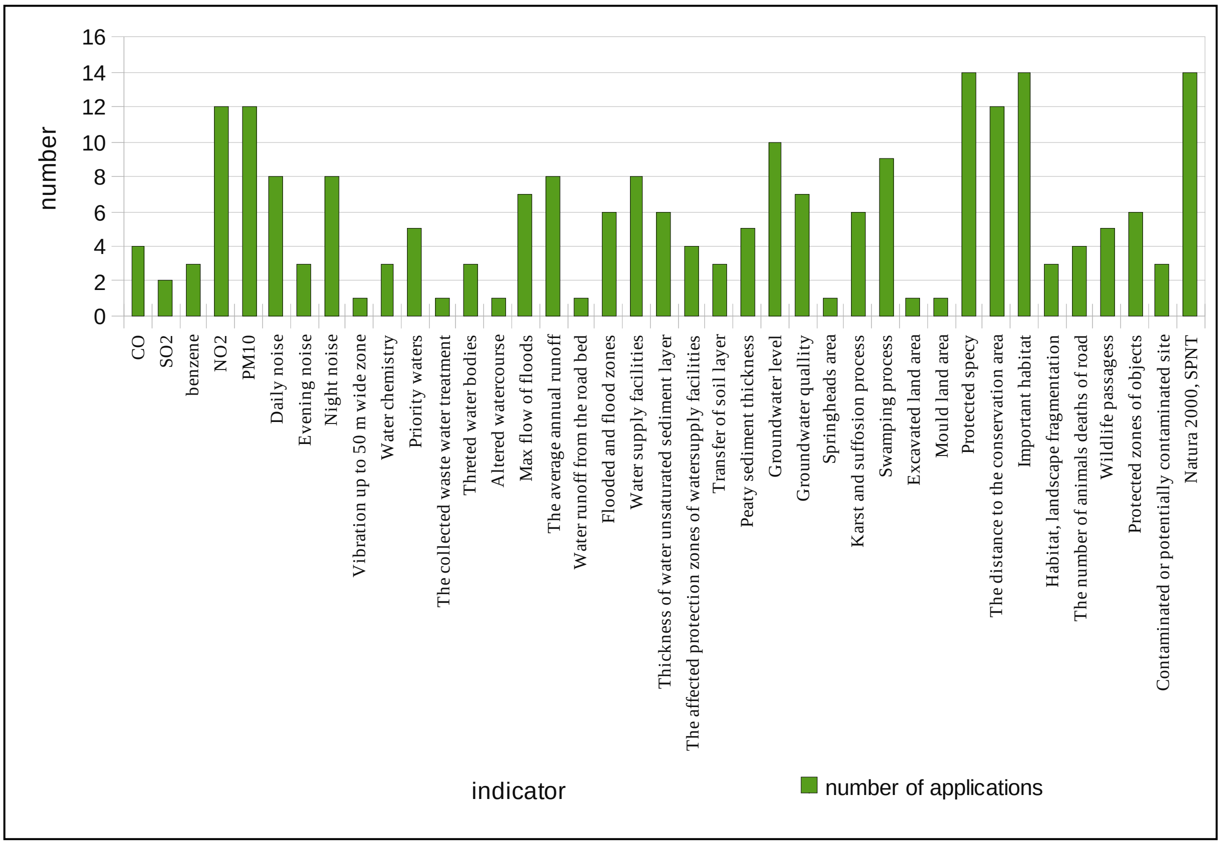


*Fig.3.* **The application of environmental indicators in EIA reports for motorway projects**

Therefore, the indicator within this research is considered to have been applied only when the evaluation was provided for it (numerical or descriptive). Results of application analysis

(Fig.3) reflect the fairness of hypothesis that unified indicator system for similar projects of economic activity such as environmental impact assessment of motorway projects will improve the quality of report and reduce the subjectivity. From the Fig. 3, it follows that 36% or 14 out of 39 of the analyzed indicators in research were used only in half (7 out of 14) of EIA reports. Furthermore, the evaluation of several environmental factors in some cases of EIA is not based on indicator analysis. Consequently, EIA are more of descriptive nature and doesn't provide unambiguous notion about possible impacts that doesn't relieve the decision making.
The results of research show that the experts' evaluation method is actually used in EIA reports and selection of environmental indicators is left to the discretion of EIA performers. Finally, it can reflect upon the quality of impact assessment of planned activity, not excluding subjectivity and superfluity. This situation clearly points out the necessity of approval of indicators and bringing forward the criteria.

## Conclusions

Any kind of economical activity by people causes environmental impact, both positive and negative, therefore it is important to assess the significance of the impact in adequate and impartial manner. The impartiality can be ensured by environmental indicators recognized by experts in particular areas. Besides, it would be preferable to use common indicator system for assessment of possible impact of each group of economic activities since the manner of impact of similar economic activities upon the same environmental factor (for example, surface water quality, air quality, eco-system quality, etc.) will be more or less alike, but the intensity and character of impact are correlated according to specific local conditions and /or applied technology. This approach would allow increase the credibility of impartiality, the assessment would be comparable, easier perceivable for public and decision makers.
The research results show that the quality of EIA in Latvia depends on qualifications and professional approach of EIA performers of this process, i.e., the choice or „not choosing" of indicators is left to discretion of experts. For the characteristics of one and the same indicator different approaches are used – ignorant, descriptive, formal or numerically evaluated that can affect the quality of EIA reports and public trust in impartiality of EIA.
Such approach doesn't provide or reduce the possibility to compare and evaluate project alternatives according to such an indicator, besides it can not be used as reference point for the status control during project implementation and of operational time. Once again, it proves the significance of indicator selection for qualitative EIA. Many literature sources point out the necessity and possibility of approving the indicators in order to avoid subjectivity and superfluity in impact assessment. The results of this research work prove the necessity of indicator validation also in Latvia.

### References

1. Steinemann A., Improving alternatives for environmental impact assessment. Environmental Impact Assessment Review Volume 21, Issue 1 [2001], Pages 3-21.
2. Androulidakis I., Karakassis I., Evaluation of the EIA system performance in Greece, using quality indicators. Environmental Impact Assessment Review 26 [2006] p. 242– 256.
3. Discoli C.A., Urban environmental impact matrices development: assessment indices incorporation. Building and Environment 40 [2005] 915–928.
4. Wang Y.-M., Yang J.-B., Xu D.-L., Environmental impact assessment using the evidential reasoning approach. European Journal of Operational Research 174 [2006] 1885–1913.
5. Van der Werf H.M.G., Petit J., Evaluation of the environmental impact of agriculture at the farm level: a comparison and analysis of 12 indicator-based methods. Agriculture, Ecosystems and Environment 93 [2002] 131–145.
6. Garrido J., Requena I., Proposal of ontology for environmental impact assessment: An application with knowledge mobilization. Expert Systems with Applications 38 [2011] 2462–2472.

7. LR MK noteikumi Nr.175 "Noteikumi par nacionālajiem vides indikatoriem". 24.02.2009., ar grozījumiem 25.05.2010.
8. Latvijas vides indikatoru pārskats 2001. LR VARAM, Latvijas Vides aģentūra, 2001, 7.lpp.
9. Gupta A.K., Sinha R., Criteria and Indicators of Sustainability: an executive summary. Executive Summary of the Proceedings of the International Training Workshop, "Criteria and Indicators of Sustainability in Rural Development: A Natural Resource Perspective", March 11-13, 1999.
10. B. ten Brink, Biodiversity indicators for the OECD environmental outlook and strategy. A feasibility study. RIVM Report 402001014, 2000.
11. www.epa.gov/indicators/whatIndicator.html
12. Guidelines for Country Studies on Biological Diversity, UNEP, Nairobi [1993].
13. Niemeijer D., de Groot R.S., A conceptual framework for selecting environmental indicator sets. Ecological indicators 8 [2008] 14-25.
14. Cloquell-Ballester V.A., Cloquell-Ballester V.A., Monterde-Diaz R., Santamarina-Siurana M.C., Indicators validation for the improvement of environmental and social impact quantitative assessment. Environmental Impact Assessment Review 26 [2006] 79-105.
15. Joa˜o E., How scale affects environmental impact assessment. Environmental Impact Assessment Review 22, 2002. p. 289–310.
16. Canter L.W., Interdisciplinary teams in environmental impact assessment. Environmental Impact Assessment Review11 [1991] 375-387.

**Anotācija.** *Ietekmes uz vidi novērtējuma (IVN) procedūra pašreizējā izpratnē Latvijā ir ieviesta 1998. gadā ar likumu "Par ietekmes uz vidi novērtējumu". Kopš tā laika IVN ir veikts virknei dažādu projektu, tai skaitā, rekonstruējamiem vai no jauna būvējamiem valsts autoceļa posmiem. Paredzēto darbību ietekmju uz vidi kvantitatīvu novērtēšanu nodrošina indikatori, kas sniedz visaugstāko iespējamo objektivitāti šajā novērtējuma procesā. Līdz ar to lēmuma pieņēmēji tiek nodrošināti ar korektu informāciju un novērtējuma rezultātiem. Latvijā indikatoru izvēlei un apstiprināšanai IVN projektos nav pievērsta īpaša uzmanība – jautājums atstāts IVN veicēju ziņā. Lai uzlabotu IVN ziņojumu kvalitāti, šajā rakstā tiek diskutēts par problemātiskajiem jautājumiem indikatoru izvēlē un indikatoru apstiprināšanas (validēšanas) nepieciešamību. Tika atlasīti 39 vides indikatori autoceļu projektu IVN, novērtēts to nozīmīgums un būtiskums, kā arī veikta šo indikatoru pielietojuma analīze 14 autoceļu projektu IVN ziņojumos. Rezultāti atklāja esošās problēmas indikatoru pielietošanā un apstiprināja pieņēmumu, ka nav vienotas indikatoru sistēmas līdzīgu saimniecisku projektu ietekmju novērtēšanā, pierādīja nepieciešamību indikatoru validēšanai, lai nodrošinātu labu novērtējuma kvalitāti.*

# OVERVIEW OF THE RIVER BASIN MANAGEMENT PLANS IN THE BALTIC REGION UNDER THE WATERPRAXIS PROJECT

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**Abstract.** *The paper provides brief overview of the river basin district management plans in the Baltic region within the WATERPRAXIS project, linked to the EU Water Framework Directive. Latvian experience in completion of the river basin district management plans is emphasized comparing to other regional cooperation partners. Article is based on the report documents, analysis of the available data and review of the development projects subject to implementation. To some extent also potential issues for discussion are outlined. Certain Baltic countries have had difficulties complying with the EU Water Framework Directive,and there are some potential areas of contention, which should be taken into account in further activities. In course of the administrative and territorial reform and compliance with other EU directives (e.g. in the renewable energy sector) modifications can be made to the status of spatial and also river basin management plans and for the purpose of sustainable development in the region.*

**Keywords:** *river basin management plans, Baltic region, WATERPRAXIS, public involvement.*

## Introduction

One of the most serious problems seen in the Baltic Sea is the eutrophication caused by nutrient loads. Practical measures have been taken to restrict them including development of the river basin management plans both on the EU and regional levels.

The study provides overview on formation of the river basin management plans in Latvia along with several other EU member states, namely, in terms of recognition of solutions to facilitate the review and the revision of planning documents under the EU Water Framework Directive and with emphasis on the project WATERPRAXIS in the Baltic region.

The following elements have been analyzed: structure of the competent authorities and coordinating bodies and their internal and external connections; participation and the role of the public and the interested parties in planning decision-making process; way to integrate and incorporate the objectives of environmental, economic and social policy of the country and region into the river basin water management plans.

The study allows the comparison of certain aspects of the existing management system in Latvia and the water resources management with similar systems operating in other European Union member states of the region.

## Materials and methods

River basic district management planning and analysis is a complex multidimensional process, hence its analysis requires an integrated approach, involving use of various types of information sources.

First these are normative and planning documents, including legislation, government reports and policy papers, which determine development of areas at different scales.

Second, information that defines processes and trends of development for the river basic district management.

Third, website information from relevant government agencies and fora is mainly used.

Fourth, telephone interviews according to given framework.

Valuable data have been obtained from reports of practitioners and plans elaborated within the WATERPRAXIS and the EU Water Framework Directive structures, such as reports and plans for Denmark, Germany, Finland, Poland, Lithuania, Sweden and Latvia.

## Results and discussion

### *Water Framework Directive*

On 23 October 2000, the Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for the Community action in the field of water policy or, in short, the EU Water Framework Directive (or even shorter the WFD) was adopted [1].
Some of the key aims of the Water Framework Directive are: expanding the scope of water protection to all waters, surface waters and groundwater; achieving "good status" for all waters by a set deadline; water management based on river basins; "combined approach" of emission limit values and quality standards; getting the citizen involved more closely [2].
The WFD requires achievement of the following environmental objectives by 2015: good ecological/chemical status of surface water bodies, good ecological potential and chemical status, good chemical/quantitative status of groundwater bodies.
WFD as a tool for performance of its assignment prescribes the river basin management plans (hereafter abbreviated as RBMP) or river basin district management plans (hereafter abbreviated as RBDMP), also procedure for development of the plans and information to be included therein. The review and the revision of the planning documents under the WFD should take place until 22 December 2015, and thereafter every six years.
Development of management plan for each river basin district (hereafter abbreviated as RBD) is assigned by national laws, however the implementation of river basin restoration measures as envisaged in the WFD have had some deficiencies. For instance, in June 2010, Denmark, Lithuania and Poland were among twelve Member States receiving a European Commission written warning for failing to submit plans for managing Europe’s river basins as required by the Water Framework Directive [3].

### *The WATERPRAXIS project*

The project WATERPRAXIS "From theory and plans to eco-efficient and sustainable practices to improve the status of the Baltic Sea" partly funded by the Interreg IVB Baltic Sea Region Programme 2007-2013 aims to improve particularly the status of the Baltic Sea by assisting the implementation of river basin management plans into practice in the Baltic Sea region. The main idea of WATERPRAXIS is that by better understanding the problems and constraints, long-term solutions and concrete pilot investments may be identified. The project partnership consists of research organisations, universities, local authorities and NGOs from Denmark, Finland, Germany, Latvia, Lithuania, Poland and Sweden. WATERPRAXIS is based on the Interreg IIIB project "Watersketch" (2004-2007) [4] as practical implementation and expansion of the initial design.
Within the WATERPRAXIS work structure WP3 stands for: Reviewing River Basin Management, Plans and Processes. River basin management plans (RBMP) from various countries are selected for analysis and the main focus is set on their expected impacts on the status of Baltic Sea. Tasks of the WP3 are: critical analysis of the implementation plan of the RBMPs; analysis of the planning process; analysis of implementation platforms and procedures and identification of critical issues for practical policy integration with policy areas of specific regional relevance [5].
A number of WATERPRAXIS criteria themes and criteria were selected until the meeting in Roskilde, 23-24 June, 2009. Subsequently, partners have selected the River Basin Districts to be enclosed in the WP3 analyses (initially without the Daugava RBD) [6].

***Brief history of the Daugava RBMP development***

Daugava River District Advisory Board was established in 2006. Public discussion of the Daugava River Area Management Plan was held from 22 December 2008 to 22 June 2009. Final version of the Daugava river basin district management plan was approved by Order No. 474 of the Minister of Environment on 21 December 2009. The Plan and program of activities included therein should ensure attainment of environmental quality objectives in the Latvian surface waters and groundwater. The principal objective of the Plan shall be to prevent deterioration of condition of the waters and to improve the surface waters and groundwater in order all the said to be in a good condition until 2015. General objectives for Daugava RBD follow WFD directive.

Analysis of the Daugava RBDMP was introduced into the WATERPRAXIS framework after the initial list compiled by Denmark, Finland, Germany, Lithuania, Poland and Sweden.

*Table.*

**Summary table of River Basin District Management Plans for Analysis** [7]
(amended with inclusion of the Daugava RBD)

| **Partner country** | **Selected river basin district** |
|---|---|
| Denmark | Zealand River Basin District |
| Finland | Oulujoki-Iijoki River Basin District |
| Germany | Oder River Basin District (actually transnational RBD of three EU member states: Poland, Germany and Czech Republic [9]) |
| Latvia | Daugava River Basin District |
| Lithuania | Nemunas River Basin District |
| Poland | Vistula River Basin District |
| Sweden | River Basin District of Bottenviken (aka Norrbotten) |

***Description of the RBM planning structure***

Outlines of the structure of RBM planning include hierarchical structure and levels, as well as key actors involved in RBMP classified as competent authorities and coordinating bodies.

Number of competent authorities responsible for RBD within different countries varies a lot since diversity should be taken into account in the planning and execution of measures; integration of water management into other policy areas such as energy, transport, agriculture, fisheries, regional policy and tourism is necessary; WFD should contribute to cooperation between memberstates [9].

In order to coordinate preparation and implementation of the river basin management plans and programs of measures, advisory boards were established for each RBD. These boards were designed to function as advisory mechanisms for the involvement of all - not only governmental – institutions and organizations concerned with the preparation and implementation of river basin management plans.

In Latvia Ministry of the Environment (present Ministry of Environment and Regional Development, hereafter abbreviated as MoEn) is responsible for RBD administration in Latvia. State limited liability company "Latvian Environment, Geology and Meteorology Centre" (hereafter abbreviated as LEGMC), subordinated to the MoEn is responsible for RBD monitoring in Latvia. LEGMC conducts continuous (i.a. surface water status) monitoring, assesses quantitative status of water bodies and human activity impact on it, submits proposals for water protection purposes, relating to quantitative status of water bodies, and

proposals concerning the assignment of water bodies to a risk group in respect of quantitative status. Institutions responsible for measures implementation in practice are: Ministry of Environment, Ministry of Agriculture, Ministry of Health, municipalities etc.
Advisory Board for the Daugava area has been established in 2006. There are 15 members in it, representing governmental bodies, municipal (development boards of the planning regions) and non-governmental organizations [10].
Primary river basin authorities - MoEn and LEGMC are active on a national level.
With administrative and economic changes revision of the existing plans may be important.
Authorities and coordinating bodies in other countries under review are similar just with some peculiarities. River basin management in Denmark (after administrative reform), Latvia and Lithuania is arranged on the national level, in Poland, Germany and Sweden on the regional or local level, in Finland mainly on the national level but the regions have had a leeway to adapt the national guidance documents to their circumstances. Reporting on the RBDM is always done on the national level. Generally the national Ministries of the Environment are involved in overall water management as the main competent authorities, certain agencies under their supervision enabling practical measures and committees, boards or councils acting as coordinating bodies.
In Poland practical tasks pertains to the National Water Management Authority and National Committees and Working Groups are involved as coordinating bodies [11]; in Lithuania Environmental Protection Agency was assigned as competent authority responsible for RBD administration [12]; in the Oder RBD International Commission on the Protection of the Oder against Pollution (abbreviated as ICPO) is assigned as an international coordination body (between Germany, Poland, and Czech Republic), while the cooperation and coordination of WFD implementation between the three German federal states in the Oder river basin (Saxony, Brandenburg, Mecklenburg-West-Pomerania) is headed by the federal state of Brandenburg [13]; in Denmark the present implementation structure is considerably more centralised than the structure before the local government reform when 14 county governments were responsible for drawing up the river basin management plans [14]; in Finland, the issues related to water quantity belong to the Ministry of Agriculture and Forestry (MoAF) supervising river basin planning within their fields of activities and having assigned the task to prepare national guidance documents on RBM planning to the Finnish Environment Institute (SYKE), which is Finland's national Center for environmental research and development [15]; in Sweden on the national level the Swedish Environmental Protection Agency and the Geological Survey of Sweden guide the River Basin District Authorities i.a. by creating regulations and guidelines.

***Methods used for reaching stakeholders and citizens***

In the course of the planning cycle of public consultation for development of the RBMP in all the countries under review, a variety of tools to inform the public and interested groups and to collect comments and opinions were used. These included: surveys; thematic brochures; guidebooks; leaflets and handouts; articles in the national, regional and industry press; media (information, advertisements provided in the press, radio and television); films; Internet web sites and online maps; meetings; seminars for the main stakeholders groups; debates; panel discussions; press conferences; fora; interviews with key actors; training. Some variations are observed in Sweden where the social network of the representatives is used as an additional way to reach stakeholders [16]; in Lithuania where Environmental Protection Agency has signed agreements with 6 NGOs working in water sector, who became information centers for implementation of the WFD and RBM plans [17]; in Finland a feedback questionnaire done by Finnish Environment Institute for the regional river basin planners about the first RBM planning process [18].

***Potential areas of concern***

Some countries have experienced certain disagreements between key players during negotiations and discussions on the RBDMP. In Sweden the most important conflict of interests in the Water Basin District of Bottenviken and its Water Councils is on hydropower. Existing hydropower plants and a potential extension of hydropower plants are also in line with the Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources. An extension of hydropower in Sweden is however in conflict with the WFD. This conflict is evident for many of the rivers in the District, even the minor ones [19]. In Lithuania agriculture and energy sectors were the main stakeholder groups which had expressed their interests. It was rather complicated to reconcile interests of water management with those of agriculture and energy sector [20]. In Finland conflicting views in the planning process concerned, according to the interviewees, mainly hydropower-related issues. The stakeholders could be divided into few groups based on their main interests: interest groups (hydropower producers, agriculture, forestry, peat production); recreational users and NGO's (fishing, nature conservation); authorities (municipalities, regional councils) [21].

Also for the above issues are potential areas of concern in the future. In addition to the said, for Latvia the Daugava river basin is of transnational nature and shared not only with the EU partners as Estonia and Lithuania, but also with non-EU countries Belarus and Russia. Therefore significant mutual efforts aimed at cooperation and inter-state relations are of vital importance.

## Conclusions

1. River basin management in Denmark, Latvia and Lithuania is arranged on the national level, in Poland, Germany and Sweden on the regional or local level, in Finland mainly on the national level but the regions have had a leeway to adapt the national guidance documents to their circumstances. Reporting on the river basin management is always done on the national level.
2. Level of centralization of the river basin management to some extent might be an issue if decisions should be taken as close as possible to the locations where water is affected or used.
3. The WATERPRAXIS Project is linked to implementation of the Water Framework Directive. Legal consequences for activities and differences related to implementation of both can be examined further.
4. In Latvia for successful attainment of goals set by the Daugava river basin district management plan transnational co-operation is important both on the EU level (with Estonia and Lithuania) and via inter-state relations with Russia and Belarus.
5. For successful attainment of goals set by the river basin management possible areas of rivalry and differences between interest groups (energy sector, agriculture, forestry) and recreational users with NGO's (fishing, nature conservation) and authorities (municipalities, regional councils) should be considered.

## Acknowledgements

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### References

1. Official Journal (OJ L 327), 22 December 2000. Available on http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CONSLEG:2000L0060:20090625:LV:HTML *(viewed 25.02.2011)*
2. http://ec.europa.eu/environment/water/water-framework/info/intro_en.htm *(viewed 25.02.2011)*

3. http://www.emwis.org/thematicdirs/news/2010/08/eu-river-basin-plan-warning/ *(viewed 25.02.2011)*
4. Available on http://waterpraxis.net/ *(viewed 25.02.2011)*
5. Račys V. WATERPRAXIS: From theory and plans to eco-efficient and sustainable practices to improve the status of the Baltic Sea. Presentation, 2010. http://www.rfkl.se/Documents/MOMENT/Presentations%20Water%20Forum/Waterpraxis.pdf *(viewed 25.02.2011)*
6. http://waterpraxis.net/downloads/Downloads/Project%20results/Results%20of%20Work%20Package%203%20WP3/waterpraxis_d3_1a.pdf *(viewed 25.02.2011)*
7. Daugava River Basin Management Plan, 2010-2015 /in Latvian: *Daugavas upju baseina apgabala apsaimniekošanas plāns 2010. – 2015.gadam*/, 2009. Available on http://www.meteo.lv/upload_file/09_upju_baseinu_apsaimniekosana/2009-12-22/Daugava/VIDMPlan_Daugava.pdf *(viewed 25.02.2011)*
8. Criteria for selection of River Basin Management Plans for analysis with Waterpraxis. http://waterpraxis.net/downloads/Downloads/Project%20results/Results%20of%20Work%20Package%203%20WP3/waterpraxis_d3_1a.pdf *(viewed 25.02.2011)*
9. Reisner R. Competent authorities -introduction and ideas for development. Presentation, 2006. Available on http://www.ccb.se/seminars/documents/ReisnerCA05.pdf *(viewed 25.02.2011)*
10. Daugava River Basin Management Plan, 2010-2015 /in Latvian: *Daugavas upju baseina apgabala apsaimniekošanas plāns 2010.–2015.gadam*/, 2009. Available on http://www.meteo.lv/upload_file/09_upju_baseinu_apsaimniekosana/2009-12-22/Daugava/VIDMPlan_Daugava.pdf *(viewed 25.02.2011)*
11. Zabrzeńska-Chaterera M., Imbierowicz S., Skrzypski J., Zbicinski I. Analysis of the Formation System of Management Plans and Water Resources Management. Warsaw, July 2010 (unpublished)
12. Jankūnaitė D., Kliučininkas L. Waterpraxis WP3: Nemunas River Basin District Management plan analysis. Kaunas University of Technology, 2010 (unpublished)
13. „Analysis of the formal structural setup: River Basin Management Plan Oder (area: Germany)", 2010 (unpublished).
14. Nielsen H. Ø., Pedersen A. B. and Frederiksen P. WP 3 Analysing River Basin Management Project. Case study Denmark – Zealand River Basin District. National Environmental Research Institute, Aarhus University, 2010 (unpublished)
15. Rytkönen A.-M., Saarikoski H., Ulvi T. WP 3 Analysing River Basin Planning Management Processes River Basin Planning in Finland – Case Oulujoki-Iijoki River Basin District. Finnish Environment Institute (SYKE),2010. (unpublished)
16. Results from analyzing River Basin Management Projects, Sweden. (unpublished)
17. Jankūnaitė D., Kliučininkas L. Waterpraxis WP3: Nemunas River Basin District Management plan analysis. Kaunas University of Technology, 2010 (unpublished)
18. Rytkönen A.-M., Saarikoski H., Ulvi T. WP 3 Analysing River Basin Planning Management Processes River Basin Planning in Finland – Case Oulujoki-Iijoki River Basin District. Finnish Environment Institute (SYKE),2010. (unpublished)
19. Results from analyzing River Basin Management Projects, Sweden, 2010. (unpublished)
20. Jankūnaitė D., Kliučininkas L. Waterpraxis WP3: Nemunas River Basin District Management plan analysis. Kaunas University of Technology, 2010 (unpublished)
21. Rytkönen A.-M., Saarikoski H., Ulvi T. WP 3 Analysing River Basin Planning Management Processes River Basin Planning in Finland – Case Oulujoki-Iijoki River Basin District. Finnish Environment Institute (SYKE),2010 (unpublished).

**Anotācija.** *Referātā sniegts īss pārskats par upju baseinu apsaimniekošanas plāniem Baltijas reģionā WATERPRAXIS projekta ietvaros, kas ir saistīti ar ES Ūdens pamatdirektīvu. Tiek akcentēta Latvijas pieredze upju baseinu rajonu apsaimniekošanas plānu izpildē salīdzinājumā ar citiem reģionālajiem partneriem. Raksta pamatā ir pārskata dokumenti, pieejamo datu analīze un izstrādājamo attīstības projektu apskats. Zināmā mērā ieskicētas arī potenciālās apspriežamās problēmas. Dažām Baltijas valstīm ir bijušas grūtības ES Ūdens pamatdirektīvas ievērošanā, un pastāv dažas potenciālās sāncensības jomas, kuras jāņem vērā turpmākajā darbībā. Administratīvi teritoriālās reformas un citu ES direktīvu (piemēram, atjaunojamās enerģijas nozarē) izpildīšanas gaitā teritoriālajos, kā arī upju baseinu apsaimniekošanas plānos un reģiona ilgtspējīgas attīstības nolūkos var tikt veiktas izmaiņas.*

**Atslēgas vārdi:** *upju baseinu apsaimniekošanas plāni, Baltijas jūras reģions, WATERPRAXIS, sabiedrības līdzdalība.*

# INFLUENCE OF WASTEWATER ON ZOOPLANKTON COMMUNITY OF THE DAUGAVA RIVER AFTER DAUGAVPILS WASTEWATER TREATMENT PLANT MODERNIZATION

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**Abstract.** *During seasonal studies 2010 (May-October, once/ thrice a month), samples of zooplankton were collected at the Daugava River section from 10 km upstream to 10 km downstream from the Daugavpils treatment plant wastewater discharge into the Daugava River. Changes in the quantitative and qualitative characteristics, saprobity index and species diversity (Shannon-Wiener index) were employed for the analysis of zooplankton community structure in the Daugava River. The Daugava River is polluted by Daugavpils wastewater, however the untoward influence of pollution on zooplankton is observed only in years and in seasons with low water level and discharge. The effect of Daugavpils wastewater pollution on changes in the zooplankton community is considered.*

**Keywords:** *hydrologic regime, large river, pollution, zooplankton.*

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## Introduction

A number of authors (e.g. Bothár, 1988; Mulani *et al.*, 2009; Gajbhiye & Abidi, 1993) are indicating to the impact of wastewater on zooplankton. Potentiality of zooplankton as bioindicator is very high (Ferdous & Muktadir, 2009; Lazareva, 2010; Escribano & Hidalgo, 2000). A great number of authors are drawing attention to possibilities of the use of zooplankton for assessing the river water quality (Bakaeva & Nikanorov, 2006; Vandish, 2000; Demenik, 1988; Kutikova, 1976; Krylov, 2005, 2006; Mathivanan *et al.*, 2007; Vanjare, 2010; Mulani, 2009; Marneffe *et al.*, 1996; Whitton, 1975).

Wastewaters from large cities, which are discharged into the Daugava River, are having their impact on ecosystems and populations of living organisms of the Daugava River (Auniņš, 1967; Matisone, 1965). The studies of 1950s and 60s on the Daugava River have shown that concentration of the dissolved substance and biogenic elements are tightly connected with the river water flow rate (Matisone, 1965). Laganovska (1963), Spriņģeri *et al.* (1999) concludes that impact of the Daugava River pollution on zooplankton can be observed at low discharge.

Notable part of pollution flows into the Daugava River within the Daugavpils city administrative territory. According to the Central Statistical Bureau data, at the beginning of 2010 the city of Daugavpils has a population of 103.922. Before 2009 the Daugavpils wastewater treatment plant has operated using mechanical and biological purification, which does not ensure complete wastewater treatment. On 18 September 2009 the advanced Daugavpils city wastewater treatment plant was opened. After the project implementation the amount of phosphorus in wastewater has decreased nearly 5 times, which ensures compliance with the EU Directive (The Ministry of Environment, 2009).

Dynamics of the zooplankton population depends on chemical factors such as ammonium, nitrates, nitrites, phosphates (Marneffe, 1996; Deksne unpublished).

The aim of the following study is to establish influence of wastewater on zooplankton community of the Daugava River after Daugavpils wastewater treatment plant modernization.

## Materials and methods

During expeditions to the Krauja – Silupe stretch of the Daugava River (4 sampling sites) in 2010, zooplankton was sampled at the right and left banks, as well as in the middle of the river (Table 1). At this stage the river is relatively shallow, 2-4 m, with low current velocity of 0.1-0.2 m $sek^{-1}$.

*Table 1.*

**GPS coordinates of the sampling sites and dates**

| Sampling site | Geographic latitude | Geographic longitude | 2010 |
|---|---|---|---|
| No.16 Krauja (10 km upstream from discharge of the Daugavpils treatment plant wastewater into the Daugava River) | 55°54.787'N | 026°40.059'E | 16 May, 2 June, 17 June, 1 July, 12 July, 30 July, 19 August, 30 August, 16 October, 30 October |
| Šūņupe (place for discharge of the Daugavpils treatment plant wastewater into the Daugava River) | 55° 52.628'N | 026° 30.093'E | 17 June, 1 July, 12 July, 30 July, 19 August, 30 August, 16 October, 30 October |
| Nr.17 1.5 km downstream of discharge of the Daugavpils treatment plant wastewater into the Daugava River) | 55°53.311'N | 026°28.401'E | 16 May, 2 June, 17 June, 1 July, 12 July, 30 July, 19 August, 30 August, 16 October, 30 October |
| Nr.18 Silupe (10 km downstream of discharge of the Daugavpils treatment plant wastewater into the Daugava River) | 55°57.322'N | 026°24.271'E | |

Samples of zooplankton were collected by filtering 100 l of river water with the 65-µm mesh-sized plankton net. Zooplankton individuals smaller than 65 µm in size were not included in this research. Collected samples were fixed in 4% formalin. A *Carl Zeiss* light microscope was used for the analysis of zooplankton; three subsamples (2 ml each) were examined at 100–400 x magnification. The qualitative study was aimed at identification of the Rotifera, Cladocera and Copepoda taxa. All the zooplankton taxa were identified using keys of Kutikova (1970), Borutsky (1960), Manuilova (1964).

Water discharge data were obtained from the company "Latvian Environment, Geology and Meteorology Centre" database.

Species diversity was calculated according to the Shannon-Wiener index (Shannon, 1948; Krebs, 1999). The analysis of similarities across sites and years was carried out using the Renkonen index.

Saprobity index (S) was calculated according to Sladechek's method, using the species – bioindicators' catalogue created by P.Cimdiņš for the Latvian conditions (Cimdiņš *et al.*, 1995).

## Results and discussion

During the 2010 studies, 71 taxa were found, among which there were 39 Rotifera, 23 Cladocera and 9 Copepoda taxa. 68% of the species found on the examined stretch of the Daugava River were indicator species of saprobity, which is a sufficient amount to consider the river pollution level according to zooplankton. Kutikova (1976) indicates that it is difficult to consider the river saprobity if there are few indicator species of saprobity in the river.

During the 2010 research, the maximum discharge as 981 $m^3$ $s^{-1}$ was observed on 15 May, the minimum discharge as 131 $m^3$ $s^{-1}$ on 19 August. During the 2010 vegetation season when the upgraded Daugavpils wastewater purification plant was already operating, the negative impact of wastewater from Daugavpils on the zooplankton was evident in the form of zooplankton abundance decline at the wastewater influx site, established only at the lowest water level (85.05 m.a.s.l.) and flow rate on 19 August (Figure 1). With a slightly higher discharge (up to ~280 $m^3$ $s^{-1}$) and water level (up to ~85.55 m.a.s.l.), decrease in numbers of zooplankton occurred 1.5 km downstream the place of wastewater discharge.

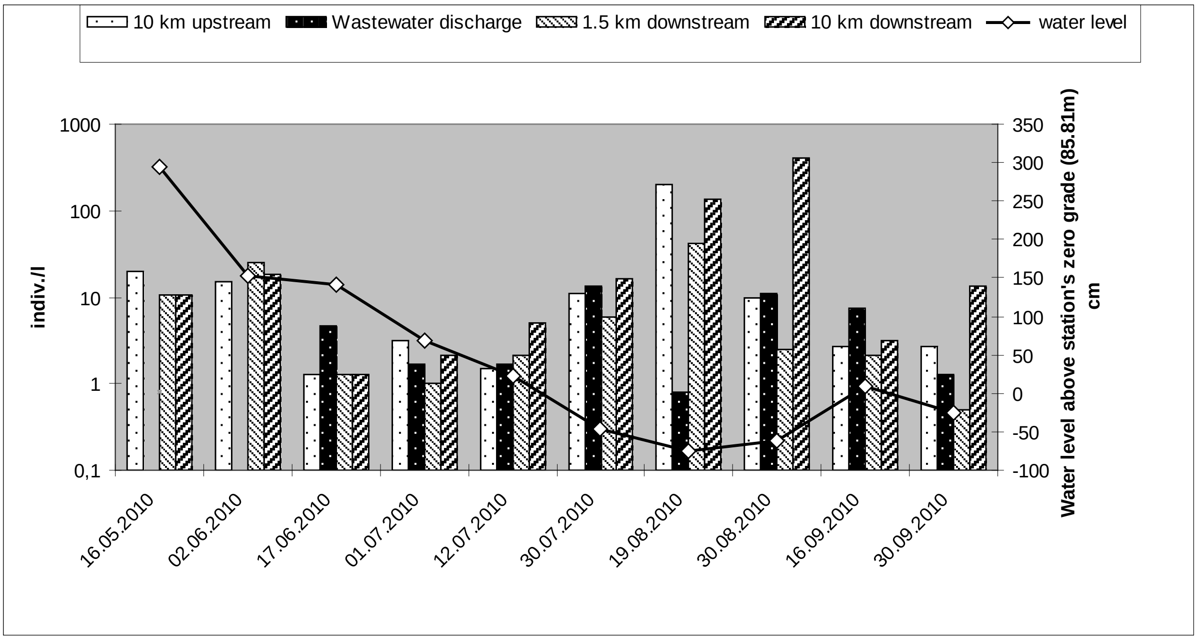


*Fig. 1.* **Abundance of zooplankton and water level during the 2010 research**

Similar conclusions when the number of zooplankton organisms in the Daugava River downstream of Daugavpils wastewater discharge decreased were made also in August 2008 at the water discharge125 $m^3$ $s^{-1}$ (Figure 2).

An excessive inflow of biogenic substances into the river is having adverse effect on zooplankton expressed as reduction in terms of species diversity and increase of the Simpson's diversity index (Kononov, 2010). The given research at water level of 85.05 m.a.s.l. has observed reduction in numbers of taxa and the Shannon-Wiener index at the wastewater influx site. Number of taxa decreased from 23 to 2, the Shannon-Wiener index decreased from 7.5 10 km upstream from the Daugavpils wastewater influx site to 2.0 at the wastewater inflow site (Figure 3). When the water level is higher (up to ~85.55 m.a.s.l.) in the same way as during the summer of *2008*, reduction in numbers of taxa and the Shannon-Wiener index is observed 1.5 km downstream from the wastewater influx site (Skutelis & Deksne unpublished).

In 2010, 2009 and 1962 (Škute,1971), when the water discharge were exceeding ~264 $m^3$ $s^{-1}$, water level was above 85.55 m.a.s.l., adverse effect of Daugavpils wastewater on the Daugava zooplankton cenoses was not evident (Figure 1, 2, 3, 4).

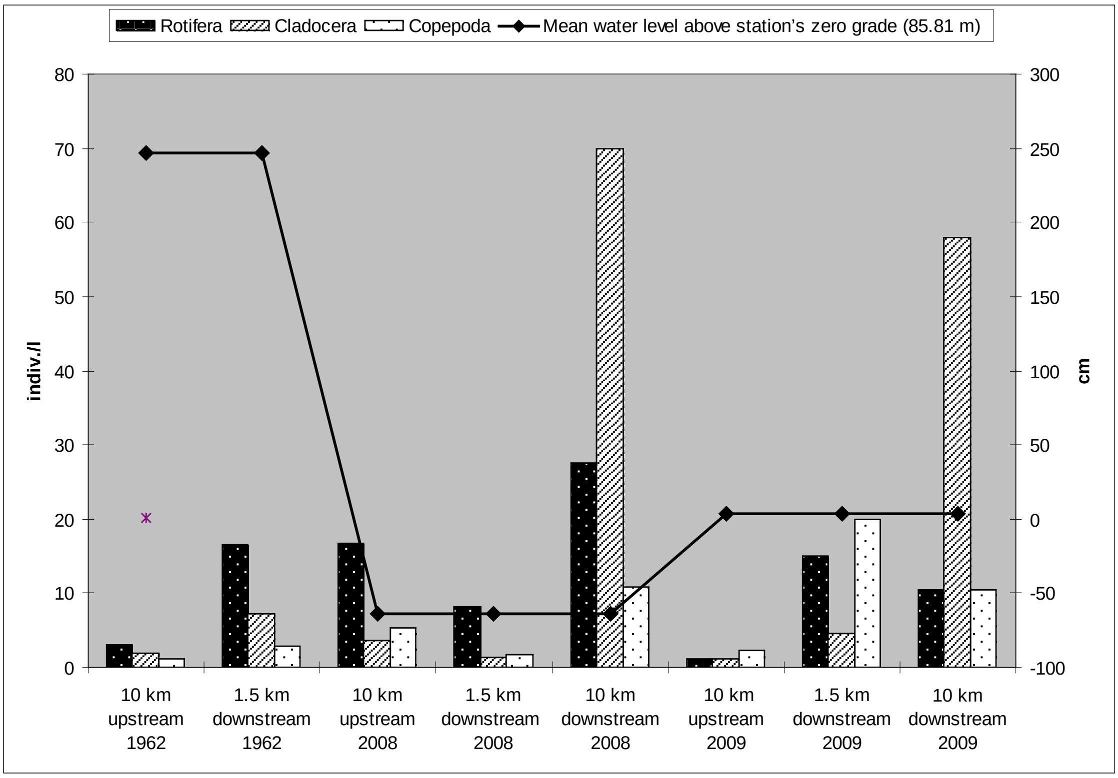


*Fig. 2.* **Abundance of zooplankton and water level during summers of 1962, 2008 and 2009**

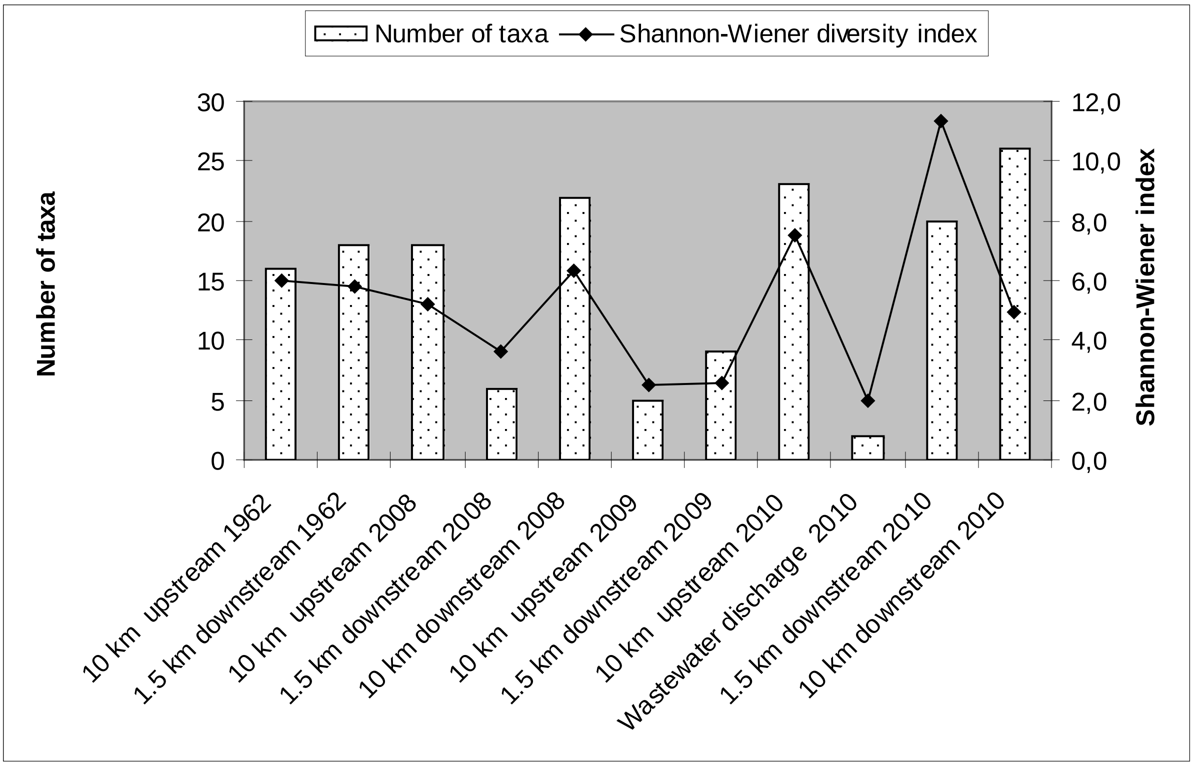


*Fig. 3.* **Number of zooplankton taxa and the Shannon-Wiener diversity index during the summers of 1962, 2008 - 2010**

In August 2010, like in the summer of 2008, reduction in the zooplankton abundance at the wastewater influx into the Daugava River and 1.5 km downstream from the Daugavpils wastewater influx site has occurred not only at the expense of dominant species, but also at the expense of reduction or even complete disappearance of the oligosaprobes, at the right bank none of the oligosaprobe species was found, while quantities of β and α-β saprobe organisms increased (Figure 4). In August 2010 at the water level of 85.05 m.a.s.l. saprobity changed from o - saprobity, which describes a slight contamination (S = 1.26) upstream of Daugavpils wastewater influx site to the β - mezosaprobity, which describes a medium-level pollution (S = 2.2) at the wastewater influx site (Figure 4). At a higher water level (up to ~85.55 m.a.s.l.) increase of saprobity occurred 1.5 km downstream from the wastewater influx site (Skutelis & Deksne unpublished).

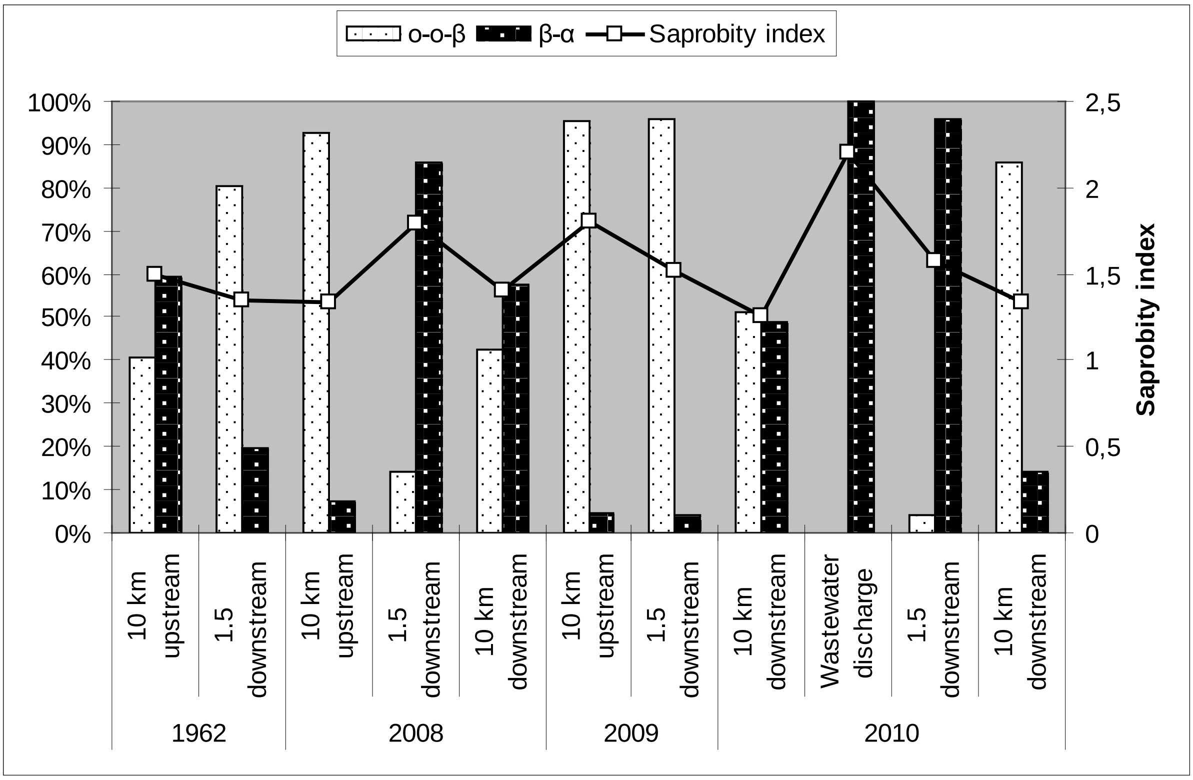


*Fig. 4.* **Percentage distribution of the zooplankton abundance according to saprobity and saprobity index in the summers of 1962, 2008 - 2010**

Zooplankton abundance and species diversity increased 10 km downstream from the Daugavpils wastewater influx site during all years and seasons (Figure 1, 2, 3). At high flow rates, which were observed in the summers of 1962 and 2009, and in the spring, autumn seasons of 2008 and 2010, zooplankton abundance and numbers of taxa increased just 1.5 km downstream from the Daugavpils wastewater influx site. Increase of zooplankton abundance and growth of diversity of species can be explained by the river self-purification processes, in this stretch of the river favorable wastewater dilution area is built up with richly developed bacteria plankton, which is very good feeding base for the development of zooplankton. Favorable condition for development of zooplankton downstream the Šūņupe River is also greater depth of the river with relatively little less stream velocity. Several authors are reporting on the importance of zooplankton in the efficiency of self-cleaning processes (Kutikova, 1976; Bakaeva & Nikonorov, 2006; Ivanova, 1976).

Upon comparison of the zooplankton cenoses on the right bank according to the Renkonen index 10 km upstream and 1.5 km downstream from the Daugavpils wastewater influx site, similarity between these sites was higher in 2009 (72%) than in 2008 (35%) and 2010 (23%) when water levels and flow rates were low, therewith the wastewater dilution degree was low and the Daugavpils wastewater adversely affected the cenoses of zooplankton, thus changing the structure of zooplankton upstream and downstream the Daugavpils wastewater influx site (Table 2). When comparing the cenoses of zooplankton in 2008, 2009 and 2010 on the right bank 10 km upstream from the Daugavpils wastewater influx site, the similarity constitutes 58%, 49% and 47%. While the similarity is lower when cenoses are compared 1.5 km downstream from the Daugavpils wastewater influx site, in 2008 and 2009 the similarity is 12% and in 2009 and in 2010 - 26%. When comparing zooplankton cenoses at the same site in 2008 and in 2010 when under the impact of wastewater at low discharge changes in cenoses are taking place, the similarity was higher - 38%. Consequently in 2008 and 2010 when there were low water levels and discharge, under the impact of wastewater there were more considerable changes in the zooplankton structure than in 2009 when the water level was high.

*Table 2.*

**Establishment of similarity according to the Renkonen index**

| | | **2008** | | **2009** | | | **2010** | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 1.5 km D | 10 km D | 10 km U | 1.5 km D | 10 km D | 10 km U | 1.5 km D | 10 km D |
| **2008** | 10 km U | **35** | 22 | **58** | 66 | 45 | **49** | 10 | 42 |
| | 1.5 km D | | 14 | 8 | **12** | 17 | 8 | **38** | 15 |
| | 10 km D | | | 10 | 33 | 43 | 50 | 19 | 43 |
| **2009** | 10 km U | | | | **72** | 33 | **47** | 0 | 10 |
| | 1.5 km D | | | | | 58 | 33 | **26** | 13 |
| | 10 km D | | | | | | 12 | 9 | 46 |
| **2010** | 10 km U | | | | | | | **23** | 18 |
| | 1.5 km D | | | | | | | | 15 |

U = upstream from discharge of the Daugavpils wastewater into the Daugava River;
D = downstream from discharge of the Daugavpils wastewater into the Daugava River.

However, it is recalled that the zooplankton dynamics depends not only on pollution and trophic status, but also on other factors (Гришанков & Степанова, 2009; Deksne unpublished).

## Conclusions

Daugavpils wastewaters pollute the Daugava River, however the adverse effects of pollution on zooplankton are exposed only in years and in seasons when water level (<85.55 m.a.B.s.l.) and discharge (<264 $m^3$ $s^{-1}$) is low. Also after modernization of the Daugavpils wastewater treatment plant the wastewater discharged into the Daugava River are affecting the zooplankton cenosis. The adverse effect of wastewater is expressed as decrease in the total abundance of zooplankton organisms, taxa and species diversity, increase of saprobity.

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**References**

1. Auniņš E. A., 1963. Calculation of ionic-salt run-off and the agrgression of water in the Daugava River. *In:* Kumsare A. J. (ed.), Hydrobiology and ichthyology of inland waterbodies in the Baltic states, Latvian SSR Academy of Sciences, Riga, 31-46. [Ауниньш Э.А., 1967. Расчёт ионно–солевого стока и агрессивности воды р. Даугавы. в кн.: А.Я. Кумсаре (Ред.).Гидробиология и ихтиология внутренних водоёмов Прибалтики. Рига: Тр. Ин-та биол. АН Латв. ССР, 31–46].
2. Bakaeva E. N. and Nikanorov A. M., 2006. Hydrobionts for the assessment of water quality, Institute of Water Problems, RAS, Nauka, Moscow, 239 p. [Бакаева Е. Н., Никаноров А. М., 2006. Гидробионты в оценке качества вод суши, Москва: Наука, 239 с.].
3. Bothár A., 1988. Results of long-term zooplankton investigations in the River Danube, Hungary. *Verhandlung Internationale Vereinigung Limnologie., 23,* 1340–1343.
4. Borutsky E. V., 1960. Key to identification of wild freshwater crawfish of the USSR and contiguous countries from fragments in fish intestines, Academy of Sciences of the USSR, Moscow, 218 p. [Боруцкий Е. В., 1960. Определитель свободноживущих пресноводных веслоногих раков СССР и сопредельных стран по фрагментам в кишечниках рыб. Москва: Изд-во АН СССР, 218 с.].
5. Cimdiņš P., Druvietis I., Liepa R., Parele E., Urtane L. and Urtans A., 1995. Latvian catalogue of indicator species of freshwater saprobity. *Proceedings of the Latvian Academy of Sciences., 1/2,* 122-133.
6. Demenik A.L., 1988. Turners as a component of zooplankton communities of rivers' ecosystems, VINITI, Minsk, 54 p. [Деменик А.Н., 1988. Коловратки как компонент сообщества зоопланктона речных экосистем. Деп. № 334-В88 (ВИНИТИ): Минсk, 54 с.].
7. Escribano R. and Hidalgo P., 2000. Spatial distribution Spatial distribution of copepods in the north of the Humboldt Current region off Chile during coastal upwelling. *Journal of the Marine Biological Association of the UK., 80,* 283-290.
8. Ferdous Z. and Muktadir A.K.M., 2009. A ***Review***: Potentiality of Zooplankton as Bioindicator. *Applied Sciences, 6(10),* 1815-1819.
9. Gajbhiye S.N. and Abidi S.A.H., 1993. Zooplankton distribution in the polluted environment around Bombay. *Environmental Impact on Aquatic and Terrestrial Habitats, Ed. by: Agrawal, V.P., Abidi, S.A.H., Verma, G.P.* 127-142p.
10. Ivanova M.B., 1976. Experience of participation of planktonic creatures in selfpurifying processes (on the example of zooplankton from the shores of the Izhora River). *In:* Skarlato O.A. (ed.), Hydrobilogical bases of water selfpurifying, Institute of Zoology, Leningrad, 36-42. [Иванова М. Б., 1976б. Опыт оценки участия планктонных животных в процессах самоочищения воды (на примере зоопланктона прибрежных учатков р. Ижоры). *В кн:* Гидробиологические основы самоочищения вод., Ленинград: Зоолог. институт АН СССР, 36-42].
11. Kononova O.N., 2010. Zooplankton of the Vichegda River tributaries with different degrees of anthropogenic load. Theses from Reports of the IV International Conference "Contemporary Problems of Hydroecology", Saint Petersburg. 89 p. [Кононова О.Н. 2010., Зоопланктон притоков реки Вычегды с различной степенью антропогенной нагрузки. Тезизы докладов IV международной конференции "Современные проблемы гидроэкологии", С.-Петербург. 89 с.]
12. Krebs J. C., 1999. Ecological Methodology. Second Edition, Addison Wesley Longman, Melno Park, California, USA, 620 p.
13. Krylov A. V., 2005. Zooplankton in plain rivers, Nauka, Moscow, 263 p. [Крылов, А. В. 2005. Зоопланктон равниных малых рек. Москва: Наука, 263 с.].
14. Krylov A.V., 2006. The changes in trophical structure of zooplankton water flow due to environmental factors. *In:* Rumjancev V.A. and Trifonova I.S. (eds), Report thesis in the International conference Bioindication in monitoring of freshwaters' ecosystems, St. Petersburg, 81-85 p. [Крылов, А. В., 2006. Изменения трофической структуры зоопланктона водотоков при влиянии ключевых факторов среды. Отв. ред. В.А. Румянцев, И.С. Тезисы докладов Международной конференции „Биоиндикация в мониторинге пресноводных экосистем" Спб., Санкт-Петербург, 81-85].

15. Kutikova L. A., 1970. Rotifera of the USSR fauna. Key to fauna of the USSR, Nauka, Leningrad, 744 p. [Кутикова Л. А., 1970. Коловратки фауны СССР. Определители по фауне СССР, издав. Зоол. Ин-том АН СССР. Вып. 104. Ленинград: Наука, 744 с. ].
16. Kutikova L.A., 1976. Water planktons' turners as the indicator of water quality. *In:* Kutikova L.A. (ed.), Methods of water biological analysis, Nauka, Leningrad, 80-90. [Кутикова Л.А., 1976. Коловратки речного планктона как показатели качества воды. *В кн.* Кутикова Л.А., (Ред.). Методы биологического анализа пресных вод. Ленинград: Зоол. ин-т АН СССР, 80-90].
17. Laganovska R., 1963. Zooplankton of the river Daugava and peculiarities of its development in connection with hydrological regime and pollution of the river, 10th Freshwater in Baltic Scientific conference., Minsk, 139 p. [Лагановска Р.Я., 1963. Зоопланктон реки Даугавы и особенности его размешщения в зависимости от гидробиологическова режима и загрезнения реки. X Научная конференция по внутренним водоемам Прибалтики. Тез. Докл.: Минск, 139 с.].
18. Lazareva V.I., 2010. Zooplankton structure and Dynamics in the Rybinsk Reservoir, KMK Scientific Press Ltd., Moscow, 183 p. [Лазарева В.И., 2010. Структура и динамика зоопланктона Рыбинского водохранилища. М: Товарищество научных изданий КМК, 183 с.].
19. Latvian Environment, Geology and Meteorology Centre. Available from http://www.meteo.lv/public/27710.html (Accessed 12 April 2011).
20. Manuilova E. F., 1964. Cladocera of the USSR fauna, Nauka, Moscow-Leningrad, 327 p. [Мануйлова, Е. Ф. 1964. Ветвистоусые рачки (Cladocera) фауны СССР. Москва-Ленинград: Наука, 327 с.].
21. Marneffe Y., Descy J.P. and Thomé J.P. 1996. The zooplankton of the lower River Meuse, Belgium: Seasonal changes and impact of industrial and municipal discharges. Hydrobiologia., 319(1), 1-13.
22. Matisone M., 1965. Biogenic run-off of the Daugava River. *In:* Kumsare A. J. (ed.), Fishery of the inland warbodies in the Latvian SSR, Science, Riga, 365-379 p. [Матисоне М., 1965. Биогенный сток реки Даугава. *В кн.* А.Я. Кумсаре (Ред.), Рыбное хозяйство внутренних водоёмов Латвийской ССР. Рига: Зинатне, 365-379 с.].
23. Mathivanan V., Vijayan P., Sabhanayakam S., Jeyachitra O., 2007. An assessment of plankton population of Cauvery river with reference to pollution. *Environ Biol., 28(2),* 523-6.
24. Mulani S.K., Mule M.B.and Patil S.U., 2009. Studies on water quality and zooplankton community of the Panchganga river in Kolhapur city. *Environ Biol., 30(3),* 455-9.
25. Shannon C. E., 1948. Mathematical Theory of Communication. *The Bell System Technical Journal., 27,* 379–423,623–656.
26. Spriņģe G., Spriņģe G., Briede A., Druvietis I., Parele E., Rodinovs V. and Urtāne L., 1999. Investigations of biodiversity in freshwater ecosystems of Latvia. *In:* Naimovičiene Ž., Raudiene L., Virbickas T. (eds), Hydrobiological research in the Baltic countries. Part I. The rivers and lakes, Institute of Ecology, Vilnius, 232-272.
27. Škute R. J., 1971. Zooplankton of the River Daugava and its role in the productivity and biological evaluating of the river. Dissertation, Tartu University, Tartu, 233 p. [Шкуте, Р. Я. 1971. Зоопланктон реки Даугавы (кроме низовий) и его роль в продуктивности и санитарнобиологической оценке реки. Диссертация. Тарту. 233 с.]
28. The Ministry of Environment, 2009. available from http://www.vidm.gov.lv/lat/informacija_presei/preses_relizes/?doc=954715.09.2009 (Accessed 17 December 2009).
29. Vandish O.I., 2000. Zooplankton as indicator of lake ecosystems' conditions (on the example of subartcical lake Imandra). *Water resources., 27(3),* 364-371. [Вандыш О.И., 2000. Зоопланктон как индикатор состояния озерных экосистем (на примере субарктического оз. Имандра). *Водные ресурсы. 27(3),* 364-371].
30. Vanjare A. I., Padhye S. M. and Pai K., 2010. Zooplankton from a polluted river, Mula (India), with record of *Brachionus rubens* (Ehrenberg, 1838) epizoic on *Moina macrocopa* (Straus, 1820). *Opusc. Zool. Budapest., 41(1),* 89–92.
31. Whitton B.A. (ed.), 1975. River Ecology. Studies in ecology, Volume 2, Blackwell Scientific Publications, US distributors: University of California Press, Berkeley, Oxford, 725 p.

**Anotācija.** *Zooplanktona paraugi ievākti 2010. gada sezonālo (maijs-oktobris/ vienreiz līdz trīsreiz mēnesī) pētījumu laikā Daugavas upes posmā 10 km augšpus līdz 10 km lejpus Daugavpils attīrīšanas iekārtu notekūdeņu ieplūdes Daugavā. Daugavas zooplanktona cenožu struktūras analīzei izmantots to kvantitatīvais (organismu daudzums, taksonu skaits) un kvalitatīvais raksturojums, saprobitātes un* Šenona-*Vīnera daudzveidības indeksa izmaiņas. Daugavpils notekūdeņi piesārņo Daugavas upi, taču piesārņojuma nelabvēlīgā ietekme uz zooplanktonu parādās tikai gados un sezonās ar zemu ūdens caurplūdumu un līmeni. Notekūdeņu nelabvēlīgā ietekme izpaužas kā kopējā zooplanktona organismu skaita, taksonu un sugu daudzveidības samazinājums, saprobitātes pieaugums.*

# COMPLEX EVALUATION OF AIR QUALITY IN REZEKNE

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**Abstract.** *Paper presents results of air ionization level measurements made in past 3 years in Rezekne city. The concentrations of positive and negative air ions with mobility factor k ≥ 0,4 cm $^2$/V·s were obtained by portative air-ion counter "Sapfir-3M" (Russia) in 8 parts of the city thrice per day. The approximate interconnections among ionization and chemical and mechanical pollution of air were analyzed. The complex evaluation of long – term air pollution impact on different parts of city is carried out using methods of lichenoindication and air ion research.*

**Keywords:** *air pollution, air ions, lihenoindication, urban ecology.*

## Introduction

The city environment is characterized by elevated atmospheric pollution relevant to high traffic intensity, concentration of industrial objects and thermal energy production. The highest pollution level is usually observed in city centers and industrial [1]. Microclimatic features of city, such as relief and character of city buildings, are very important for pollution dispersion. For example, during the winter season in Rezekne city, which is situated on a lowering in relief, in anticyclonic conditions the arctic smog can be observed.

Emission data from stationary pollution sources were obtained according to methodical regulations approved by The Ministry of Environmental Protection and Regional Development, whereas the evaluation of traffic pollution needs data about weekly, daily and hourly traffic intensity. [2]

In observing the air quality of city environment, several methods can be used, for example: 1) analyzing data from stationary pollution sources; 2) measuring traffic flow intensity in city streets; 3) using bioindication of air quality; 4) summarizing data from air quality monitoring stations; 5) obtaining information about the state of human health, 6) measuring concentrations of light air ions in different city regions.

Since the end of the 20th century, the environmental pollution in Rezekne created by stationary pollution sources has significantly decreased: from 2669 tons of emissions in 1998 to 1317 tons in 2005. In 2009, only 219 tons of polluting substances have been detected mostly $NO_x$ and CO. [3] It can be explained by the decline of industrial production (factories create only 13 per cents of stationary source emissions) and by the replacement of fuel oil by natural gas and wood chips in heat supply enterprises. Unfortunately, there are no emission calculations from low power heating systems, such as private houses, therefore the actual air pollution level created by stationary sources in Rezekne city is definitely higher and the dispersion of it is much weaker.

Until 2007, the intensity of traffic flows in city streets was increasing constantly but currently it tends to become stable or even decrease. Moreover, since 2005 the technical state of vehicles has significantly improved.

Hence, it can be declared that in the first decade of the 21th century the air quality in Rezekne city has ameliorated. It should be mentioned that the proportion of motorcars in Rezekne is approximately 83 – 85 per cents, whereas the number of bicycles is less than 1per cent of listed vehicles. Therefore it can be assumed that it is still possible to improve the air quality of the city in the future.

The long-term influence of pollution is presented quite precisely by lichenoindication data because the lichens are universally recognized to be very sensitive bioindicators that demonstrate the territorial differentiation of air pollution. The lichenoindication of air quality in Rezekne city is taking place since 2001.

A new method that is rarely used in observing the air quality in cities is the measuring of light air ion concentration. It is known that air ions have an effect on human health and well-being and interact with aerosol particles and chemical gasiform air pollution that is adsorbed on these particles. There are many studies in literature affirming that environmental air ion concentration levels and balance can affect a wide range of biological organisms, including humans. Elevated negative air ion levels are reported to have beneficial effects on humans, for example enhanced feeling of relaxation, reduced fatigue, stress, irritability, depression and tenseness level. Increased positive ion levels are reported to have no effect, or deleterious effects. [4, 5, 6] To ensure human health and well-being, the minimal concentration of negative and positive ions is necessary $400 ions/cm^3$ [7].

The ion polarity is characterized by unipolarity factor K, which is the relation of concentration of positive and negative ions in $1 cm^3$ of the air.

$$K = \frac{n^+}{n^-}$$

The article presents an integrated evaluation of air quality, basing on lichenoindication, traffic flows and light air ion concentration data.

## Materials and methods

### *Lichenoindication*

Lichenoindication is a bioindication using the lichens. The extinction of lichen and the decrease in its biodiversity indicate an elevated air pollution level, therefore the lichens are one of the most popular bioindicators. Lichens are highly diverse, that is why the identification of species is not always simple. The lichens are commonly divided into three main groups – crustose, foliose and fruticose lichens. The species of lichens respond differently to air pollution. Sensitive species disappear in conditions of even low pollution level while more resistant species survive in relatively high pollution. Usually, fruticose lichens disappear first, they are followed by foliose lichens and finally by crustose lichens. There is some regularity – the wider is the diversity of lichens and the more trunk surface is covered with lichens; the clearer is air in the given territory. The broad-leaved trees, such as maples, limes, ashes and elms, are more appropriate for the studies of lichens, whereas conifers are not appropriate for it. For lichen studies only grown-up trees are useful, because the covering of lichens on saplings has not developed yet.

Rezekne city map was divided into squares. The length of one edge was 500m. In each square, the flora of lichens on ten deciduous trees was inspected. The lichens were studied at the altitude of 1.3 – 1.5 m on the side the most covered with lichens. A transparent 20 x 20 cm polythene square, divided into 100 small quadrants, was put to the trunk of the tree. This method facilitates the defining of percentage of lichen covering on the trunk.

The air quality observations made in relation to the lichen covering on tree trunks are shown in the left lower corner of figure 2. Air pollution level is estimated to be low in places where all the three lichen groups are present, average in the places where two lichen groups are present and high in the places where only one lichen group (mostly crustose lichens) is present.

### *Traffic flow intensity measuring*

The measurements of traffic flow intensity were taken on weekdays, on the biggest street junctions of Rezekne city, counting the transport units crossing the given junction in a period of one hour. The measurements were taken three times a day: 8.00 - 9.00, 13.00 - 14.00 and 17.00 - 18.00. The counting of transport units was performed mostly on the junctions situated on the main arterial roads of Rezekne city – Atbrivosanas aleja and Darzu street, as well as on Latgales street that is partially used for transit traffic in direction of Dagda and Ludza. The traffic flow measurements for the period 2007 – 2010 are summarized in the map of complex air quality evaluation (Figure 2).

***Air ion measuring***

To evaluate air ion level and dynamics of its changes, measurements of light air ions concentration in different places of Rezekne city were made. The bipolar air ions counter "Saphire-3м" was used. Air ion counter is intended to provide separate and simultaneous measurements of negative and positive air ion concentration in 1 $cm^3$ of air with mobility factor $k \geq 0{,}4\ cm^2 V^{-1} s^{-1}$. Minimum resolution of the counter is 10 ions/ $cm^3$. Air flow rate through the aspirating camera while measuring the air ion concentration is $(230 \pm 23)$ l/min.

Each time in every measuring point 10 measurements of positive and negative ions were taken using 16 sec averaging mode. The ion counter was placed perpendicularly to the wind flow in order to avoid measurement inaccuracies caused by sudden wind blasts in the aspirating camera.

The air ion concentration measurements taken in different seasons in the period 2009 – 2010 are summarized and analyzed. The aim is to study the interaction between pollution and air ions and to clarify how the anthropogenic pollution influences the concentration of positive and negative air ions.

A wide network covering the whole city, including industrial zones, residential neighborhoods, recreational areas, main streets and junctions was estabilished (see figure 1).

Breaf characterization of measurement points.

1st test point – Rezekne Meat processing factory vicinity. It has not been considered to be particularly contaminated, but there is often a specific odor in this area. A railway and an important road junction are located nearby.

2nd test point – parking at the pharmacy "Lana". Located nearly the only monitoring station in Rezekne, situated in the city centre along the main street.

3rd test point – parking next to the intersection of Atbrivosanas and Latgale streets – the busiest intersection in Rezekne. Traffic intensity is high, in the mornings and evenings traffic jams tend to occur. The central bus station is located in this part of city.

4th test point - private residential area opposite Miera street. Quiet territory with low traffic intensity. A large cemetery resembling a park is located nearby.

5th test point is located on the territory of the Hospital of tuberculosis and resembles a quiet park with mixed tree plantations.

6th test point - neighborhood of the railway station Rezekne II. Considered to be one of the most polluted areas in Rezekne (not only air, but also soil and water). There is an active movement of passengers and goods. Stacijas street, one of the major city streets, is located along the station.

7th test point - parking at the Rezekne Secondary School #5. Represents the concentration of air pollution in the residential area of the Northern part of the city.

8th test point - parking at the factory of electrical tools "REBIR". Represents the industrial zone of the Northern part of the city.

## Results and discussion

Lichenoindication does not provide data about short-term changes of air pollution that can be very inconsistent in time. Nevertheless, this method provides information about long-term influence of air pollution in one particular part of the city.

It can be seen that the biggest lichen covering on tree trunks and the lowest air pollution level is observed in the Southern part of the city with many trees and green zones where the

cottage-type buildings prevail and where there are no trunk roads. The covering of lichens on tree trunks overcomes 60 per cents.
The big lichen covering located in the Northern part of the city is mainly observed in the territory of storehouses and allotments. The high percentage of lichen covering in some other squares of the city, for example near the river, is related to the absence of air pollution sources, with the exception of allotments in the Western part of the city where the railway is relatively close. It can be presumed that the pollution created by this railway is dispersed by western winds above the city territory. Generally, the city territory is dominated by average air pollution related to the motor transport, the small boiler houses and probably to the relatively equable pollution dispersion from big boiler houses. High or very high air pollution level was observed mainly along the railways, near the railway stations and in the industrial city zones situated mostly in the Northern part of the city. In this part, the covering of lichens on tree trunks usually does not overcome 20 per cents and all the species of lichen are resistant to pollution.
All the three lichen groups (crustose, foliose and fruticose lichens) are simultaneously present only in some squares of the Southern part of the city and slightly along the river coasts. The tree trunk covering with crutose and foliose lichens is typical for all the city territory. In some squares along the railways, only crutose lichens are present. Along the city streets the population of foliose lichens is also poor. It is possible that the precision of obtained results in some city squares was influenced by the lack of trees suitable for lichenoindication.
According to the data from Road Traffic Safety Directorate (CSDD), in 1998-2010 the number of registered motorcars in Rezekne has increased by 28 per cents, whereas the number of lorries has decreased by 25 per cents and the number of buses has fallen more than twice [8]. The figure2 shows the averaged traffic flow intensity from the most important junctions of Rezekne. The comparable data of years 2007 and 2010 are shown in table 1.

*Table 1.*

**Traffic intensity in the streets of Rezekne**

| **Street junction** | **The average number of vehicles per 1 hour** ( on working day) | | |
|---|---|---|---|
| | **Year 2007** | **Year 2010** | **Designation in the map** |
| Atbrivosanas street – Latgales street | 1074 | 1139 | A |
| Atbrivosanas street – Lubanas street | 942 | 1042 | B |
| Atbrivosanas street – Maskavas street | 908 | 896 | C |
| Latgales street – Darzu street | 473 | 457 | D |
| Latgales street – Ludzas street | 496 | 501 | E |
| Kr. Barona street – Liepu street | 213 | 192 | F |
| Ludzas street – Raznas street | 552 | 530 | G |
| Rigas street – Vilakas street | 382 | 366 | H |

The calculations of transport units reflect the load of given streets. Rezekne has some particularities defining its traffic flow. There are two bridges over Rezekne river used for the motor transport. So the main traffic flow is on Atbrivosanas, Darzu and Latgales streets.

Air ion concentration during the whole measurement period and almost in all the test points showed large fluctuations. Concentration of positive and negative ions can vary from zero to hundreds of ions per $cm^3$ even among 10 measurements taken consecutively. Air ion concentration is greatly influenced by meteorological factors, such as wind speed and direction, temperature, and changes of relative humidity. The flow of air masses creates turbulence mixing the different layers of atmosphere and contributing to the pollution migration between them. Despite the high instability of air ion concentration during individual measurements, in long-term the average values are very important to provide more accurate information about air energetic saturation level that characterizes the air of the particular test point.

It is known that the air pollution in city is rising during the day. The pollution level starts to increase rapidly at approximately 8:00 and reaches the culmination at approximately 17:00 to decrease again in the nighttime due to the natural air purification. This cycle depends to a great extent on the traffic intensity. It is proved by data obtained in the monitoring station on Brivibas street in Riga. The concentration of carbon dioxide and benzene is in close correlation with changes in the quantity of cars on the street in twenty-four hours time. The concentration of sulphur dioxide is less related to the motor transport than to the industrial sector – the activity of boiler houses of different size and type. Therefore the level of this kind of pollution is relatively constant day and night. [9] It can be assumed that these regularities of air pollution changes exist not only in Riga but also in the other largest cities (it should be remarked that Rezekne is the 7th largest city in Latvia).

Unlike the mentioned air pollution, the concentration of light air ions has a tendency to decrease during the day. It permits to assume that air ions are important for the processes of air purification. The charge of air ions, interacting with the pollutant molecules, stimulates their mutual attraction and formation of bigger aggregates, and accelerates their sedimentation from air environment (see figure 1). First of all, it relates to the mechanical pollution components - various solid-state and liquid aerosols. The high adsorption capacities of gasiform substances on the aerosols reduce the amount of pollutant gases in atmosphere. Air ions can promote different chemical reactions in the atmosphere also. Especially strong decrease of ions during the day characterizes the measure points located near pollution sources crated by traffic. Besides, the rapidest decrease usually concerns the concentration of negative ions. It can be explained by the different structure of positive and negative ions. Negative ions are smaller but with higher mobility, consequently they can intervene in the process of air purification more rapidly and actively. It is important to mention, that in the points distant from pollution emission sources (e.g. Tuberculosis hospital), the decrease of ion concentration level during the day is not strong or does not even manifest itself.

The highest values of unipolarity coefficient K are observed near the railway station “Rezekne II”, on the junction of Latgales Street and near the Meat processing factory. In these measure points the pollution created by traffic and partially the industrial pollution dominate. The lowest values of coefficient K are observed on the Miera Street and near the Hospital of tuberculosis where the pollution sources are minimal. Intermediate values of K can be observed in the city center and in the Northern part of the city (see the map.). It is probable that in these city parts the characteristic air pollution of intermediate level is manifesting itself as well.

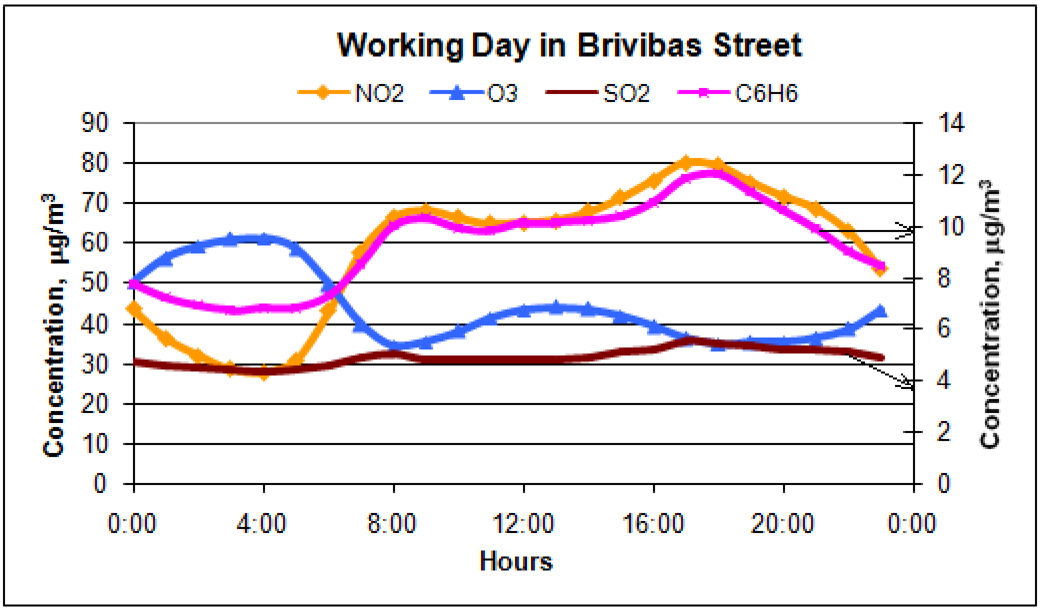


*Fig. 1.* **Dynamic of atmospheric pollution concentration** [10]

Speaking about complex evaluation of air quality, there are some aspects to be mentioned. Lichenoindication, ion measuring and counting of transport units correspond with each other relatively well. The maximal coverage of lichens on tree trunks and the minimal value of K is observed in the points with minor traffic flow (see junctions F, G and points 4 and 5 in figure 2). The average level of air ionization is not high in these points as well. It can be explained by the lack of anthropogenic ionization sources. It is known that the automobile exhaust gases also produce positive and negative air ions in almost similar proportions [11]. In these measure points the natural ionization level is preserved and its ion production and depletion rate is typical for parks and forests. The level of air ion concentration is not high but these ions are more "salubrious" because the negative ions prevail over the positive ones.
A low level of lichen coverage is located in the environs of railway. The vicinity of railway station "Rezekne II" encompasses the junction with the third the most intensive traffic flow, the lowest level of lichen coverage and the highest value of coefficient K. All these conditions indicate that there is a relatively high level of air pollution in this area (see squares D6, F6, E6, junction B and measure point 6 in figure 2). Intermediate lichen coverage is usually observed along the streets, whereas the lowest level of lichen coverage is located along the railway. It allows presuming that air quality is more influenced by railway than by motor transport in the city.
The traffic flow is the most intensive in the junction A (see figure 2). On average, this junction is traversed by 1124 motor cars per hour. Besides, the lowest total concentration of air ions is observed in the measure point that is located near this junction. Nevertheless, the value of coefficient K 0,95 is considered to be average and should not be regarded as unfavourable for human health because the amount of positive and negative ions in 1 $cm^3$ is almost balanced. It can inferred that a great part of air ions recombine taking part in the self-purification of air where the negative ions act a little bit more actively than the positive ones. Basing on the lichenoindication, the level of air pollution in this area is intermediate and does not reach the level of air pollution observed near the railway station or along the railways.
In the Northern part of the city there are two measure points 7 and 8 that should be mentioned. The point 7 is located near Rezekne Secondary school $N^{\#}5$ and it represents the residential area. It is significant that basing on lichenoindication, the level of air pollution in this area is low and there is the highest total concentration of air ions (see table 2), what is beneficial

effect for human health. The park that is situated in the South, as well as the relief protect this point from the influence of railway pollution, whereas the building defends it from the pollution created by motor transport. The measure point 8 is located in the industrial zone and it is more subjected to the motor car pollution from the junction C. This point is characterized by one of the lowest ion concentration levels and the lichenoindication data reveal that the level of air pollution in this area is high.

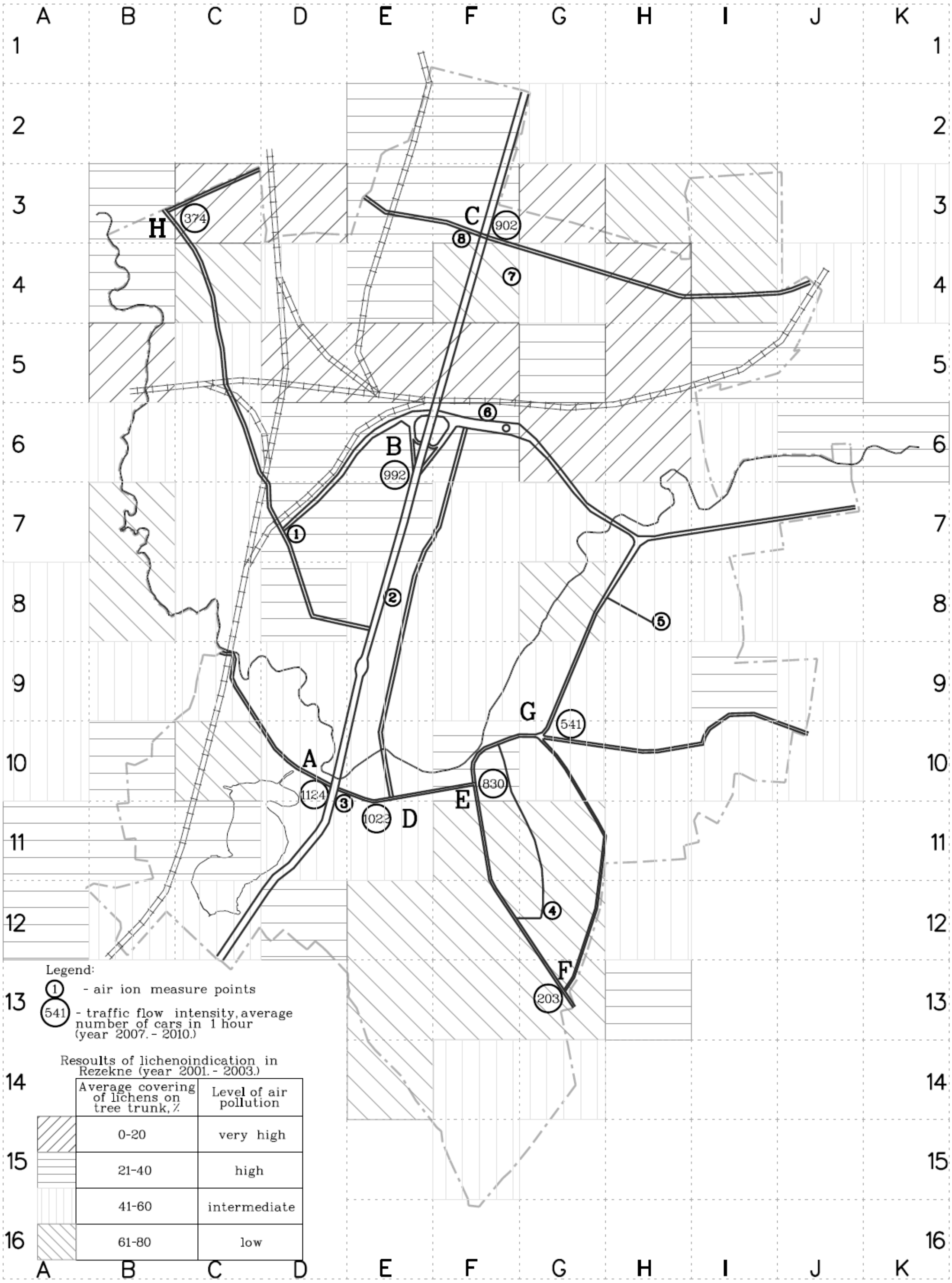


*Fig. 2.* **The map of complex air quality evaluation in Rezekne**

*Table 2.*

**Summary of air ion concentrations and unipolarity factor K (2009 – 2010)**

| **Measure points** | Negative | Pozitive | Total | K |
|---|---|---|---|---|
| 1. Meat proc.plant | 279 | 264 | 543 | 0,95 |
| 2. Pharmacy "LANA" | 259 | 210 | 469 | 0,81 |
| 3. Latgale Street | 227 | 216 | 443 | 0,95 |
| 4. Miera Street | 288 | 214 | 502 | 0,74 |
| 5. Tuberculosis hosp. | 269 | 195 | 464 | 0,72 |
| 6. Rezekne II | 219 | 238 | 457 | 1,09 |
| 7. Sec. School #5 | 333 | 274 | 607 | 0,82 |
| 8. REBIR | 259 | 212 | 471 | 0,82 |

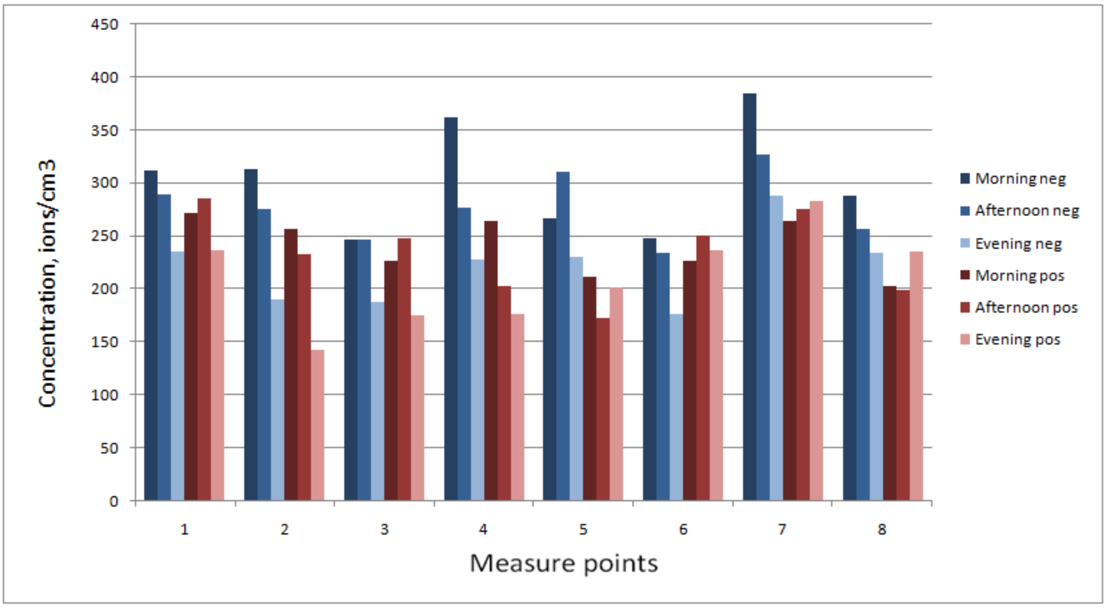


*Fig. 3.* **Average air ion concentrations in different daytime (2009 – 2010)**

**Conclusions**

1. Data obtained by lichenoindication, ion measuring and counting of transport units correspond with each other and all these elements can be used to obtain a common picture of air quality in the city and to interpret its changes.
2. The quality of city air is more influenced by railway than by motor transport. According to lichenoindication, the highest level of air pollution was observed along the railway, whereas the railway station Rezekne II is the only measure point were positive ions prevail over negative ones in long-term and where the total ionization level is one of the lowest in the city. Therefore the environs of railway and railway station can be considered to be unfavourable for human health.
3. The level of air pollution influences the total concentration of air ions and the unipolarity coefficient K. The highest is the level of pollution, the lowest is the total concentration of air ions and the highest is the value of K.
4. Air ions promote the processes of air natural purification.

## Acknowledgements

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## References


1. Vides zinātne. Red. M. Kļaviņš. Rīga: LU Akadēmiskais apgāds, 2008. 412 lpp.
2. Ietekmes uz vidi novērtējums. Rīga: Ietekmes uz vidi novērtējuma Valsts birojs, 2002. 100.lpp.
3. Vides rādītāji Latvijā 2009. gadā. Statistisko datu krājums. Rīga: LR Centrālā statistikas pārvalde, 2010. 21.lpp.
4. Kreuger A P, Reed E J. Biological impact of small air ions. Science, 193, 1209-13. 1976.
5. Danze, J.M. L'ionisation de l’oxygene. http://www.delvaux-danze.be/ioniation.htm , viewed 16.08.2009.
6. Air ion effects on human performance. http://www.static-sol.com/library/articles/air%20ion%20effects.htm, viewed 19.08.2009.
7. SanPiN 2.2.4.1294-03 Sanitary and Epidemiologial Norms. Ministry of Health of Russian Federation. (June 16, 2003)
8. Transportlīdzeku sadalījus pilsētās un novados. http://www.csdd.lv/?pageID=1296470925, viewed 01.03.2011.
9. Unpublished materials of Latvian Environment, Geology and Meteorology Centre , 2009. g.
10. *Gaisa piesārņojuma mērījumu rezultāti Rīgā 2003. – 2004., 2005., 2006. un 2007. gadā.* Rīga: Rīgas Domes Vides departamenta Gaisa aizsardzības nodaļa, 2008.
11. Jayaratne E.R., Ling X., Morawska L.(2010) Ions in motor vehicle exaust and their dispersion near busy roads. Atmospheric Environment 44, 3644-3650.

# II

# RENEWABLE ENERGY

# HYDROELECTRIC POWER PLANTS' RESERVOIRS AND THEIR IMPACT ON THE ENVIRONMENT

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**Abstract.** *The paper presents the analysis of different types of impact the hydroelectric power plants' reservoirs could make on the environment. Hydroelectric power plants (HPP) produce ecologically safe energy and correspond to the modern striving for sustainability because they are operated on renewable energy sources. At the same time they can provoke various potential dangers for the environment. The objective of the investigation is to demonstrate the interrelation between the type and structure of a hydroelectric power plant and the way its reservoir may impact on the nature surrounding the plant. These effects may be direct and indirect, positive and negative and vary from insignificant that can be easily fixed to those that are irreversible and catastrophic. The latter should be taken into account during the design of HPP.*

**Keywords:** *HPP reservoir, environmental impact, sustainability, renewable energy.*

## Introduction

Hydroelectric power plants (HPP) are operated on renewable energy sources. This energy appears in the atmosphere and on the surface of the planet as a result of interaction of specific substances and forces. It always exists in the nature and does not require any special expenses for being released. Consequently, HPP are a rather attractive type of power stations.

Depending on their capacity, HPP can be classified as large, medium, and small. In Russia, large HPP were most intensively built and put into operation in the second half of the last century. The reasons for this were a great need for the electrical energy and major advantages of HPP in comparison with other types of power stations. Among these advantages, there are low cost of energy production, high efficiency and maneuverability of units, significant automation in the basic equipment' operation, a small number of technical personnel, and others.

## HPP structure and its role in the environmental impact

HPP can perform their basic functions only as a part of an energy unit or a hydro complex, which includes supporting structures and a reservoir. Moreover, the component parts (HPP, supporting structures and a reservoir) are interrelated, functionally supplement one another and significantly influence the surrounding environment. For example, the height of the supporting structures determines the power of the HPP, as well as the area of the territory covered by the reservoir. The parameters of a reservoir impact on the amount of manufactured electric power, and its depth and temperature conditions impact on flora and fauna. The mode of a HPP operation and its capacity affects the constructive decisions on supporting structures and water spillway conduits, as well as the range of a water-level change in the reservoir and the banks processing.

With the examination of the problems, related to the impact of reservoirs on the environment, it is necessary to consider their special features. Figures 1 and 2 represent the general views of reservoirs.

*Fig. 1.* **The reservoir of a mountain hydro-power plant (China)**

It is obvious that reservoirs made on mountain rivers actually do not process banks; however, they do affect to a significant degree the temperature conditions of the river in comparison with the natural conditions, and they also influence an oxygen content in the water flow and a quantity of suspended deposits in it.

*Fig. 2.* **The reservoir of a lowland hydro-power plant (Poland)**

Large reservoirs of river-bed HPPs, on the other hand, substantially influence the wash-out of coasts, since they very frequently are located of the soft grounds.

*Fig. 3*. **Coast wash-outs on the Saratov HPP Reservoir (the Volga) near Samara (Russia)**

## Classification of environmental effects

The impact of reservoirs on the environment should be classified into direct and indirect. The direct impacts are caused by the fact of creation and the very existence of a reservoir. The indirect influences manifest themselves implicitly through certain factors of specific functions of a hydro-power plant. Both direct and indirect effects can be positive and negative.

### Direct impacts

One example of the reservoirs' direct positive impacts on the environment is the seasonal regulation of river flow: a considerable decrease of the freshet discharge due to the water accumulation in the reservoir provides territories protection from flooding in the freshet season, and a water release during the low-water period makes it possible to assuredly supply different users from down the river with water and also to ensure the required navigable depths in the river. Slowing down the flow of water in the reservoir (reduction in the rate of flow in the supported section of river) is the same type of influence. As a result, in winter time, the ice is more rapidly formed, and consequently, more favorable conditions are created for wild animals to walk on the ice.

A change in the load on the earth's crust due to the concentration of significant volumes of water on a limited earth's surface is an example of the direct negative influence of the reservoir. Similarly, flooding of territories, especially the ones suitable for agriculture or rich in minerals, processing of the reservoir banks and such are other examples of direct negative impacts.

### Indirect impacts

Indirect positive effects of a reservoir on the environment are: a more active manifestation of the water self-cleaning effect in the reservoir, guaranteed amounts of water from the reservoir for the public water supply and agricultural needs, the use of the reservoir for fish breeding and activities of fish farms, the organization of recreational zones, and so forth. Included in here is the possibility of using the reservoir as an emergency reserve for a rapid power supply for the public in case of emergency and failure of other electrical stations, power system, or electric power lines.

The indirect negative effects include the pollution of water by organic materials because of poorly executed preparation and deforestation of the bed of the reservoir; wash-out and processing of banks in the lower part of the HPP complex because of a frequent water-level change resulted from daily regulation of water. An additional indirect effect is that the water is polluted by petroleum products because of the leaks in the equipment components in the HPP and their penetration into the water stream, a change in water temperatures in the lower part of the HPP and others.
It should be noted that one and the same indirect effect of the reservoir on the environment can have simultaneously both positive and negative impacts. For instance, the use of the reservoir as an emergency reserve besides the positive side noted above has a negative one too – a sharp increase of the water level in the lower part of a HPP will aggravate the erosion of the bank slope.

## Conclusions

From what was mentioned above it can be concluded that such large technical structures, as reservoirs of hydroelectric power plants, can have rather diverse influences on the environment. The rate of their impact also varies: from insignificant and easily fixed to those that are irreversible and catastrophic.
When a HHP already operates, it is very important to exclude any possibility of the most dangerous - irreversible - negative environmental impacts of reservoirs and probability of occurrence of catastrophic impacts. At the same time, it is necessary to foresee possible minimal and reversible negative impacts already at the design stage of a future plant and provide protective measures to minimize future negative effects.

### References

1. Бальзанников М.И., Ахмедова Е.А., Шабанов В.А. Концепция развития береговой линии реки в пределах крупного города / Вестник Волжского регионального отделения Российской академии архитектуры и строительных наук. Вып. 7. – Н.Новгород: ННГАСУ, 2004.
2. Патент РФ 2237129, МПК Е 02 В 3/02, Способ защиты берегового откоса от разрушения / Ю.М. Галицкова, М.И. Бальзанников, В.А. Шабанов; Опубл. 2004, Бюл. № 27.

# MECHANICAL PROPERTIES OF COMPOSITE BIOMASS BRIQUETTES

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**Abstract:** *In the handling and usage processes, sufficient density and durability of biomass (straw, read) briquettes should be provided. For the briquettes density standards determined the value ρ > 1.0 g·cm$^{-3}$. In the densification process usually fine grinded particles are used, what significantly increases energy consumption for stalk material cutting. Calculated energy consumption for common reed cutting to sizes less than 3 mm was > 7 kJ kg$^{-1}$ but for size 20 mm it was approximately 1 kJ kg$^{-1}$. The goal of the investigation was to obtain the necessary density and durability of briquettes of larger biomass particles by arranging them. The orientation of straw or reed stalks had to promote binding by the pressing operation. The long stalk linking, in the picture of coloured stalk briquettes sections, is good visible. Crushing force dependence on particle size for arranged structure briquettes is stated in laboratory experiments. The specific splitting force of arranged structure coarse chopped wheat straw and reed briquettes reaches value 35 N mm$^{-1}$. It is approximately the same as industrially produced wood briquettes. Splitting force of the hemp stalk briquettes reaches 115 N·mm$^{-1}$.*

**Keywords** *stalk materials, biomass conditioning, biomass briquettes, durability*

## Introduction

There are several herbaceous energy species, currently considered in Europe – miscanthus, red canary grass and switch-grass. Also as a biofuels provided for combustion include agricultural waste, forest residue, bark, common reed and peat.

Biofuels and especially – herbaceous biomass, contain more alkali metals (mainly potassium and sodium) than coal and peat. Alkali metals lower the ash melting point and upon reaction with chlorine, also contained in biomass, have a strong corrosive effect on heat exchangers [1]. Strategies for minimizing deposition problems include co-firing biofuels with “cleaner” fuels. Suitable “clean” fuels include certain types of coal or peat, which contain large amounts of inert species such as silica or alumina in their ash. By blending peat with chips or herbaceous biomass also sulphur content of the fuel is increased, sulphates are formed instead of chlorides, and the risk of corrosion is avoided [2].

Using peat with woody or herbaceous biomass has also other advantages - peat addition increases density and durability and lowers energy consumption for stalk material densification (briquetting, pelleting) [3, 4]. Particle size and shape are also of great importance for briquetting. It is generally agreed that biomass material of 6-8 mm size with 10-20% powdery component (< 4 mesh) gives the best results [5]. Calculated energy consumption for common reed cutting to mention size was > 5 kJ kg$^{-1}$ but for size 20 mm it was approximately 1 kJ kg$^{-1}$ [3].

The goal of the investigation was to obtain the necessary density and durability of reed-peat and straw-peat briquettes of larger biomass particles by arranging them. The orientation of straw or reed stalks had to promote binding by the pressing operation.

The basic standards for the solid biofuels developed Technical Committee - CEN/TC 335 Solid Biofuels. Standard EN 14961: Solid Biofuels – Fuel Specification and Classes determine the briquettes density ρ = 0.8-1.2 g·cm$^{-3}$. The density of ρ > 1.0 g·cm$^{-3}$ is recommendable for high quality wood briquettes. This value had been used for evaluation of herbaceous material densification results.

To guarantee the quality of biomass briquettes in the handling and usage process, sufficient durability of briquettes have to be provided. In Latvia durability of solid biofuels briquettes is

regulated by standard: Solid Biofuels - Methods for the determination of mechanical durability of pellets and briquettes - Part 2: Briquettes LVS EN 15210-2:2010. Here the durability is the measure of the resistance of densified fuels towards shocks and/or abrasion as a consequence of handling and transportation processes. The test sample is subjected to controlled shock by collision of briquettes against each other and against the walls of a defined rotating test chamber. The durability is calculated from the mass of sample remaining after separation of abraded and fine broken particles. The size of the sample shall conform to the requirements of corresponding technical specifications and shall be at least 15 kg.
As the pressing operation with oriented stalks was carried out on laboratory equipment, productivity of it was low. Therefore durability of briquettes has to be characterized by different method where small amount of briquettes are sufficient.
In previous experiments shear strength of briquettes was examined. Shear strength tests were performed for determining ultimate shear tests for briquettes with particles size 0.5 - 3 mm. Ultimate shear stress was determinated in direction perpendicular of briquetting direction [4].
Shear tests is not suitable for briquettes with particle length 50 – 300 mm. For laboratory experimental testing of briquettes crushing strength should be examined [6, 7].
For experimental testing wheat straw, hemp stalks, reed and reed composition with peat briquettes were produced by biomass pressing in closed die.

## Materials and methods

Wheat straw, hemp stalks, reed and reed composition with peat biomass densification experiments had been carried out by means of hydraulic press equipment in closed die (Fig. 1). Pressure and piston displacement measurement data were collected on the PC using Picolog software. Chopped to different length stalks with moisture content 10% -14% was used for densification.

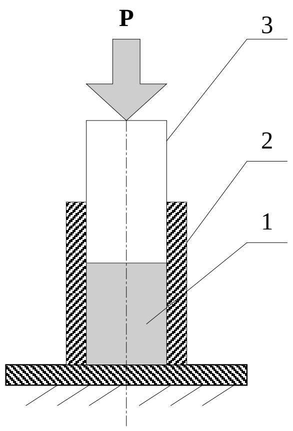
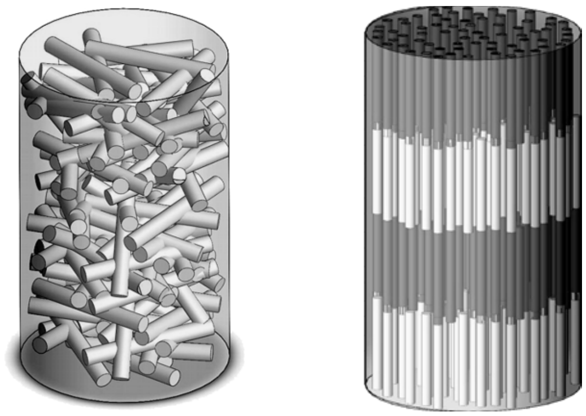



*Fig. 1.* **Scheme of densification**
1 – stalk material composition,
2 – closed die, 3 - piston



a b

*Fig. 2.* **Arrangement of stalk material in closed die before briquetting**
a – unarranged, b – arranged

Experimentally were tested briquettes of straw, reed and hemp stalks. Length of straw particles was 30, 60 and 100 mm, reed stalks - 30, 60, 150 and 300 mm and hemp stalks - 150 and 300 mm. Experiments was carried out with unarranged straw and reed stalks, arranged straw, reed and hemp stalks and with flattened and arranged reed stalks. Stalk flattening was performed with two rotating cylinders.
Stalk material particles with certain length was arranged in closed die as it is presented in Fig. 2b. Arranged particles were located in direction of longitudinal axe of die. Displacement between ends of particles in different layers was approximately from 5 to 15 mm. Particles

was slightly compacted in arranging process to obtain the same mass of material for every rerun. After arranging particles was compacted by hydraulic press with the maximum pressure 158 Mpa for 62 mm diameter and 212 Mpa for 36 mm diameter briquettes. Length, diameter of briquette and weight was measured. Density of briquettes was calculated on the basis of dimension measurement and weighing. For comparison 30 mm length straw and reed particles was placed in briquetting die without arranging (Fig. 2a) and pressed with maximum pressure 158 MPa.

Mechanical strength of the briquettes is characterized by the force necessary for its destruction [5, 7]. The briquette of circular cross section is exposed to the pressure force as shown in Fig. 3, i.e. its direction is perpendicular to its axis of symmetry. Briquette was placed on support plate of testing machine and compression force *F* was applied to briquette in the direction perpendicular of briquetting direction. This force is gradually increased until the briquette disintegration and splitting. The destruction force intensity was investigated for 11 samples of each composition. Obtained force – deformation diagrams (Fig. 4) were analyzed for all kinds of tested biomass and average crushing force was calculated.

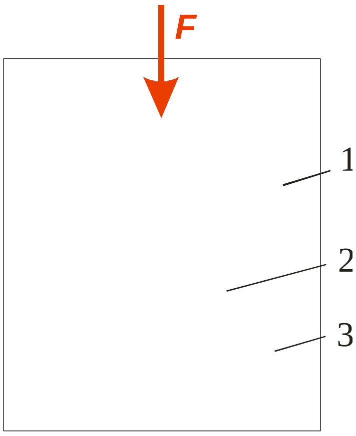



*Fig. 3.* **Scheme of compression**
1 – compression plate, 2 – briquette,
3 – support plate

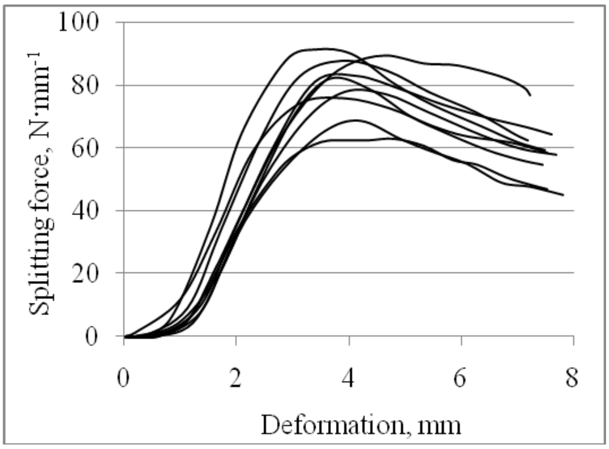



*Fig. 4.* **Force – elongation diagram for not flattened reed stalks, 300 mm length**

Diameter of briquettes produced in experimental pressing device was 36 and 62 mm. Length of briquettes varies according closed die filling capacity before pressing. It depends on biomass stalk diameter, flattening and density. Average length of briquettes (diameter 62 mm) was 60 mm and for diameter 36 mm length of briquettes varies from 34 to 85 mm.

To compare durability of different length briquettes, specific splitting force was calculated:

$$F_s = \frac{F}{L}, \qquad (1)$$

where $F_s$ – specific splitting force, $N \cdot m^{-1}$; $F$ – splitting force, *N*; $L$ – length of briquette, *mm*.

Compression tests were carried out on Zwick and GUNT testing equipment. Zwick materials testing machine TC-FR2.5TN.D09 have force resolution 0.4%, displacement resolution 0.1 µm and the maximal testing force 2.5 kN.

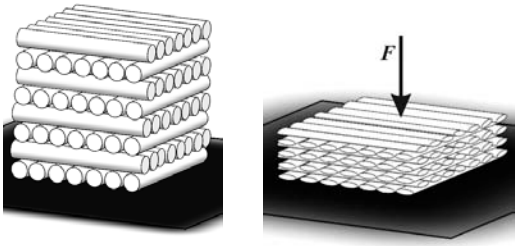
GUNT 20 materials testing machine have force resolution 1%, displacement resolution 10 µm and the maximal testing force 20 kN.

For comparison industrially produced wood briquettes and pure peat briquettes was tested in the same way.

## Results and discussion

In previous densification experiments of chopped straw, common reed stalk material particles and compositions with additives was stated that compacted with pressure 230 MPa compositions of straw particles from two fineness groups (2 – 3 mm and < 0.5 mm) have density > 1.0 g·cm$^{-3}$, if fineness proportion (amount of particles < 0.5) exceed 25% [4]. Density 1.0 g·cm$^{-3}$ has been obtained in densification of straw and reed stalk material particle compositions with peat, if peat proportion exceeds 20%. Density of briquettes made from coarse chopped material (particle size more than 3mm) were significantly less than 1.0 g·cm$^{-3}$. Fine communition of stalk material significantly increases energy of grinding. Increasing of particle length from 1 to 100 mm decreases specific cutting energy up to 40 times. Roughly shredded straw or reed material does not provide necessary density and durability of briquettes, if material is unarranged in the closed die before cold briquetting.

The scope of investigation was to find method how to increase density and durability of coarse chopped material briquettes. If particles are inserted in briquetting die without arranging they lay down perpendicularly of pressing direction. Pressing force compact particles, but sharp adhesion between them does not occur because of hard and glossy outside surface of the stalks. To confirm this hypothesis experimental test was carried out. Reed stalk particles were arranged in perpendicular layers (Fig. 5) and compressed between two flat surfaces. Length of particles was 50mm, pressing force 300kN. After sample of stalks was released adhesive force between them was not stated.




a b

*Fig. 5.* **Pressing process of perpendicularly arranged reed particles**
a – arrangement of particles before pressing,
b – pressing process

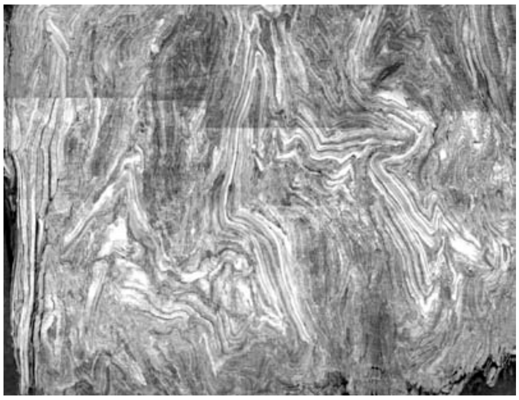


*Fig. 6.* **Cross-section of reed stalk briquette with colour particles**

To increase density and strength of briquettes necessary maximize bonding surface area between particles. Suitable arrangement of straw and reed particles in briquetting die allows changing deformation directions of particles. The stalk material curves and adhesion between particles increases (Fig. 6).

Arranged particles were located in direction of longitudinal axe of die according Fig. 2b. Displacement between ends of particles in different layers was approximately from 5 to 15mm. Particles were slightly compacted in arranging process to obtain the same mass of material for every rerun.

Results of investigation of briquettes density dependence on arranged particle size is presented in Fig. 7. Increasing particle length from 30 to 100 mm does not affect significantly density of briquettes if diameter of briquettes is 62mm. Density of arranged straw briquettes varies between 939 kg·m$^{-3}$ (100 mm) and 928 kg·m$^{-3}$ (30 mm). It is less then recommended 1.0 g·cm$^{-3}$ and dependence on the length is less than 1.3%.

Density of arranged reed briquettes varies between 927 kg·m$^{-3}$ (length of particles 30mm) and 947 kg·m$^{-3}$ (60mm). Density dependence on the particle length for reed briquettes does not exceed 3%. The density of flattened reed stalks briquettes is >1000 kg·m$^{-3}$. It shows that arranging and previously densification has good influence on briquettes density.

The addition of peat to wheat straw and reed particles increases density of briquettes. Fig. 8 presents the changes of briquettes density depending on peat content. The addition of 30% peat increases density of briquettes till ~1000 kg·m$^{-3}$. Significant reed+peat briquettes density depending on material length was not stated (Fig. 8).

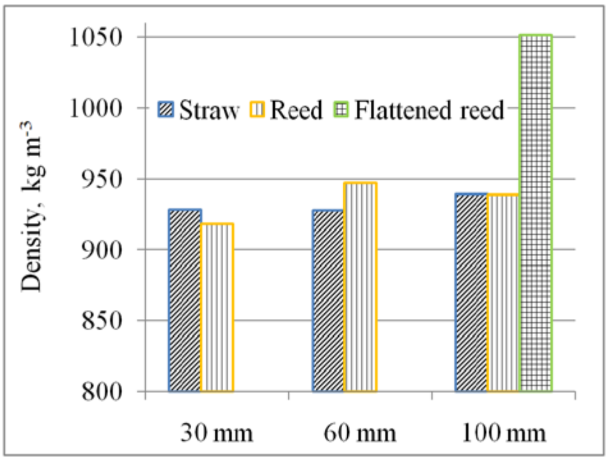



*Fig. 7.* **Briquette density dependence on the length of particles**

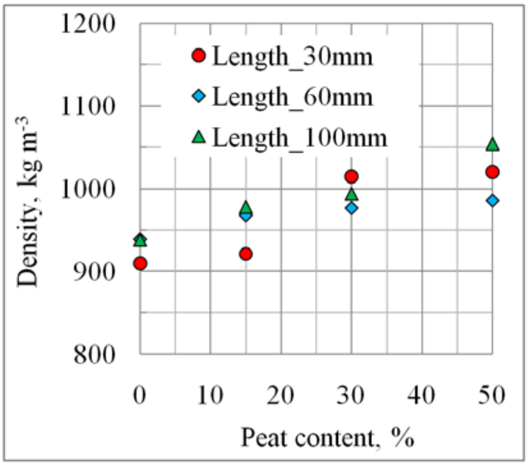
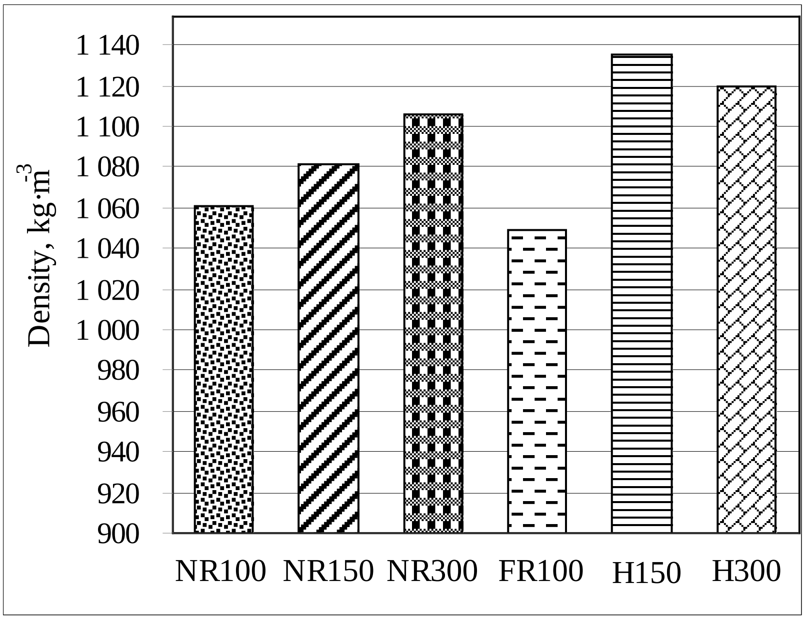



*Fig. 8.* **Briquette density dependence on the peat content**

Density investigation for briquettes with diameter 36 mm were carried out for different length of reed and hemp particles. Increasing no flattened reed particle length from 100 to 300 mm increases density of briquettes from 1060 to 1130 kg·m$^{-3}$ (Fig. 9). It is equal with density of reed - peat composition briquettes with peat content 50% (Fig. 8)




NR100 – not flattened reed, length 100 mm
NR150 - not flattened reed, length 150 mm
NR300 - not flattened reed, length 300 mm
FR100 - flattened reed, length 100 mm
H150 – hemp stalks, length 150 mm
H300 – hemp stalks, length 300 mm

*Fig. 9.* **Density of briquettes with diameter 36 mm**

Density of flattened reed briquettes is equal for both diameter briquettes. Density of hemp stalk briquettes significantly exceeds recommend 1000 kg·m$^{-3}$ and reaches 1135 kg·m$^{-3}$.
Durability test was carried out using ZWICK and GUNT material testing equipment. Diameter of closed dies for briquetting was 60 and 35 mm which let obtain briquettes with diameters accordingly 62 and 36 mm. As a result of tests briquette splitting force dependence on briquette deformation was stated (Fig. 4). Evaluation of average splitting force for all reruns stated dependence of disintegration force on the particle length.
Fig. 10 presents dependence of the splitting force on the particle length for wheat straw and reed made from arranged structure briquettes. Increasing of durability by increasing of particle length was stated for reed briquettes, but for straw briquettes change of splitting force was not significant. Comparing unarranged reed stalks (length 30 mm) briquettes showed low specific destruction resistance 6 N·mm$^{-1}$. Briquettes from flattened and arranged reed stalks showed good results. The splitting force of briquettes was 1.3 times higher than for not flattened stalk briquettes. Splitting force represented in Fig. 10 was stated for briquettes with diameter 62 mm.

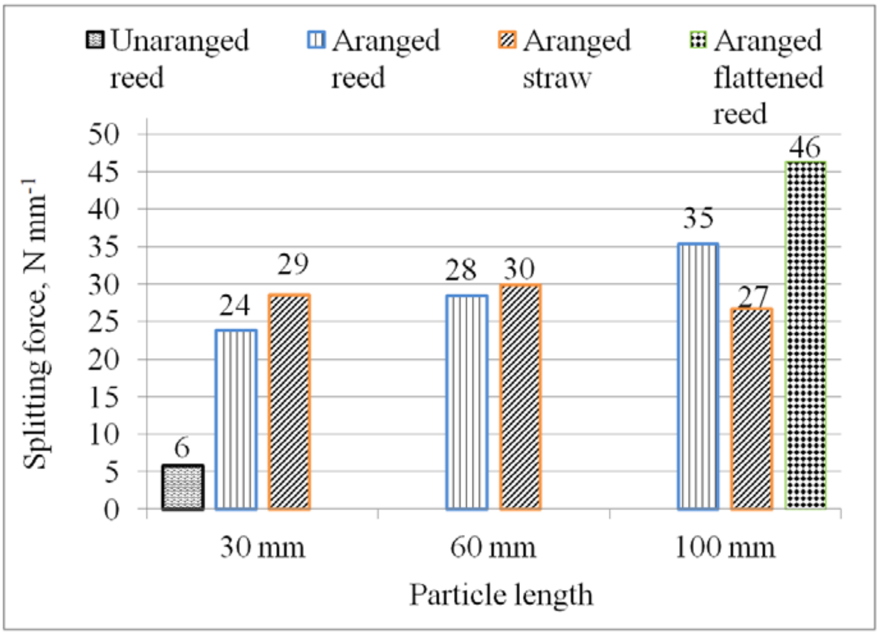



*Fig. 10.* **Dependence of specific splitting force on particle length for straw and reed briquettes with diameter 62 mm**

Peat additives let substantially increase splitting force of reed briquettes (Fig. 11). The addition of 15% peat increases durability of briquettes from 1.2 to 1.3 times for all lengths of particles. Increasing addition of peat till 30% and more, increases durability of briquettes, but splitting force dependence on particles length is not significant (Fig. 11).

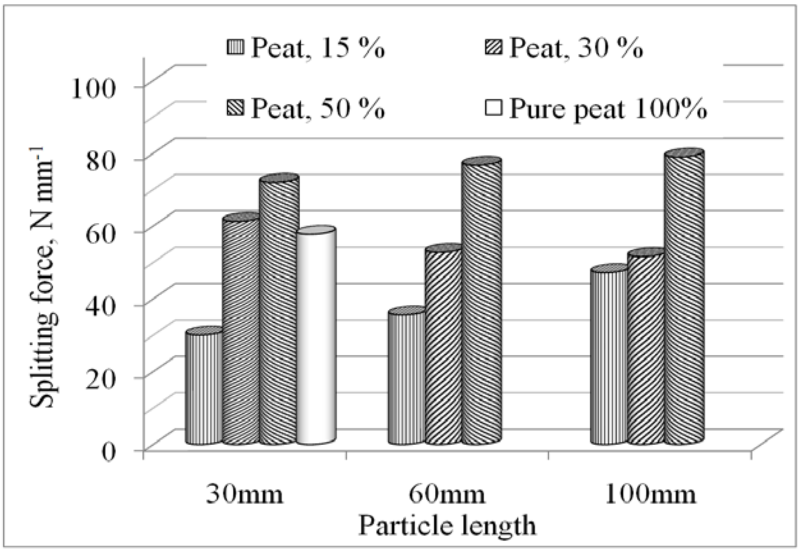
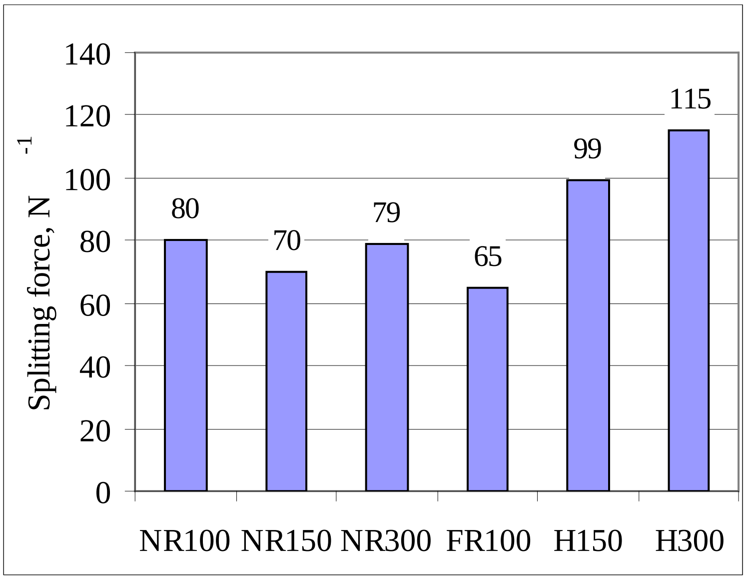



*Fig. 11.* **Specific splitting force dependence on peat additive for reed+peat compositions (diameter of briquettes 62 mm)**

For comparison industrially produced wood, unarranged reed and wheat straw and pure peat briquettes were tested using the same method. Specific splitting force for wood briquettes reaches 38 $N \cdot mm^{-1}$ and this value can be taken as a base for comparison of experimentally made briquettes. Pure peat briquettes showed splitting force 55 $N \cdot mm^{-1}$.

Unarranged reed particle (length 30 mm) briquettes show specific splitting force approximately 6 $Nmm^{-1}$. The same value of splitting force was obtained for wheat straw (30 mm) unarranged briquettes destroying.

Splitting force for briquettes with diameter 36 mm was stated for different particle length of reed and hemp stalks (Fig. 12).




NR100 – not flattened reed, length 100 mm
NR150 – not flattened reed, length 150 mm
NR300 – not flattened reed, length 300 mm
FR100 – flattened reed, length 100 mm
H150 – hemp stalks, length 150 mm
H300 – hemp stalks, length 300 mm

*Fig. 12.* **Specific splitting force for briquettes with diameter 36 mm**

Splitting force of no flattened reed particles varies from 70 to 80 $N \cdot m^{-1}$. The same value of splitting force was stated for reed – peat briquettes with diameter 62 mm, if peat content reaches 50% (Fig. 11). Splitting force stated for pure reed stalk briquettes with particle length

100 mm (diameter 62 mm) was only 35 $N\cdot m^{-1}$ (Fig. 10). Reed stalk flattening decreases splitting force compared together with no flattened reed stalks till 65 $N\cdot m^{-1}$ (Fig. 12).
Significant increasing of splitting force was stated for hemp stalk briquettes. Splitting force for hemp stalk particles with 300 mm length reaches 115 $N\cdot m^{-1}$.

## Conclusions

1. Addition of 30% peat to coarse chopped straw or reed arranged structure briquettes increases density to recommended value 1.0 $g\cdot cm^{-3}$. Decreasing of the diameter of the briquette let exceed recommended density for pure reed and hemp stalk briquettes. Density of the hemp stalk briquettes reaches 1135 $kg\cdot m^{-3}$ for particle length 300 mm.
2. Increasing peat proportion in arranged structure straw and reed briquettes till 50% increases splitting force 2 – 3 times.
3. Destroying force of arranged structure coarse chopped wheat straw and reed briquettes with diameter 62 mm reaches value 35 $N\cdot m^{-1}$. It is approximately the same as industrially produced wood briquettes.
4. Decreasing of the diameter of the briquettes from 62 to 36 mm increases splitting force of the pure reed stalk briquettes approximately 2 times.
5. Arranged structure of biomass particles in briquetting die is recommended for significant increasing durability of stalk material briquettes.
6. Flattening of the herbaceous biomass stalks before briquetting arranged briquettes increases density of the 62 mm diameter briquettes to more than 1.0 $g\cdot cm^{-3}$ and splitting force 1.3 times.

### References


1. Kavalov B., Peteves D. *Bioheat applications in the European Union*: An analysis and perspective for 2010. Luxembourg: Office for Official Publications of the European Communities, 2004. 122 p. ISBN 92-894-8730-5.
2. Alakangas E., Agar D., Leppänen M. *Report of the seminar presentations and study tour* [online]. Biomass Logistics and Combustion [viewed 2011-01-15]. Accessible: *http://www.opet-chp.net/download/wp3/summerschoolreport.pdf*
3. Kronbergs E., Kakitis A., Smits M., Nulle I. Biomass conditioning for solid biofuel compositions. In: *Proceedings of 2nd International Baltic Bioenergy Conference*. Germany, Fachhochschule Stralsund – University of Applied Sciences. Stralsund: LAiV, 2006, p. 81 – 90.
4. Kakitis A., Nulle I. Durability of stalk material briquettes. In: *Proceedings of the International conference "Scientific achievements for wellbeing and development of society"*, March 4-5, 2004,– Rēzekne, pp. 26 – 31.
5. Grover P.D., Michra S.K. *Biomass briquetting*: Technology and practices. Bangkok: FAO Regional Wood Energy Development Programme in Asia, 1996. 48 p.
6. Plištil D., Brožek M., Malaták J., Hutla P. (2005): Mechanical characteristics of standard fuel briquettes on biomass basic. Research in Agricultural Engineering, 51: 66–72.
7. Brožek M., 2001. Briketování nekovového odpadu. In: Sborník z mezinárodní konference XIV Diamatech.Krakow, Univerzita Radom: 84–87.



**Anotācija.** *Transportēšanas un lietošanas apstākļos biomasu (salmu, niedru, kaņepju stiebru) briketēm ir nepieciešams nodrošināt pietiekamu blīvumu un mehānisku izturību. Standartos rekomendētais brikešu blīvums ip>1.0* $g\cdot cm^{-3}$. *Gan granulu, gan brikešu ražošanā, stiebru smalcināšana ir viens no energoietilpīgākajiem procesiem. Tāpēc lietderīgi izvēlēties atbilstošo stiebru masas daļiņu smalcināšanas pakāpi atkarībā no izgatavošanas tehnoloģijas. Tā kā granulu diametrs ir robežās no aptuveni 4 mm līdz 25 mm, tad ir nepieciešama ļoti smalka smalcināšana un tas nozīmē, ka tiek patērēta liela enerģija produkta ražošanas sākuma stadijā. Iepriekš veiktajos eksperimentos tika konstatēts, ka niedru smalcināšanas enerģija, ja daļiņu lielums nepārsniedz 3 mm, ir > 7* $kJ\cdot kg^{-1}$, *bet 20 mm daļiņu lielumam enerģijas patēriņš bija aptuveni 1* $kJ\cdot kg^{-1}$. *Pētījuma mērķis ir sasniegt nepieciešamo blīvumu un mehānisko noturību ar sakārtotām, 30 līdz 300 mm garām, biomasas daļiņām. Sakārtoti salmu un niedru stiebri nodrošina to savstarpējo saķeri kompaktēšanas procesā. Garu stiebru saistīšanās labi redzama iekrāsotu stiebru daļiņu briketes šķērsgriezumā.*

*Pētījumi tika veikti ar sakārtotas struktūras, rupji smalcinātu kviešu salmu, niedru un kaņepju stiebru briketēm. Briketes tika izgatavotas presējot doto biomasu metāla cilindrā. Tika izgatavotas divu izmēru briketes, ar diametru 62 mm un 36 mm. Briketēšanas spiediens – attiecīgi 158 un 212 Mpa.*

*Laboratorijas eksperimentos veikti sakārtotas struktūras brikešu mehāniskās izturības pārbaude. Rupji smalcinātu kviešu salmu un niedru brikešu īpatnējais sagraušanas spēks sasniedza 35 $N \cdot mm^{-1}$, kas ir aptuveni tāds pats kā rūpnieciski ražotai kokskaidu briketei. Kaņepju stiebru brikešu īpatnējais sagraušanas spēks sasniedza 115 $N \cdot mm^{-1}$. Lai uzlabotu salmu un niedru brikešu sadegšanas īpašības un samazinātu korozijas risku kurtuvju elementiem, rekomendējama kūdras pievienošana brikešu sastāvam. Eksperimentāli tika noteikta kompozītu brikešu (niedres + kūdra) noturība. Šādu brikešu blīvums pārsniedza rekomendējamo 1.0 $g \cdot cm^{-3}$. Brikešu sagraušanas spēks, atkarībā no daļiņu izmēra, bija robežās no 70 līdz 78 $N \cdot m^{-1}$.*

# MECHANICAL PROPERTIES OF HEMP (*CANNABIS SATIVA*) BIOMASS

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**Abstract.** *In Latvia approximately of 14.6% of unfarmed agricultural land can be used for herbaceous energy crop growing. Herbaceous energy crops would be as the main basis for solid biofuel production in agricultural ecosystem in future. Herbaceous energy crops as hemp (Cannabis sativa) are grown in recent years and can be used for solid biofuel production. Experimentally stated hemp stalk material ultimate tensile strength the medium value is 85 ± 9 N mm*$^{-2}$*. The main conditioning operation before preparation of herbaceous biomass compositions for solid biofuel production is shredding. Therefore hemp stalks were used for cutting experiments. Cutting using different types of knives mechanisms had been investigated. Specific shear cutting energy for hemp samples were within 0.02 – 0.04 J mm*$^{-2}$*. Hemp stalk material density was determined using AutoCAD software for cross-section area calculation. Density values are 325 ± 18 kg m*$^{-3}$ *for hemp stalks. Specific cutting energy per mass unit was calculated on basis of experimentally estimated values of cutting energy and density.*

**Keywords:** *energy crops, hemp, mechanical properties.*

## Introduction

Latvia has target [1] in 2020 for renewable energy resources to be 40% in gross final consumption of energy. In 2005 EU biomass accounted for 66 % [2] of renewable primary energy production. Biomass has relatively low costs, less dependence on short-term weather changes and it is possible alternative source of income for farmers. Herbaceous energy crops would be as the main basis for biofuel production in agricultural ecosystem in future. There is not problem in Latvia that if bioenergy crops are encouraged, then less land will be available for growing food. In 2005 year investigation was stated that 14.6% of agricultural land [2] of Latvia was unfarmed. Therefore herbaceous energy crop growing on these lands can provide sustainable farming practice. Sources of renewable energy are also by-products of hemp (Cannabis sativa) straw of the process of fiber extraction and the whole plants of hemp cultivated for biomass. Hemp and waste hemp residues after processing can be used for production of solid biofuel pellets and briquettes.

The main conditioning operation before compacting of herbaceous biomass in shape of pellets and briquettes is shredding. It is size reduction of biomass stalks and residues by cutting operation. In Latvia hemp growing as biomass for solid fuel production is new activity. For this reason mechanical properties of different varieties of hemp have to be investigated in order to develop shredding equipment design methodology. Mainly shear strength of hemp samples were investigated in order to find methods for cutting (shredding) with minimal energy consumption. The main hypothesis for cutter design is that cutting method has to be used with minimum of energy consumption by reducing frictional forces to a minimum. Different cutting knives mechanisms have to be investigated for energy consumption evaluation. The objective of this study is to determine cutting properties of hemp stalk materials and energy efficiency of cutting knives mechanisms.

## Materials and methods

Herbaceous biomass as hemp is prospective stalk materials for solid biofuel production in Latvia. For production of solid biofuel mainly herbaceous plant stalks are used. Hemp (Cannabis sativa) in Latvia is cultivated only in recent years and it mechanical properties are not broadly investigated. Cross-sections of hemp stalks show the complicated structure (Figure 1) of this material. It can be noticed that hemp stalks have significant woody part – resource for solid biofuel production.

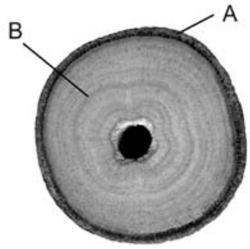


*Fig.1.* **Hemp stalk cross-section**
(A - fibrous layer, B - woody part)

As sample materials for investigation of cutting properties eight varieties of hemp were used in experiments. Average biomass yield in DM (in 2010) of hemp varieties are presented in Table 1.

*Table 1.*

**Hemp biomass in DM yields**

| Hemp variety | Yield, t $ha^{-1}$ |
|---|---|
| Bialobrzeskie | 14,0 |
| Felina 32 | 13,2 |
| Epsilon 68 | 15,8 |
| Benico | 12,7 |
| Uso - 31 | 14,4 |
| Futura 75 | 16,9 |
| Fedora 17 | 15,9 |
| Santhica 27 | 16,4 |

Hemps, with moisture content ~10%, were used for density calculation and experiments for investigation of mechanical properties.
Mostly hemp stalk material cross-section shape is irregular; therefore cross-section area can't be calculated by using geometry equations. For irregular cross-section area calculation AutoCAD software functions "Spline", "Region"and "Object properties" (Figure 2) had been used. The scanned hemp stalk sross-section images in real measurements for area calculation were used. Bouth border lines of cross section were marked with function "Spline". With function "Region" the area included in border lines is marmed. For bouth regions in "Object properties" areas in $mm^2$ are shown. The difference between outside border region area and inside border region area is a real hemp stalk cross-secrion area. By using function "Substract" is possible to cut out inner region from outer region. In that way in "Object properties" is shown real hemp stalk cross-section area.
Cross-section area was calculated from data obtained from direct measurement with sliding caliper (accuracy ± 0,01 mm). Hemp stalk cross-section area was used in material density and mechanical properties calculations. In density calculations for each stalk test piece were determined cross-section areas for both stalk ends. By multiplication of average area and length the volume of each test piece was found. Volume values were used for density calculation.

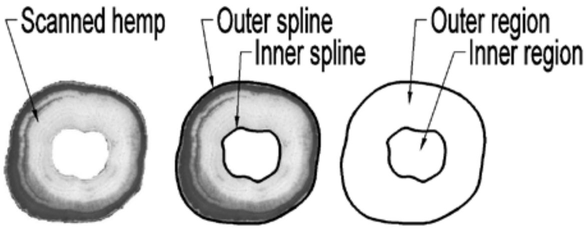


*Fig.2.* **Cross-section area calculation in AutoCAD software**

Ultimate shear strength and energy consumption for stalk cutting has been investigated using the Zwick materials testing machine TC-FR2.5TN.D09 with force resolution 0,4% and displacement resolution 0,1 µm and the maximal force for testing 2,5 kN. For shear cutting parameter determination original cutting device has been designed. For all experiments the displacement speed of cutting knives did not exceeds 50 mm $min^{-1}$. Cutting device was equipped with five different cutting knives mechanisms (Figure 3).

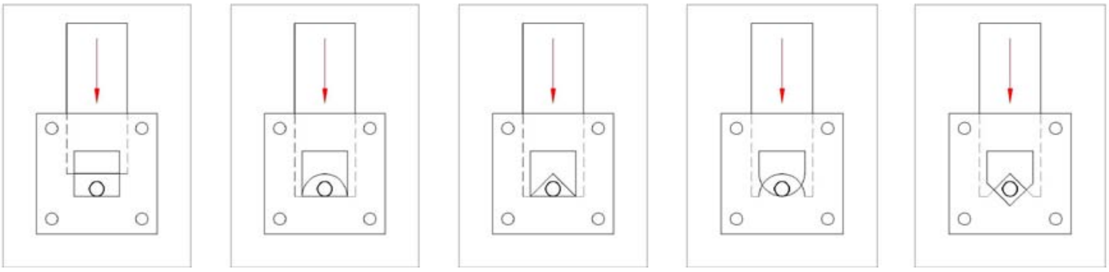


*Fig.3.* **Shear cutting knives mechanisms**

Ultimate shear strength was calculated:

$$\tau_C = \frac{F_C}{A} \qquad (1)$$

where: $\tau_C$ - ultimate shear strength, N $mm^{-2}$;

$F_C$ - maximal cutting force, N;

$A$ - cutting area, $mm^{-2}$.

Specific cutting energy was determined:

$$E_{SC} = \frac{E_C}{A} \qquad (2)$$

where: $E_{SC}$ - specific cutting energy, J $mm^{-2}$;

$E_C$ - cutting energy, J;

$A$ - cutting area, $mm^{-2}$.

Displacement and stress data were collected and processed by using Zwick software program TestXpert V9.01. The energy consumption was obtained by integrating force – displacement diagram. Specific cutting energy consumption was investigated for all varieties of hemp. For investigation of each knives mechanism were used 15 samples of every plant stalk material variety.

Results of cutting experiments were processed by Microsoft Excel program.

The cutting (chopping) energy $E$ for stalk material mass unit is calculated [3] using equation:

$$E = \frac{E_{SC}}{L_C \cdot \rho} \tag{3}$$

where: $E$ - cutting energy per mass unit, J kg$^{-1}$;
$L_C$ - length of stalk cut, mm;
$\rho$ - stalk material density, kg mm$^{-3}$.

Ultimate tensile strength for hemp stalk has been investigated using the GUNT 20 materials testing machine with force resolution 1% and displacement resolution 10 µm and the maximal force for testing is 20 kN. For average ultimate tensile strength determination original clamping part has been designed (Fig. 4).

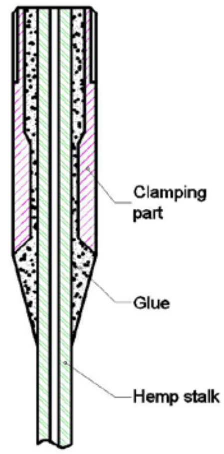

*Fig.4.* **Hemp stalk gripper mechanism**

Ultimate tensile strength was calculated:

$$\sigma = \frac{F_P}{A} \tag{4}$$

where: $\sigma$ - ultimate tensile strength, N mm$^{-2}$;
$F_P$ - maximal tensile force, N;
$A$ - stalk cross-section area, mm$^{-2}$.

## Results and discussion

Hemp stalk material ultimate shear cutting strength and specific cutting energy is shown in Table 2. Average specific cutting energy for hemp stalks is within 0.02 – 0.04 J mm$^{-2}$.Hemp stalk material ultimate shear cutting strength and specific cutting energy is shown in Table 2. Average specific cutting energy for hemp stalks is within 0.02 – 0.04 J mm$^{-2}$.

*Table 2.*

**Hemp and common reed stalk material mechanical properties**

| Sample | Cutting mechanism | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | № 1 | | № 2 | | № 3 | | № 4 | | № 5 | |
| | $\tau_{max}$, N mm$^{-2}$ | E, J mm$^{-2}$ | $\tau_{max}$, N mm$^{-2}$ | E, J mm$^{-2}$ | $\tau_{max}$, N mm$^{-2}$ | E, J mm$^{-2}$ | $\tau_{max}$, N mm$^{-2}$ | E, J mm$^{-2}$ | $\tau_{max}$, N mm$^{-2}$ | E, J mm$^{-2}$ |
| Bialobrzeskie | 14.9 | 0.021 | 15.3 | 0.023 | 11.8 | 0.030 | 14.1 | 0.024 | 15.5 | 0.037 |
| Felina 32 | 15.8 | 0.025 | 17.0 | 0.026 | 14.4 | 0.035 | 15.6 | 0.031 | 13.5 | 0.037 |
| Epsilon 68 | 13.8 | 0.020 | 15.9 | 0.022 | 13.8 | 0.028 | 14.6 | 0.023 | 14.4 | 0.029 |
| Benico | 18.9 | 0.031 | 19.4 | 0.029 | 18.8 | 0.045 | 18.9 | 0.032 | 19.0 | 0.043 |
| Uso - 31 | 16.6 | 0.030 | 17.1 | 0.032 | 13.4 | 0.039 | 17.8 | 0.039 | 13.3 | 0.047 |
| Futura 75 | 17.5 | 0.030 | 18.4 | 0.030 | 15.9 | 0.041 | 17.3 | 0.034 | 16.1 | 0.042 |
| Fedora 17 | 13.5 | 0.022 | 14.3 | 0.021 | 12.3 | 0.029 | 12.6 | 0.022 | 13.1 | 0.028 |
| Santhica 27 | 17.0 | 0.030 | 17.7 | 0.029 | 15.4 | 0.037 | 16.4 | 0.029 | 16.4 | 0.038 |
| Average for hemp | 16.0 | 0.026 | 16.9 | 0.026 | 14.5 | 0.036 | 15.9 | 0.029 | 15.2 | 0.038 |

The cutting knives mechanisms № 1 and № 2 are approved as the most energy efficient, where the average cutting energy consumption for hemp stalks is minimal (0.026 ± 0.003 J mm$^{-2}$). Cutting knives mechanism with round shape (№ 2) is recommended because the rounding in cutting knives are increasing nip angle. Increased nip angle improve the biomass shredder technical parameters by reducing rotation speed deviation and wear of cutting and counter knives.

The cutting mechanism № 3 is recommended then it is necessary to reduce cutting force values, because minimal average ultimate shear strength is 14.5 ± 1.9 N mm$^{-2}$. For all cutting knives mechanisms cutting parameters depend on material deformation process during cutting. The ultimate shear strength values are decreasing if bevel angle for knives is increased. But increased bevel angle causes significant material deformation, therefore specific cutting energy is increasing.

Specific cutting energy of hemp stalks with mechanism № 2 is shown in Figure 4. It can be noted that specific cutting energy is increasing if hemp sample cross-section is increased.

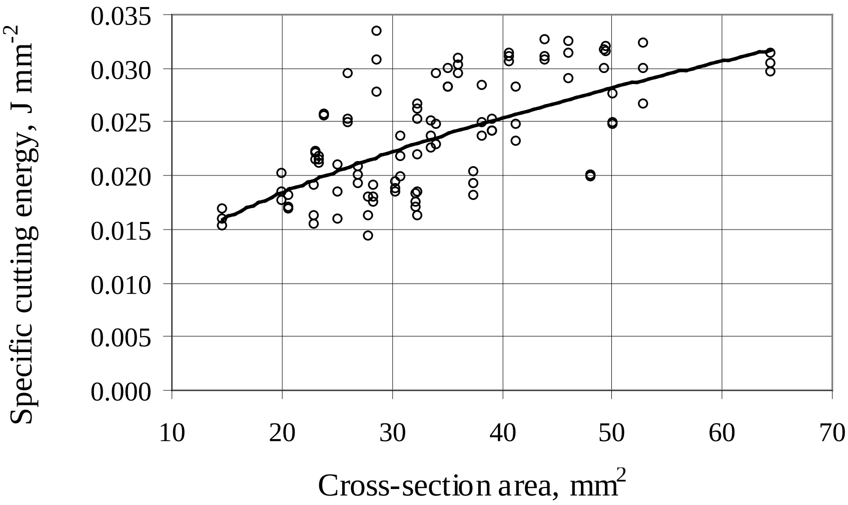


*Fig.4.* **Specific cutting energy of cutting mechanism № 2**

Ultimate tensile strength of different hemp varieties samples depending on cross-section area is shown in Figure 5. The average hemp stalk material ultimate tensile strength is calculated 85 ± 9 N mm$^{-2}$.

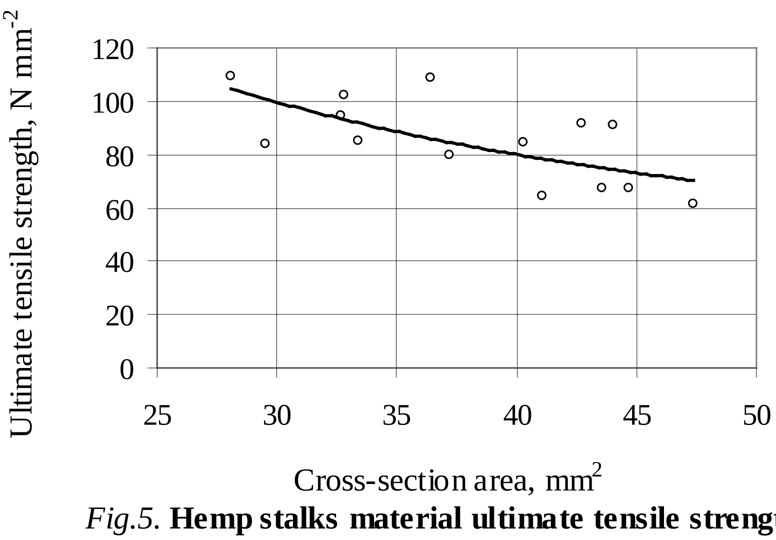


*Fig.5.* **Hemp stalks material ultimate tensile strength**

The trendline shows that hemp test piece area increasing causes decreasing of ultimate tensile strength. Figures 4 and Figure 5 shows that there is significant dependence between stalk mechanical properties and ratio of cross-section area and perimeter. For all hemp samples there are tendency of specific cutting energy growing and ultimate tensile strength decreasing, if cross-section area is increasing.
Investigated hemp stalk material density is shown in Table 3.

*Table 3.*

**Hemp biomass density**

| Hemp variety | Density, kg $m^{-3}$ |
|---|---|
| Bialobrzeskie | 300 |
| Felina 32 | 340 |
| Epsilon 68 | 310 |
| Benico | 340 |
| Uso - 31 | 320 |
| Futura 75 | 340 |
| Fedora 17 | 300 |
| Santhica 27 | 360 |

The average calculated hemp stalk material density is 325 ± 18 kg $m^{-3}$. These values are used in cutting knives mechanism cutting energy per mass unit calculation (Figure 6). It can be noticed that for hemp varieties Fedora 17 and Bialobrzeskie have the least values of density (300 kg $m^{-3}$) and also the least value of specific cutting energy (0.021 and 0.023 J $mm^{-2}$) with cutting knives mechanism № 2. It can be concluded that the minimum values of specific cutting energy are for hemp samples with least values of density.
On basis of calculated stalk material density specific cutting energy per mass unit (Figure 6) is determined. Specific cutting energy per mass unit is growing considerably when shredding size is less than 30 mm for hemp stalk material.

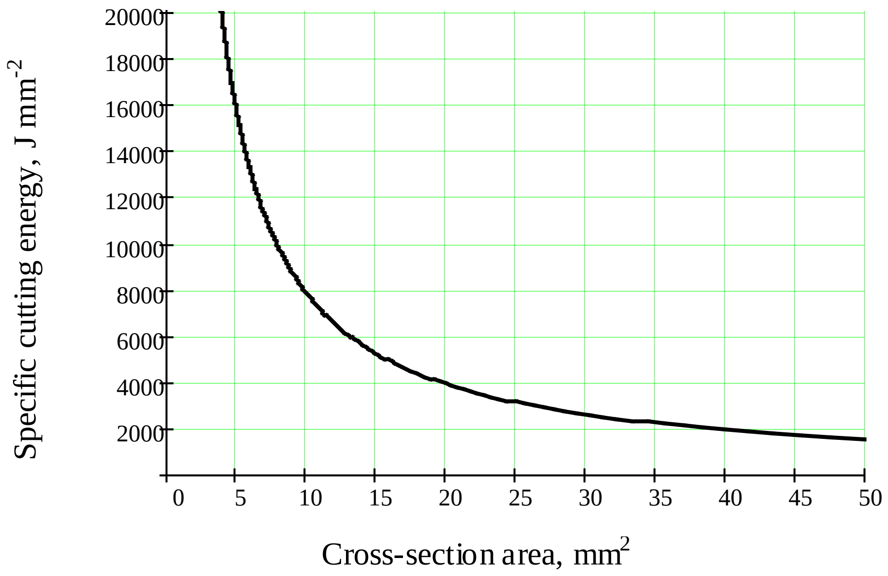


*Fig.6.* **Hemp stalk material cutting energy**

## Conclusion

Average specific shear cutting energy is within 0.02 – 0.04 J mm$^{-2}$ for hemp stalks.
The cutting knives mechanism № 2 is approved as the most energy efficient, where the average cutting energy consumption for hemp stalks is 0.026 ± 0.003 J mm$^{-2}$.
The cutting mechanism № 3 is recommended then it is necessary to reduce cutting force values, because minimal average ultimate shear strength is 14.5 ± 1.9 N mm$^{-2}$ for hemp samples.
The average hemp stalk material ultimate tensile strength is 85 ± 9 N mm$^{-2}$.
For all hemp samples there are tendency of specific cutting energy growing and ultimate tensile strength decreasing, if cross-section area is increasing.
The average calculated hemp stalk material density is 325 ± 18 kg m$^{-3}$.
Hemp varieties Fedora 17 and Bialobrzeskie have the least values of density (300 kg m$^{-3}$) and also the least value of specific cutting energy (0.021 and 0.023 J mm$^{-2}$) with cutting knives mechanism № 2.

## Acknowledgment

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### References

1. Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC (Text with EEA relevance).
   http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:32009L0028:EN:NOT,
   (Accessed on 30.03.2010).
2. Land politics statement for years 2008. – 2014. The Order of the Cabinet of Ministers of the Republic of Latvia Nr. 613 (in Latvian), http://www.mk.gov.lv, (Accessed on 30.03.2010).
3. Srivastava AK, Goering CE, Rohrbach RP. Engineering principles of agricultural machines. ASAE Textbook Number 6. Pamela De Vore-Hansen, Editor, Books&Journals. 1993. p. 601.

**Anotācija.** *Latvijā aptuveni 14.6% no lauksaimniecībā neizmantojamās platības var tikt izmantota enerģētisko stiebraugu audzēšanai. Enerģētisko stiebraugu audzēšana lauksaimniecībā nākotnē varētu būt kā galvenais cietā kurināmā ražošanai nepieciešamais izejvielu avots. Sējas kaņepju (Cannabis sativa) audzēšana Latvijā notiek tikai pēdējos gados un varētu tikt izmantota kā izejviela cietā kurināmā ražošanai. Eksperimentāli noteiktā kaņepju stiebru robežizturība stiepē ir 85 ± 9 N mm$^{-2}$. Kā galvenā apstrāde pirms cietā kurināmā ražošanas ir smalcināšana, tādēļ kaņepju stiebri tika izmantoti griešanas pētījumos. Griešanas pētījumos tika izpētīti pieci dažādi griešanas mehānismi. Īpatnējā griešanas enerģija kaņepju stiebraugiem bija robežās no 0.02 – 0.04 J mm$^{-2}$. Kaņepju stiebraugu materiāla blīvums tika noteikts, izmantojot datorprogrammā AutoCAD aprēķinātos stiebra šķērsgriezuma laukumus. Kaņepju stiebru materiāla blīvums ir 325 ± 18 kg m$^{-3}$. Stiebru materiāla griešanas enerģija uz masas vienību ir aprēķināta, izmantojot eksperimentāli iegūtās materiāla blīvuma un īpatnējās griešanas enerģijas vērtības.*

# THE CHEMICAL CONTENT OF DIFFERENT ENERGY CROPS

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**Abstract.** *The paper presents the data of gaseous and alkali elements in above-ground biomass of energy crops. The investigations objects were Phalaris arundinacea L., Populus nigra, Artemisia vulgaris, Sylphium perfoliatum, Sida hermaphrodita, Dactylis glomerata, Salix viminalis, Medicago sativia L. The aim of the research: to evaluate the amount of chemical elements in energy crops. Evaluating the energy crops it can be seen, that the most alkaline metals are contained in Sida hermaphrodita, and the least in Sylphium perfoliatum L.*

**Keywords:** *chemicals elements, energy crops.*

## Introduction

In the last few years greater attention has been given world-wide to the importance of biomass for obtaining energy due to the increased demand. Biomass- a biological extracted constituent from the sectors of agriculture and forestry; also from related products, refuse and remains (amongst them- substances originating from plants and animals), as well as from waste from manufacturing and households. It consists of organic substances, which are formed as a result of photosynthesis at present, in contrast to the fossil fuels, which were formed millions of years ago [1]. At present the meadows and pastures of Europe, which up to now guaranteed food stocks for animals, fulfil new functions as environmental stabilizers and as an additional option for renewable energy resources, also forming new directions for research in the cultivation of plants [2].

Energy crops are used widely in various sectors of the economy. They also have a positive effect on the environment, they reduce soil erosion and contamination with chemical substances, they can be grown in soil which cannot be used for food crops [2, 3, 4, 5]. Energy crops have different demand for quality than food and agricultural plants. The alkali metals contented in plants are important factor, as increased amounts facilitate corrosion in heating systems.

The aim of the research: to evaluate the amount of chemical elements in energy crops.

## Materials and methods

Energy crops were tested in the following locations and under the conditions described in Table 1.

The lucerne samples were taken according to the standard requirements GOCT [6]. The chemical analysis of lucerne was carried out at the Mykolayiv State Agrarian University laboratory "Облгосплодородие" according to generally accepted animal husbandry methods.

Carbon (C), Oxygen (O), Nitrogen (N), Hydrogen (H), and Sulphur (S) were established at Klaipeda University with the element analyser *Vario Macro CHNS-0*. Potassium (K), calcium (Ca), sodium (Na) and silicon (Si) concentrations (two replications) in energy crop samples were established with the inductively coupled plasma optical emission spectrometer *Perkin Elmer Optima 2100 DV* in the Rēzekne Higher Education Institution Chemical laboratory.

*Table 1.*

**Trials' methods in 2010**

| **Country** | | **Latvia** | **Lithuania** | **Ukraine** |
|---|---|---|---|---|
| Soil type | | Humi-podzolic gley soil | *Eutri-Endohypostagnic Albeluvisol*, *ABj-n-w-eu*; texture – moraine loam (clay 12-14%) | Southern black earth with little humus.Remainder-slightly alkaline, with a heavy loamy soil |
| Soil composition | $pH_{KCl}$ | 5.8 | pH 4.25-4.8 | 6.4-6.7 |
| | OM, % | 5.2% | - | 2.8-3.0 % |
| | $P_2O_5$ | 20 mg $kg^{-1}$ | 35 – 120 (A-L method) | 85 mg $kg^{-1}$ |
| | $K_2O$ | 90 mg $kg^{-1}$ | 144 – 225 (A-L method) | 180 mg $kg^{-1}$ |
| Pre-crops | | Bare fallow | fallow | Bare fallow |
| N:P:K fertilizers | | N:P:K 5:10:25, 400 kg $ha^{-1}$ | 60:60 (P:K) kg $ha^{-1}$ | P 120 kg $ha^{-1}$ |
| Sowing time | | 12$^{th}$ August in 2008; 29$^{th}$ April in 2009 | 14$^{th}$ July in 2009 | 27$^{th}$ March in 2008 |
| Seeding rate | kg $ha^{-1}$ | 70 | 15 kg $ha^{-1}$ v.s (viable seeds) | 2-3 kg $ha^{-1}$ |
| Sort or/and varieties | | *Phalaris arundinacea* L. - 'Marathon' | *Phalaris arundinacea* L. - 'Chieftain'; *Dactylis glomerata* L. - 'Amba' | *Medicago sativa L* 'Sinskia' (Синская) |
| N fertilizer rate | kg $ha^{-1}$ | N0, N30, N60, N90 | N0, N60, N120 | N15 |
| N fertilizer time | | 21$^{st}$ April 2010 | 14$^{th}$ April (N60 (for 2$^{nd}$ and 3$^{rd}$ treatments)) and 21$^{th}$ July (N60 (for 3$^{rd}$ treatment)) | 1-3$^{th}$ July |
| Harvesting time | | 6$^{th}$ October | 1$^{st}$ cutting 28$^{th}$ June (*Dactylis glomerata*) and 7$^{th}$ July (*Phalaris arundinacea*); 2$^{nd}$ cutting – 30$^{th}$ September (both species) | 27$^{th}$ July- 8$^{th}$ August Or 8$^{th}$ - 24$^{th}$ August Or 20-30$^{th}$ September |
| Trial plots | | 16 $m^2$ | 14 $m^2$ (for grasses) | 30 $m^2$ |
| Replication | | 3 | 3 | 4 |

**Meteorological conditions in Viļāni.** The air temperature from April to August in the plant growth period was greater than the long-term average, except for September. During April, July and August the precipitation was less than 50% of the long term average indicators. In

June the rainfall amount was 75.7mm. While the long-term average indicator was 75mm.During May and September the rainfall amount was near the norm.

**Meteorological conditions in Vėžaičiai.** There was much precipitation in May (indistinctive for spring period) and the rainy period continued until the middle of June. Periodically hot with heavy rainfalls weather continued until the second half of August. For the mentioned period, the average temperature and amount of precipitation were higher than annual. September was a rainy month (excepting the 2$^{nd}$ decade) and the average temperature, slightly lower than the long-term average. During the April-September period, the amount of precipitation was 620.2 mm (annual average 427.1 mm), the sum of average temperatures - 2246ºC.

**Meteorological conditions in Mykolayiv.** The lengthy cool spring hindered the surface biomass development during May. The average air temperature from March to August was 16.8 C, the amount of precipitation 267.7 mm.

## Results and discussion

The data of our investigation showed the following chemical content in reed canary grass: nitrogen (N) 3.282% - 4.307%, sulphur (S) -0.224% to 0.259%, hydrogen (H) - 6.009% to 6.761%, carbon (C) - 41.31% to 45.93%, oxygen (O) - 40.85% to 47.463% in reed canarygrass in Latvia (Fig.1). Three elements - C, H and S - are inflammable. As Oxygen (O) and Nitrogen (N) are the internal ballast of the fuel, as these elements do not burn, and do not produce heat and reduce the flammable element percentage content. Oxygen is important as a promoter of combustion. Fuels which have a greater oxygen content fire-wood and peat, catch fire and continue to burn easily. The amount of nitrogen in solid fuels (fire-wood and peat) is small 0.5 - 2.5 % [7]. N supplementary fertilisers significantly influenced ($p<0.05$) the N, C and O content. Only the sowing period ($p<0.05$) influenced the nitrogen, carbon and oxygen content in plants.

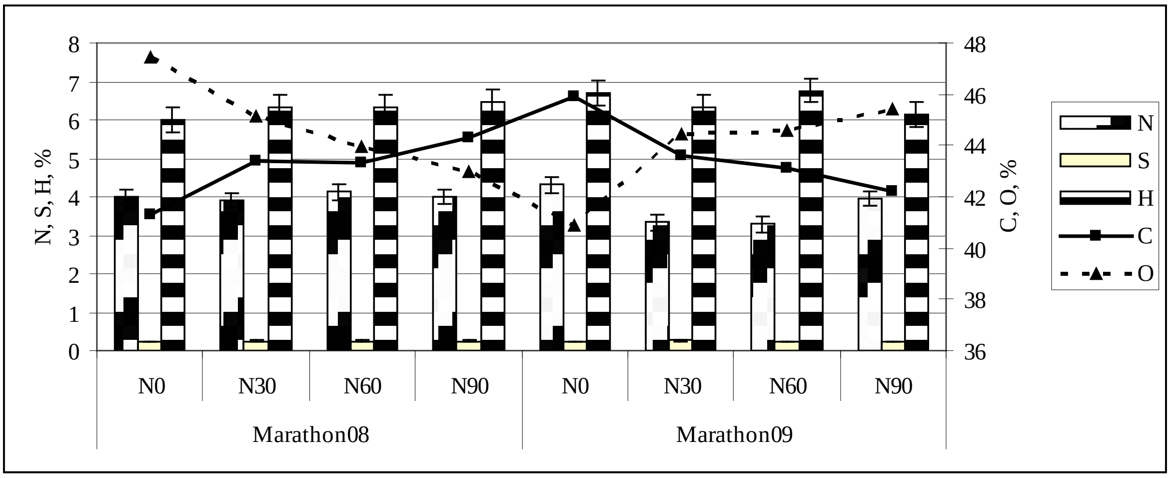


*Fig.1.* **The Carbon (C), Oxygen (O), Nitrogen (N), Hydrogen (H), and Sulphur (S) contents for the reed canary grass variety 'Marathon' second year crop in Latvia 2010, %**

The sulphur content in coal is from 1% to 4%. In petroleum sulphur content is from 0.3% to 3% [1]. In our research the sulphur content for reed canary grass variety 'Marathon' is smaller than the amount found in oil, which confirms, that the biomass plants do not endanger the surrounding environment.

The ash content in lucerne ranged from 7.9 to 13.9%, but in woodpulp from 12 to 28%, dependant on the plant segment (Fig.2). The chemical element content in lucerne is dependant on the plant segment ($p<0.05$).

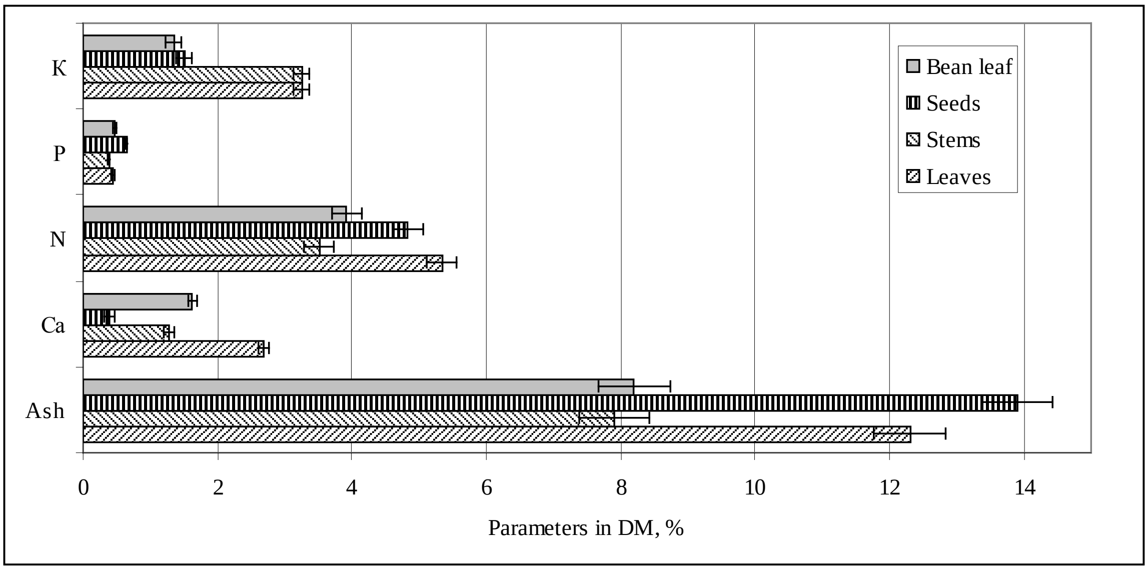


*Fig.2.* **The ash and chemical elements in *Medicago sativa* L. dry matter, %**

The crop yield in the southern Ukraine was 4.7 - 5.0 t $ha^{-1}$ and yield and chemicals elements was dependant on the amount of precipitation in the plant growth period [8].
Comparing five energy crops, it is obvious, that the most alkali metals are contained in *Sida hermaphrodita*; meanwhile in *Sylphium perfoliatum* – the least. (Fig.3). N fertilizer rates were significantly ($p<0.05$) the chemicals elements in energy crops.

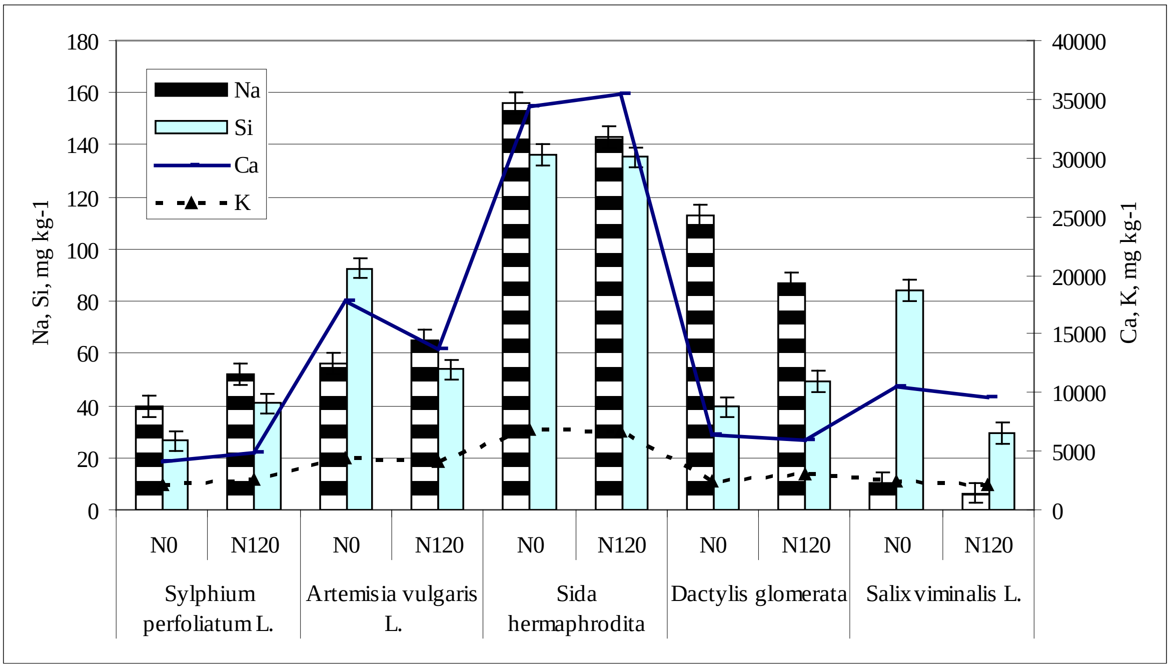


*Fig.3.* **The chemical content of different energy crop plants in Lithuania**

Calcium (Ca), sodium (Na) and silicon showed that it in Latvia higher than Lithuania in reed canary grass (Fig.4). That shows not only the influence of climatic conditions, but also influence of the soil pH content, and the plant variety.

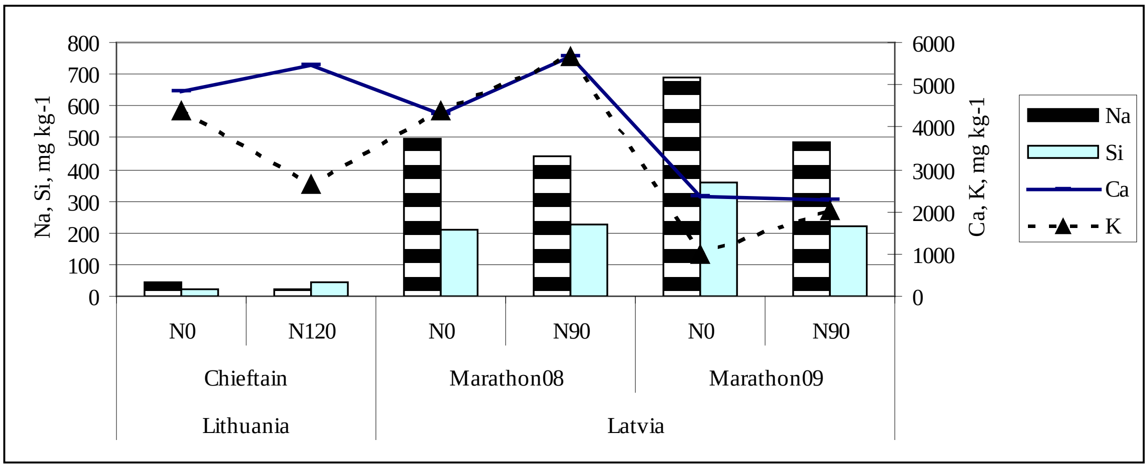


*Fig. 4*. **The chemical content of reed canarygrass depends on the agro-climatic conditions and the N fertilizer rate**

Comparing the reed canary grass grown in Latvia according to the chemical content, it can be seen that it contains more alkali metals than other energy crop plants, which is not desirable when used for biofuel production (Fig. 3, Fig.4). Straw, cereals, grass and grain can contain comparatively large amount of Cl, S and alkali metals, which have a significant relationship for corrosions and sediment formation [9]. Silicon connections strengthen the plant stems, therefore averting plant collapse [10]. An increased dose of fertilizer, rainwater and other contaminants from groundwater pollution caused by nitrates significantly degrades the soil properties, reducing its fertility [11, 12].

## Conclusions

The reed canary grass grown in Latvia contains a larger amount of alkali metals, than the energy crop plants grown in Lithuania, therefore the conditions of sowing must be carefully assessed. The ash content in lucerne is from 7.9% - 13.9%, but in woodpulp from 12% - 28% dependant on the plant segment. The chemical content of lucerne is dependant on the plant segment ($p<0.05$). In the Ukraine for the growing lucerne the N content was 3.5% - 5.34%. The N content in Latvia for the growing reed canary grass ranges from 3.282% to 4.307%, which is greater than what was found in other research; but the S is in a range of 0.224% to 0.259%, which is less than in fossil fuel. The sowing period t ($p<0.05$) influenced the nitrogen, carbon and oxygen content in the plants. Evaluating the energy crop plants grown in Lithuania, it can be seen, that the most alkaline metals are in *Sida hermaphrodita*, but the least in *Sylphium perfoliatum* L.

## Acknowledgment

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## References


1. Vides zinātne. Kļaviņš, M., Nikodemus, O., Segliņš, V. u.c. Rīga: Latvijas Universitāte, 2008, 599 lpp. (in Latvian).
2. Кулаковская, Т., Кургак, В., Адамович, А. Основные направления исследований и экологические аспекты развития лугопастбищного хозяйства в Европе. Корми і кормовиробництво. Міжвідомчий тематичний науковий збірник. Випуск 67, Вінниця, 2010,135-142 с. (in Russian).
3. Enerģētisko augu audzēšana un izmantošana. Adamovičs A., Agapovs J., Aršanica A. u. c. Rīga: Valsts SIA „Vides projekti", 2007, 190 lpp. (in Latvian).
4. Sanderson, M.A., Adler, P.R. Perennial Forages as Second Generation Bioenergy Crops. International Journal of Molecular Sciences. Vol. 9. No. 5, 2008, p. 768-788.
5. Wrobel, C., Coulman, B. E., Smith, D. L. The potential use of reedcanarygrass (*Phalaris arundinacea* L.) as a biofuel crop. Acta Agriculturae Scandinavica, Vol. 59, 2009, p. 1-18.
6. ГОСТ 13.586.3-83. Правила приемки и методы отбора проб. Срок действия с 01.07.84. (in Russian).
7. Cars, A. Energoresursi. Rīga: SIA Baltic Communication Partners. 2008, 102 lpp. (in Latvian).
8. Антипова, Л. К. Виробництво насіння люцерни в Степу України : моногр. / Л. К. Антипова. – Миколаїв: МДАУ, 2009, 227 с. (in Ukrainian).
9. Biedermann, F., Obernberger, I. Ash-related problems during biomass combustion and possibilities for a sustainable ash utilisation. 2005, [tiešsaiste] [skatīts 2010. g. 21. janv.]. Pieejams: www.bios-bioenergy.at/uploads/media/Paper-Biedermann-AshRelated-2005-10-11.pgf.
10. Zelčāns, G., Lukevics, E. Silīcijs dzīvajā dabā. Rīga: Zinātne, 1976, 75 lpp. (in Latvian).
11. Bramley, R. G. V. Cadmium in New Zealand agriculture. New Zealand Journal of Agricultural Research. Vol. 33, No. 4, 1990, p. 505-519.
12. Минеев В. Г. Агрохимия и биосфера. 1984. 245 с. (in Russian).


## Kopsavilkums


*Pētījuma mērķis: novērtēt ķīmisko sastāvu dažādiem enerģētiskajiem augiem. Pētījuma objekti: Phalaris arundinacea L., Populus fascigiata, Artemisia vulgaris, Sylphium perfoliatum, Sida hermaphrodita, Dactylis glomerata, Salix viminalis, Medicago sativa L. Mūsu pētījumā iegūtais N saturs miežabrālim svārstās robežās no 3.282% līdz 4.307%, S – 0.224% - 0.259%, H – 6.009 – 6.761%, C – 41.31% – 45.93%, O – 40.85% - 47.463%. Sēra daudzums miežabrāļa šķirnei 'Marathon' ir mazāks par naftā esošo sēra daudzumu. Pelnu saturs lucernā ir no 7.9 – 13.9%, bet kokšķiedras - 12 - 28% atkarībā no auga daļas. Ķīmisko elementu daudzums lucernā ir atkarīgs no auga daļas (p<0.05). Visvairāk sārmu metālu satur Sida hermaphrodita, bet vismazāk Sylphium perfoliatum L. Sārmu metālu daudzums augos ir svarīgs faktors, jo to klātbūtne veicina korozijas veidošanos apkures sistēmās.*

# RESEARCH ON DECREASE OF OUTSIDE AIR HEAT PUMP PASSIVE EVAPORATORS ICE-COVER

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**Abstract.** *Two years (2009-2010) experience of the experimental use of alternative energy sources in technological processes of agriculture is analyzed. Water was heated by an outside air heat pump with passive evaporators, and used for new born piglets resting place floor heating. Experimental data were obtained by the reckoning consumption of electric energy for the operation of the heat pump's compressor and electric heater, and by a heat meter registering the consumed heat energy.*
*The obtained data show that the outside air heat pump with passive evaporators is working successfully during summer months, when the coefficient of performance (COP) of the heat pump exceeds 3.5. When the outside temperature decreases under +10°C, the heat pump evaporators become covered with hoarfrost and ice. The value of the COP and produced amount of heat energy reduce, and the electric heater often switches on. During the experimental research one of the heat pump evaporators was supplied with a ventilator, air flow from which was washing the surface of the evaporator's plates. So the satisfactory operation of the heat pump was provided till December 10, 2009 and November 25, 2010.*

**Keywords:** *coefficient of performance, heat pump, ice coverage.*

## Introduction

In order to widen the use of renewable energy sources in Latvia, detailed investigation, advance and support on technological investigation issues is needed. Particularly it concerns the use of heat pumps in the climatic conditions of Latvia. It is important to find out its place in the energy supply system for today and future [1]. Producers and disseminators of heat pumps are organizing impressive reclamation campaigns with recommendations on the use of heat pumps for living house heating, particularly when heated floors are introduced. The heat energy can be taken from the ground, water or air. An attention deserves the latest projects, realised in Latvia, about the use of heat pumps, where the heat is taken from the sea (Salacgriva) and the lake (Katvari).

The efficiency of an outside air heat pump essentially depends on the air temperature. The heat transformation ability is determined by coherence [2]:

$$COP = \frac{T_H}{T_H - T_L}, \tag{1}$$

where $COP$ – coefficient of performance of the heat pump;
$T_H$ – highest (necessary for consumer) temperature, °C;
$T_L$ – lowest (heat source) temperature, °C.

The heat pump's coefficient of performance (COP) is smaller at lower value of the outside air temperature. It is exactly when the need for heat is the highest. Therefore in case when the heat pump is not able to produce the necessary amount of heat energy, additional heat producing advices are envisaged.

Conditions, different from living houses are in warmed domestic animal cattle-sheds, where intensive ventilation system is working. There polluted inside air is delivered out from the premises and the fresh and clean air is brought in. With the polluted air considerable amount of heat is lost. At the same time in order to maintain the necessary temperature inside the sucking and weaned piglet premises, all the year round electric heaters or heating boilers are used. The fossil energy consumption rises and the environment becomes spoiled.

By setting up pigsties with heat pumps of an appropriate power, during the period of hot weather it is possible to provide for heating piglets resting place floor without using additional heaters. Working out the solution of recovering the heat from brought out by ventilation system polluted but warm air, it could be possible to provide for heat pump operation at lower outside temperature, that is, during the heating period also. As a result the consumption of fossil energy would be diminished.
The objective of the research is to ascertain the suitability of the use of outside air heat pump for piglets resting place floor heating, putting particular attention to the possibility of providing for high heat transmission coefficient (COP) of the heat pump during could and frosty weather conditions.

## Materials and methods

For the experimental investigation an outside air heat pump with passive evaporators has been used. The compressor of the heat pump is driven by the electric motor of 5 kW power. The power of produced heat energy is up to 17 kW. The power of additional electric heater is 12 kW. The heat pump was installed at one of sows farrowing sections with two compartments, where 96 farrowing places are set. The passive evaporators are places outside the piggery, but compressor and other equipment – inside the piggery. The hot water, heated by the heat pump up to 45-50˚C by means of a circulation pump through the pipe system to each of farrowing pens with heating floor panels has been delivered. The heat load of each of heating panels is 180 W.
During the experimental investigation the panels' surface temperature within the limits of 35-36˚C has been kept. The circulation pump operation regime after the back flow water temperature has been controlled, keeping it within the limits of 36-38˚C.
Data about the produced amount of heat energy and consumed electric energy for heat pump compressor's and electric heater operation have been registered. The efficiency of the heat pump operation during certain periods has been estimated, establishing the COP and energy transfer coefficients using coherencies [1]

$$COP = \frac{Q}{P_c} \tag{2}$$

$$K = \frac{Q}{P} \tag{3}$$

where $K$ – energy transfer coefficient;
$Q$ – produced amount of heat energy, kWh;
$P_c$ – electric energy consumed for compressor's operation, kWh;
$P$ – total consumption of electric energy, kWh.

For the registration of the consumed electric energy two 3-faze electric meters has been used, with the accuracy 0.01 kWh. One of them registered the electric energy consumed for the operation of the heat pump's compressor, and another one, additionally consumed electric energy by the electric heater. Produced amount of heat by the use of heat meter SONOMETER$^{TM}$1000 (accuracy 1 kWh) has been measured. The heat meter allows in every time moment to read of the efficiency of the hot water flow, the temperature of the heated floor inflow and outflow water, and the heat energy power as well. Average daily and monthly outside air temperatures during the experiment from the data base of the State Meteorological Service has been taken [3].
In order to carry out the experimental investigation on the possibility of the decrease of hoarfrost and ice coverage of the heat pump evaporators, one of them was provided for a ventilator (efficiency 1.2–1.4 $m^3/s$), which air flow on the evaporators' plates has been directed.

## Results and Discussion

The heat energy, produced by the heat pump, was used for piglets resting place floor panels' heating. From the data given in Table 1, about the exploitation parameters of the heat pump obtained in 2009 and 2010, firstly, direct relationship between the outside air temperature and COP of the heat pump is seen. Secondly, during the warm months of the summer – July and August, the consumption of heat is essentially smaller. The heat pump all the necessary amount of heat is able to produce with breaks at COP >3.5. At the temperature under 10 °C and down to the positive temperature above 0 °C, the character of the operation of the heat pump changed. Particularly it is seen from the data about October and November, when the average temperature was 5-6˚C and the evaporators' plates started to be covered with hoarfrost and ice. The demand of heat for keeping the floor temperature in the necessary level increases also. The heat pump's compressor in the majority was working continuously. Not always the ice thawed from the heat evaporator plates, when the temperature in the middle of a day increased. As a result the COP of the heat pump felt down to 2.8–2.6. The common heat transfer coefficient reduced to 2.3–2.6. In certain time periods, particularly in nights, the electric heater switched on. The hoarfrost of radial placed evaporators' plates increased so intensively that the evaporators entirely were covered by the ice and visually took a cylindrical shape.

*Table 1.*

**Exploitation indexes of the heat pump with passive evaporators in 2009 and 2010**

| Months | Average outside air temperature, °C | | Specific heat consumption, kWh/h | | Compressors' common | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | COP | | K | |
| | 2009 | 2010 | 2009 | 2010 | 2009 | 2010 | 2009 | 2010 |
| May | - | 11.0 | - | 8.46 | - | 3.00 | - | 2.95 |
| June | 14.0 | 14.9 | 10.01 | 9.98 | 3.06 | 3.23 | 3.06 | 3.20 |
| July | 17.4 | 21.5 | 5.27 | 5.45 | 3.32 | 3.67 | 3.32 | 3.67 |
| August | 16.0 | 18.8 | 9.16 | 7.48 | 3.25 | 3.55 | 3.25 | 3.35 |
| September | 13.6 | 11.5 | 8.13 | 9.51 | 3.24 | 2.90 | 3.24 | 2.90 |
| Oktober | 5.0 | 4.9 | 9.75 | 12.87 | 2.63 | 2.78 | 2.34 | 2.49 |
| November | 4.8 | 6.1 | 10.13 | 11.29 | 2.58 | 2.85 | 2.01 | 2.62 |
| December | 3.5 | - | 9.78 | - | 2.33 | - | 2.09 | - |
| Average | 10.6 | 12.7 | 8.89 | 9.29 | 2.91 | 3.14 | 2.76 | 3.02 |

Technical solutions for the diminishing of the hoarfrost and taking off the ice from the evaporators' plates have been looked for. They are based on the direction of the warm air flow on the evaporators' plates. The first investigations in the exploitation season of 2009 have been carried out. Around one of the evaporator blocs an isolation square box, where by means of a ventilator from one side the air from outside or the pigsty ante-room has been blown in. The average increase in heat energy power by 0.8 - 3.2 kW has been obtained and the thaw of hoarfrost has been furthered [4]. During the further work this principle has been changed. The additional air flow was directed parallel to the evaporator's plates. It was completed placing the ventilator above the evaporator's block and by means of a special cone moving the air flow to the evaporator's plates (Fig.1). In order to intensify the process, the possibility to cover the evaporator's block from both outside and inside with special screens has been envisage.

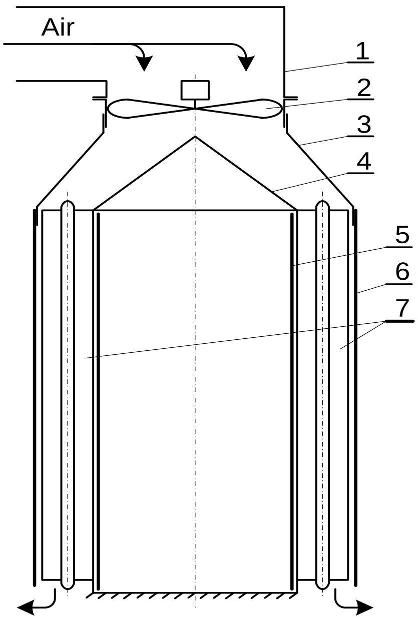


*Fig.1.* **Scheme of screens for air flow movement parallel to evaporator plates:**
1 – air canal; 2 – ventilator; 3 – cover; 4 – cone; 5 – inside screen (movable); 6 – outside screen (movable); 7 – evaporator's block

*Fig.2.* **Ventilator above the heat pump evaporator**

Experimental results on the promotion of the ice thaw from the evaporator's plates by short time moving the air flow to evaporator's plates, and by long time moving the air flow to evaporator's plates in order to improve the heat pump operation. Results in Table 2 when the air flow is directed to the evaporator's plates, corresponds to regime "1". Period of time from September 1 to September 9 the heat pump was working in constant regime "0". Consumption of heat on the average was 9.5 kWh/h at the COP = 2.80. In the morning of September 9 at the outside air temperature 9 – 10˚C the evaporator's plates were covered by the hoarfrost, and the heat pump was working continuously with heat power 9.6 – 10.4 kW, at the COP = 2.58. In the next morning (September 10) at similar weather conditions switching on the ventilator and starting to direct the air flow to the evaporators plates, during several minutes the heat power from 10.4 kW increased to 12.5 kW. The compressor switched off and the thaw of the evaporator's plates started. When the compressor switched on next time, the heat power rose up to 13.8 kW. After some time when the ventilator was switched off, the heat power diminished a little, because the evaporator plates already were free from hoarfrost. Similar examination was repeated several times. The main gain from the additional switching on and off of the ventilator is to contribute to the thawing of the evaporators' plates, which after that improves the parameters of the neat pump for longer time.
Greater effect has been reached at additional operation of the ventilator in the first week of October (2009), when the temperature lowered under 5–8˚C. On October 9 the ventilator has been operating all the day round (Fig.2). At the heat consumption 12.8 kWh/h the reached heat power was 15.2 kW at the COP = 3.08, including the energy consumed for the ventilator's operation K = 2.64).
The two last rows in Table 2 reflect the average results of the long term operation of the heat pump at outside air temperature 5-6˚C. From October 5 to 10 when the ventilator was out of operation, the compressor's COP on the average was 2.53. As for some time the electric heater has been operating, the common energy transfer coefficient was K = 2.26.

From October 10 till November 4 the ventilator was operating constantly. Therefore the hoarfrost essentially reduced, the air flow around the evaporator's plates was more intensive and the electric heater did not switch on. In result at the average heat consumption 12.2 kWh/h the compressor's COP increased up to 2.89, and including the ventilator's consumed power, the common coefficient K was 2.58.

*Table 2.*

**Increase in heat pump operation results in September-October, 2010 coursed by outside air flow**

| Date | R | Time, h | Outside air temperature, $^oC$ | | | Q, kWh/h | N, kW | COP | K |
|---|---|---|---|---|---|---|---|---|---|
| | | | average | min | max | | | | |
| Sept. 1 – 9 | 0 | 216 | 12 | 9 | 18 | 9.5 | | 2.80 | 2.80 |
| Sept. 9 | 0 | 2 | 9 | | | 10.0 | 9.6 – 10.4 | 2.58 | 2.58 |
| Sept. 10 | **1** | **0.35** | **10** | **10** | **10** | **10.0** | **12.5 – 13.8** | | |
| | 0 | 6 | 13 | 10 | 15 | 10.0 | 13.8 – 12.3 | 3.16 | 3.13 |
| Sept. 10 –13 | 0 | 65.5 | 15 | 13 | 18 | 9.98 | 12.3 – 10.2 | 3.14 | 3.14 |
| Sept. 3 | **1** | **3.5** | **17** | **14** | **19** | **8.00** | **13.2** | **3.04** | **2.97** |
| Oct. 6 | 0 | 2.4 | 4 | 4 | 6 | 11.25 | 11.3 | 2.49 | 2.49 |
| | **1** | **0.15** | **6** | **6** | **6** | | **11.3 – 14.2** | | |
| | 0 | 0.5 | 6 | 6 | 6 | | 14.2 – 11.4 | | |
| Oct. 7 | 0 | 7.7 | 5 | 3 | 8 | 12.76 | 14.2 | 2.50 | 1.94 |
| | **1** | **0.7** | **8** | **8** | **8** | **12.86** | | **3.10** | **2.77** |
| Oct. 7 – 8 | 0 | 21.2 | 4 | 2 | 8 | 10.87 | 10.5 | 2.51 | 2.51 |
| Oct. 8 – 9 | 0 | 18.4 | 5 | 3 | 9 | 11.45 | 12.6 | 2.11 | 1.77 |
| Oct. 9 | **1** | **7** | **7** | **3** | **9** | **12.8** | **15.2** | **3.08** | **2.64** |
| Oct. 5 –10 | 0 | 110 | 6 | 2 | 11 | 11.99 | | 2.53 | 2.26 |
| Oct. 10 – Nov. 4 | **1** | **599** | **5.3** | **2** | **8** | **12.19** | **10 - 14** | **2.89** | **2.58** |

Designations: R – regimes, 0 – without air flow, 1 – with outside air flow, N – produced heat power, Q – consumption of heat energy, COP – compressor's coefficient of performance, K - common energy transfer coefficient.

In Table 3 experimental results when outside air temperature was under +6$^oC$, and the evaporator was heated by outside or inside air flow using a ventilator (November, 2010), are presented.

On November 4 afternoons at the outside air temperature +9$^oC$ the heat power reached 14.3 kW. During the night temperature decreased and in the morning November 4 it was only +3$^oC$. The evaporators were slightly cowered with hoarfrost and the heat power has diminished to 9.9 kW. At switching on the ventilator with outside air flow after 5 minutes the heat power increase by 1,2 kW and later reached 13.7 kW, although hoarfrost of the evaporator's plates did not thaw. When warm air (+10$^oC$) from the ante-room was blown to the evaporator, fast hoarfrost thaw started and the heat power increased up to 15.7 kW. At switching the ventilator off and on repeatedly, the heat power changed correspondingly. Similar investigations several times during a week have been carried out. Always it resulted in the increase of produced heat power and the COP of the heat pump.

*Table 3.*

**Evaporator's heating by outside or inside air flow in November, 2010**

| **Date** | **R** | **Time, h** | **$T_{out}$, °C** | **Q, kWh/h** | **N, kW** from – up to | **N, kW** difference | **COP** | **K** |
|---|---|---|---|---|---|---|---|---|
| 4 –5 | 0 | 17 | 6 | 11.53 | 14.8 – 9.9 | - 4.9 | 2.54 | 2.54 |
| 5 | **1** | **2.9** | **5** | **12.76** | **13.7** | **+ 3.8** | **2.67** | **2.42** |
| | 3 | 0.6 | 10 | | 15.7 | +5.8 | | |
| | 0 | 2.9 | 7 | 12.50 | 13.4 | - 2.3 | 2.73 | 2.73 |
| | 3 | 0.5 | 10 | | 14.5 | + 4.6 | | |
| 5 – 6 | **2** | **21.8** | **6** | **11.19** | **14.6** | | **3.13** | **2.74** |
| 6 – 8 | 1 | 48.5 | 2 | 12.10 | | | 2.67 | 2.39 |
| 8 | 0 | 1.75 | 3 | 10.86 | 10.7 | | 2.52 | 2.28 |
| 8 –10 | **2** | **41.3** | **8** | **11.42** | **15.6** | **+ 4.9** | **2.85** | **2.54** |
| 10 | 0 | 0.4 | 4 | | 10.8 | - 4.8 | | |
| 10 – 12 | **1** | **46.9** | **5** | **10.68** | **13.6** | **+ 2.8** | **3.15** | **2.75** |
| 12 | 3 | 0.25 | 9 | | | | | |
| 12 – 15 | 0 | 72 | 8 | 10.07 | | | 2.98 | 2.98 |

Designations: R – regimes, 0 – without air flow, 1 – with outside air flow, 2 – with outside and inside air flow, 3 – with inside air flow only, $T_{out}$ – average outside air temperature, N – produced heat power, Q – consumption of heat energy, COP – compressor's coefficient of performance, K - common energy transfer coefficient.

Experimental results, when the outside air flow was directed to the evaporator covered by screens, in Table 4 are presented. One of experiments on October 6 when outside temperature reached +7°C has been carried out. In the morning both evaporators were covered by hoarfrost. In the afternoon at 13.10 p.m. the ventilator was switched on. In 10 minutes the heat power of the non-covered evaporator increased from 11.3 kW to 14.2 kW. After switching off the ventilator in 25 minutes the heat power diminished to 11.3 kW and the evaporator's plates did not thaw. After that a row of experiments have been carried out using the screens around the evaporator from outside and inside. Warm air flow (+12°C) from the ante-room was delivered to the evaporator. Fast heat power increase started, reaching its maximum at 15.4 kW. The COP of the heat pump increased accordingly from 2.5 to 3.4. When the screens were taken off the indexes decreased (Table 4).

*Table 4.*

**Experimental results when the evaporator covered by screens (2010)**

| Date | R | Time, h | $T_{out}$, °C | Q, kWh/h | Heat power, kW | COP | Common K |
|---|---|---|---|---|---|---|---|
| Nov. 6 | 0 | 2.9 | 5 | 11.25 | 11.3 | 2.49 | 2.49 |
| | 1 | 1.7 | 12* | 13.33 | 11.3 – 15.4 | 3.14 | 2.82 |
| Nov. 8 | 0 | 5.5 | 4 | 10.90 | 10.6 | 2.29 | 2.07** |
| | 1 | 1,7 | 10* | 13.25 | 10.6 – 14.3 | 3.1 | 2.78 |

Designations: R – regimes, 0 – without air flow, 1 – with inside air flow, $T_{out}$ – average outside air temperature, Q – consumption of heat energy, COP – compressor's coefficient of performance, K - common energy transfer coefficient, * - air temperature in ante-room, ** - for short time the electric heater is switched on.

The process of the investigation in Fig.2 is shown. Steep increase in the heat power just after switching on the ventilator in Fig.3 is seen. Similar results in repeated experiments are obtained. The evaporator block with opened screens after thawing in Fig.4 is given. On the left side (Fig.4) another evaporator's block is seen, which at the same time did not thaw.

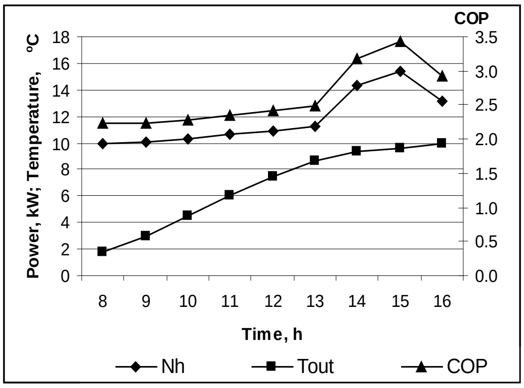


*Fig.2.* **The gain of the COP and heat energy power $N_h$ of the heat pump: $T_{out}$ – outside air temperature**

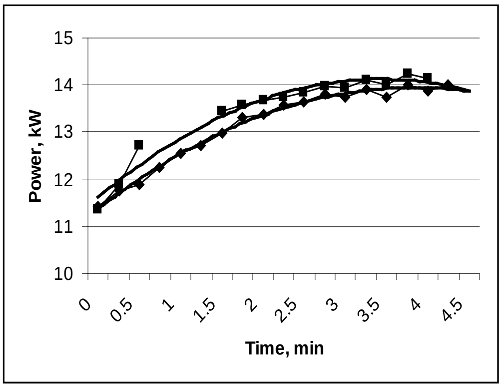


*Fig.3.* **The dynamics of the gain in power during 4 minutes after the start of warm air flow: upper curve – with screen, lower - without screen**


*Fig.4.* **The evaporator block with opened screens after thawing**

## Conclusions

From our two years investigation results about the possibility of the use of an outside air heat pump for piglets resting place floor panels heating, the following is concluded:

1. In summer period at the outside air temperature above 10–12$^o$C the coefficient of performance of a heat pump is above 3 and the heat consumption 5–9 kWh/h. The evaporators of the heat pump are not covered by hoarfrost.
2. At outside air temperature 3-10$^o$C the heat demand increases. The heat pump operates constantly or with small breaks. The evaporators start to be covered by hoarfrost. The exploitation indexes of the heat pump decreases. The heat transfer coefficient becomes fewer than 2.5.
3. At the positive outside air temperature within the limits of 2-5$^o$C the evaporators coverage by hoarfrost increases, and without additional undertakings to this, the heat pump operation is not useful.
4. The thawing of the hoarfrost using additional air flow in successful only in the outside temperature interval 6-12$^o$C.

5. At the outside air temperature under 12$^{o}$C it is recommended to blow the heat pump evaporators by warmed air flow. In our experimental examination the obtained gain of the heat power was by 3.7-4.1 kW, and the COP of the heat pump increased by 0.6-0.7 on the average.
6. The investigation has shown that the blowing of the evaporators by warmed air can prolong the operation of the heat pump at lower outside temperature period. In our experimental pigsty using the transformed by a heat pump the heat energy for piglets resting place floor heating from May till the middle of November (2010) the economy was about 1180 €.
7. Our experimental investigation has shown that using the worm air from a pigsty ventilation system for evaporators warming, the heat pump operation is possible even at negative outside temperature.


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## References


1. Blumberga D. Heat pump. R.: RTU. 2008. 140 p. (in Latvian).
2. Reay D., Macmichael D. Heat Pumps. M.: Energoizdat. 1982. 220 p. (in Russian).
3. http://www.meteo.lv (in Latvian).
4. Ilsters A., Ziemelis I., Zagorska V. Warming of Piglets Resting Places by Air Heat Pump in Dependence on Outside Air Temperature. Proceedings of the 9th International Scientific Conference “Engineering for Rural Development”, Jelgava, Latvia, 2010, pp. 106 – 111.

# ENERGY PRODUCED BY SOLAR BATTERY AND PERSPECTIVES OF IT'S USAGE IN LATVIA

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**Abstract:** *Many alternative energy sources can be used instead of fossil fuels. The decision as to what type of energy source shoud be utilized in each case must be made based on economic, environmental, and safety considerations. Because of the desired environmental and safety aspects it is widely believed that solar energy should be utilized instead of other alternative energy forms it can be used sustainably without harming the environment. The paper deals with the solar photovoltaic module capacity recording device whose load characteristic is similar battery charging load characteristic. As a result, the device will record the amount of energy retrieved from the module battery. In 2009th with this device was recorded solar module PVM10/12PF power and charged batteries are retrieved energy levels in the months and year as a whole.*

**Keywords:** *Solar electricity, photo-electric modules, batteries, system.*

## Introduction

Currently there are three known methods for direct conversion of solar electric energy: photo-electric, thermo-electric and thermo-electronic.

Thermoelectric converter (generator), works on the Zeebeka effect, as follows: the electrical circuit, which consists of various materials managers, resulting electromotive force (EDS), on the condition of the driver circuit contact points are at various temperatures. Usually thermoelectric generators consists of a thermo battery, consisting of in series and parallel closed thermopile and thermocouple of a high and the hot end heat exchanger. In order to further exploit the opportunities for thermocouple, thermoelectric generators equipped with solar energy concentrators and sun trackers. Thermoelectric generators have an efficiency of around 15% and power some hundreds of kW [1].

Heat can directly convert in electrical using thermionic converters, which operate on termoelectron emission effect. It is known that a vacuum heated surfaces (cathode) emits electrons that are going through interelectrode room into the anode, creating a current of the external circuit. Saturation current density down converter Richardson equation. Good termoemission material is coated with tungsten cesium. Power production is not required external EDS, where the heated metal surface apply with a lower electron leaving the necessary work. Such a system can generate electricity like a semiconductor p-n junction. From the energy point of view, such devices are ineffective.

The most widely used photo-electric converters [2] – photo-electric modules (Module), which consists of individual, usually in series of semiconductor photo-electric elements (Cell) The size and number determine currents and voltage value, which provides the module. Connecting in series and parallel photo-electric modules, a photo-electric modules, solar cells (Array).

The most common in the world is silicon (Si) solar cells, which, depending on the technologies of production (depending on the arrangement of silicon atoms in crystal), can be a mono-crystalline, poly-crystalline and amorphous. The corresponding solar energy conversion factors to these elements are as follows: [3]: (12 – 15); (11 – 14); (6 – 7). At the poly-crystal group usually are added (thin film) solar cells, the structure consists of glass, silicium precipitation from the gaseous materials.

To determine and compare the installed capacity of solar cells and modules, during testing the output power measured at the standardized test conditions: the intensity of radiation - 1000

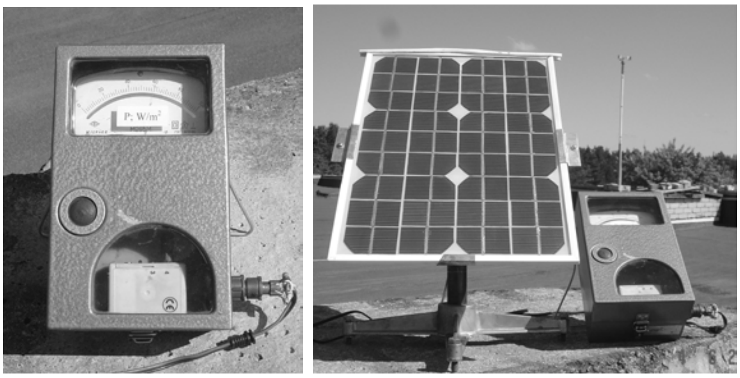
W/m$^2$, radiation spectrum - AM 1.5 (shown light type and color), the temperature + 25 ºC . AM 1.5 corresponds to solar radiation spectrum, if the beam angle to the horizon is 45°. Power, the battery produced under these conditions denoted by Wp (peak power) and it is the power of the solar battery produced in optimum conditions.

Solar cells produced power is measured in W/m$^2$ and it depends on the type of radiation (the spectrum) the intensity of radiation and module temperature. More power solar battery produced when irradiated direct, cell surface being perpendicular to the sun's rays, minimum – from reflections (diffuse radiation) and the electric light, it is a vivid impression of light, solar cell produces more electricity than in the shade and the electric lighting.

Designing and implementing the autonomous solar power system, the question arises as solar electric power capacity operating conditions in a given area, it is necessary to know the data on the solar power produced in the nature, characteristics and long term (per year) of the battery load the electric power generated Wh. To develop this challenge, a photo-electric solar power module recorder was made and in 2009 was registered produced power of module PVM10/12PF.

**Matherials and methods**

Set up solar photo-electric power modules recorder is given on Fig.1 a). The device work with the photo-electric module PVM10/12PF see Fig.1 b). Photo-electric module PVM10/12PF technical data aggregated into Table 1.



a) b)

*Fig.1.* **a) The overview of solar photo-electric power modules manufactured by a recording device; b) Capacity recording devices into the photo-electric module PVM10/12PF**

Photo-electric power module registration principal scheme shown on Fig.2. It consists of the capacity of a recording device 2 which is connected to the photo-electric module and a data recorder 3 (Hobo module). Capacity recording device based on the equivalent battery, it is a load, the curve similar to the battery charging power curve. Therefore Hobo registered capacity and the amount of energy can be considered as a battery charger and rechargeable battery power you have downloaded the amount of energy. Device battery equivalent of a DC parametric stabilizer 4 with a series of switch current limiting ballast resistance R1, which is removed from the data recorder and the supply voltage to be proportional to the photo-electric power module manufacturers. To increase the power stabilizer, it created a transistor-based VT, which collector-base circuit dissconect stabilitrons, but the base-emitter circuit - resistance R3.

Table 2 gives the device electrical characteristics. Figures columns of U and I obtained experimentally, it is the replacement of photovoltaic modules with a variable DC voltage source and measuring the corresponding voltage to the circuit. The figures in other columns of the table have been calculated mathematically. Table with the $P_b$ has identified capacity, which is recorded HOBO and measured mikroammeter PA (Fig.2). The Fig.3 shows the device VA curve obtained using the column I, and U numbers of Table 1.

*Table 1.*

**Technical data of Mono-crystal photo-electric module PVM10/12PF**

| Nr | Parameter | Symbol | Dimension | Value |
|---|---|---|---|---|
| 1st | The peak power | $W_p$ | W | 10 |
| 2nd | Nominal voltage | U | V | 12 |
| 3rd | Wp point voltage | $U_{Wp}$ | V | 17 |
| 4th | Wp point current | $I_{Wp}$ | A | 0.6 |
| 5th | A short-circuit current | $I_{\bar{\imath}s}$ | A | 0.8 |
| 6th | The surface area | L | $m^2$ | 0.1 |
| 7th | Transformation factor | $K_p$ | % | 12 – 15 |
| 8th | Size | depth*height*depth | mm | 280*365*6 |
| 9th | Mass | M | kg | 0.4 |

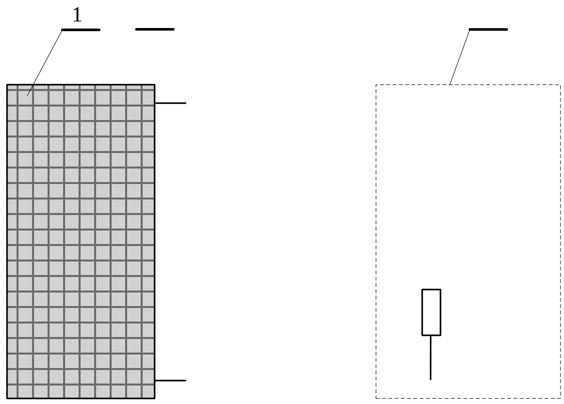



*Fig.2.* **Principal scheme of photo-electric power module registration process**

$R_1$ = 1,45 Ω; $R_2$ = 12 k Ω; $R_3$ = 240 Ω; VD – Д814Д; VT – KT808

*Table 2.*

**The parameter table of recording device of the photo-electric power module**

| U, V | I, A | P=I*U ($L=0,1m^2$) | P=10IU, $W/m^2$ | U=I*R (HOBO) | $P_b$=100*U $W/m^2$ |
|---|---|---|---|---|---|
| 13.03 | 0.002 | 0.026 | 0.26 | 0.0029 | 0.29 |
| 13.32 | 0.011 | 0.146 | 1.46 | 0.0159 | 1.59 |
| 13.5 | 0.021 | 0.28 | 2.8 | 0.0304 | 3.04 |
| 13.88 | 0.1 | 1.4 | 14 | 0.145 | 14.5 |
| 14.23 | 0.24 | 3.41 | 34.1 | 0.348 | 34.8 |
| 14.8 | 0.5 | 7.4 | 74.0 | 0.725 | 72.5 |
| 15.2 | 0.7 | 10.64 | 106.4 | 1.015 | 101.5 |

Using the considered device, photo-electric module output recorded throughout 2009. year. The data recorder used to record two channels of HOBO device, one power and one to record temperature. Therefore, in order to restart HOBO (the data from HOBO are removed) only once a month, registration of data taken at intervals of 12 min. To obtain the photo-electric module power Pb W/m$^2$ (see Table 2) the processing of data in Excel, Hobo registered voltage value multiplied by 100.

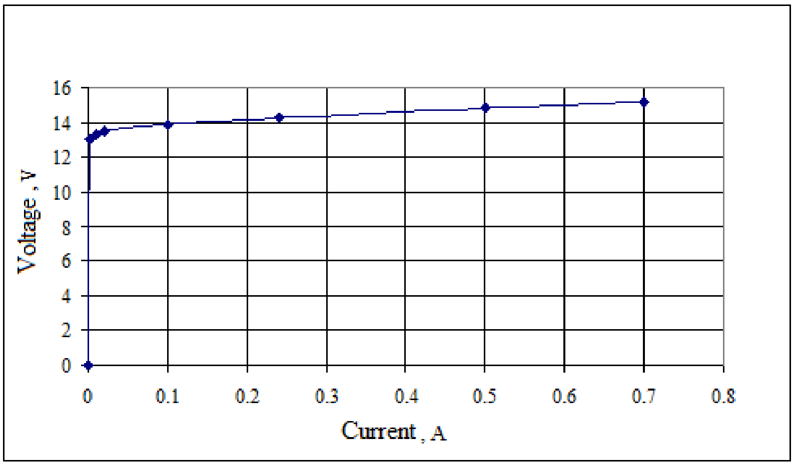



*Fig.3.* **Photo-electric module, power recorders Volt-Ampere characteristic**

## Results and discussion

With Hobo data recorder data from the photo-electric module PVM10/12PF capacity shown with chart tables. Processing data in Excel, we can get power in the form of a chart graphic to any period: hourly, daily, weekly, etc.

On Fig.4. given the photo-electric module, power diagram, 2009 21st April, when, as seen in day has been entirely free of clouds and photo-electric module PVM10/12PF, the day has produced 0.67 kWh/m$^2$. Found that in April there have been the most favorable weather conditions for the solar cells produce electrical energy module PVM10/12PF in April (see Fig.6) has produced 16.1 kWh/m$^2$, which is the best indicator of the entire 2009th during the year. Relatively favorable conditions for electric energy production remained until October, because even in September (see Fig.7) obtained 11.79 kWh/m$^2$ per month. Inimic weather adverse conditions have been during the winter months, for example, in January (Fig.5) and November (Fig.8) is 18 days and more, the power module was less than 10 W/m$^2$.

In general, the module per year (see Fig.9, converted to 1 m$^2$ surface with $W_p$ = 100 W) has produced 101.9 kWh/m$^2$ power, of which 82.63 kWh/m$^2$, or 81.1% produced by April till September.

In assessing the results of the reliability of the data point of view, it should be noted that the resulting amount of energy should be regarded as the batteries are not downloaded, but no battery is connected directly to the module.

On real working conditions will be energy losses [4] on the battery to 25%, as well as pipelines and the rest of the solar equipment as a result, the resulting amount of energy will be lower.

According to [5], photo-electric module energy output:

$$E = k \cdot W_p \frac{E_g}{1000} \tag{1}$$

where: $k$ – the coefficient, in summer k = 0.5, in winter k = 0.7;

$E_g$ – Global output energy under consideration period;

$W_p$ – peak power of the used photo-electric module.

In our case, assuming full-year k = 0.6; E = 0.6*10*1040000*1000$^{-1}$ = 6240 Wh = 6.24 kWh. Since our module has an area of 0.1 m$^2$, then the 1 m$^2$ (Wp = 100 W) energy produced

expected will be 62.4 kWh per year (if Wp = 1 kW), the 624 kWh per year which is significantly lower than that recorded by the device.
In [6] at the factors "k" is the numerical value of 0.75. In this case, from 1 $m^2$ (Wp = 100W) actually get the amount of energy will be around 78 kWh per year, but from Wp = 1 kW of power is expected to be around 780 kWh per year, which could be regarded as a reliable, if due allowance for the above energy loss.

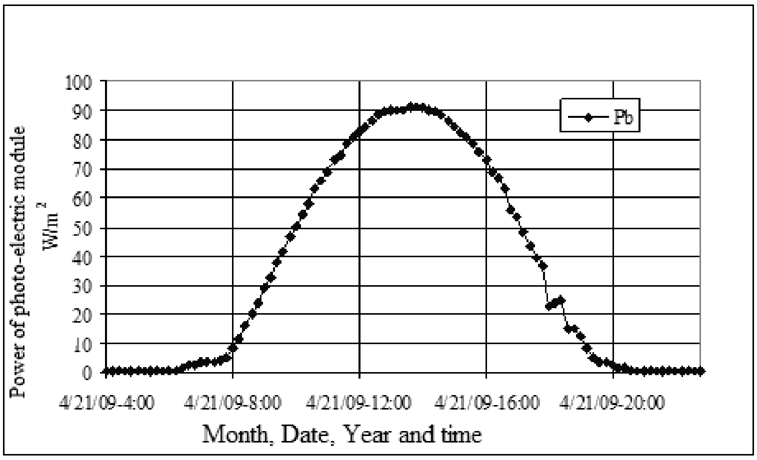



*Fig.4.* **Photo-electric power module diagram 2009, 21st April**

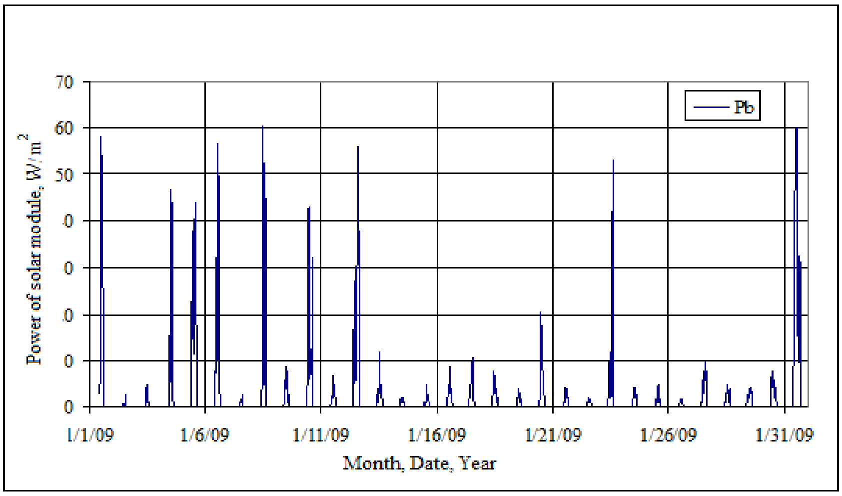



*Fig.5.* **Photo-electric power module diagram and power diagram energy output in January, 2009th**

Analyzing data from the economic point of view we see that 100 Wp module to the surface of 1 $m^2$ (per loss) during the year has produced about 78 kWh of electricity and bring in (price 0.073 Ls) 5.7 Ls.
As noted at [7], now cost per kW of installed peak capacity in Latvia are about 5,500 to 6,000 euro (average of 4000 Ls). This price includes all the equipment, the planning and installation. Given that one of the peak power kW our circumstances, can produce around 780 kWh per year in monetary terms corresponds to 57 Ls, the solar installation payback period will be 4000/57 = 70 years. Given that the solar battery life is 30 - 40 years, the state subsidies, such as buying batteries for energy produced at a higher tarif, solar battery for use in Latvia as a realistic basis.
The world's major focus is on reducing the prices of the batteries, which strives for:

Construction of the sun following solar battery [8] equipment; increasing the battery energy conversion factor, using the high-quality, multi-layer GaInP / GaInAs / Ge structure of photo-electric elements, which size 2*2 mm and the Fresnel lens on those, up to 1000 times the solar capacity, thus reducing the cost of equipment installed capacity up to 2 $ per W [9].
Encouraging, photovoltaic main construction material, pure (99.999) silicon extraction technology (chlorine free) [10] by reducing the production cost of silicon 2-fold, thus reducing the silicon and solar batteries on the market price.
Building and developing thin film solar [11] photo-electric modules: the copper-gallium diselenid (CIGS), kp = 20% Cadmium-tellurium (CdTe ), kp = 16%, amorphous silicon (a-Si: H), kp = 10%; nanocristalic silicon Si, kp = 10%, and other materials.

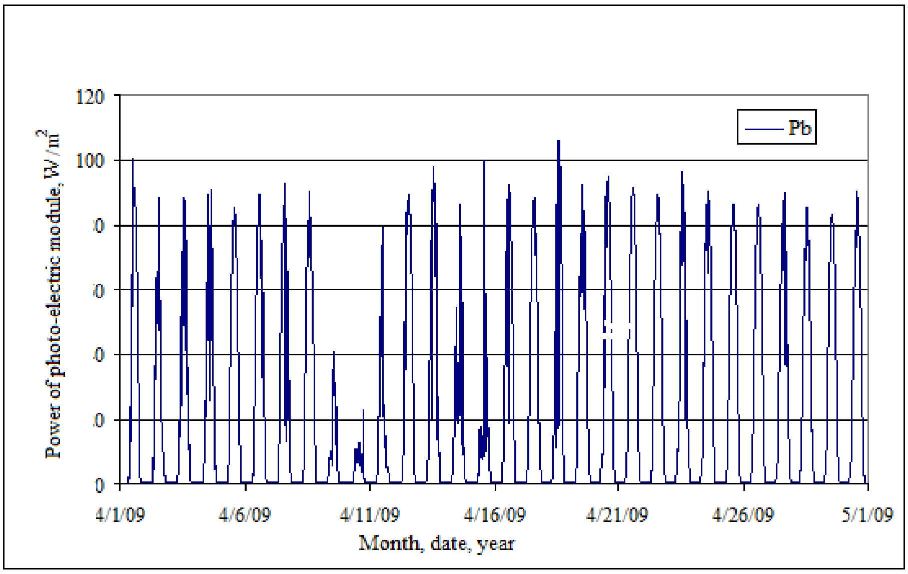



*Fig.6.* **Photo-electric power module diagram and power diagram energy output in April, 2009th**

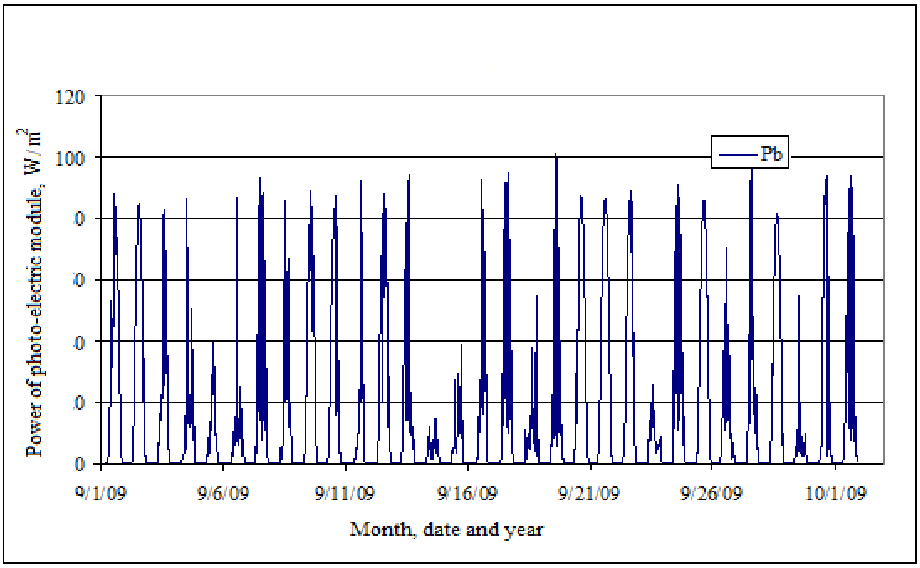



*Fig.7.* **Photo-electric power module diagram and power diagram energy output in September, 2009th**

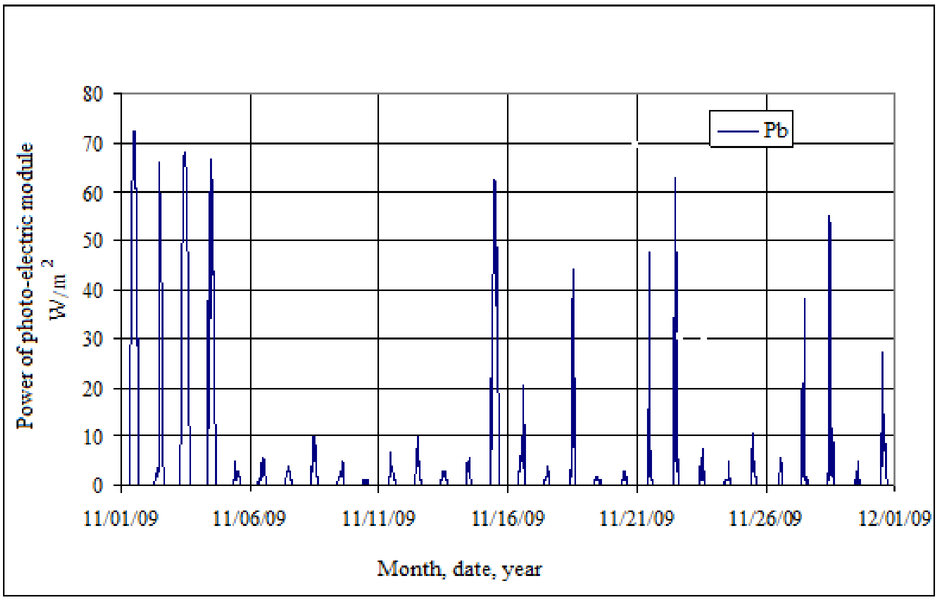



*Fig.8.* **Photo-electric power module diagram and power diagram energy output in November, 2009th**

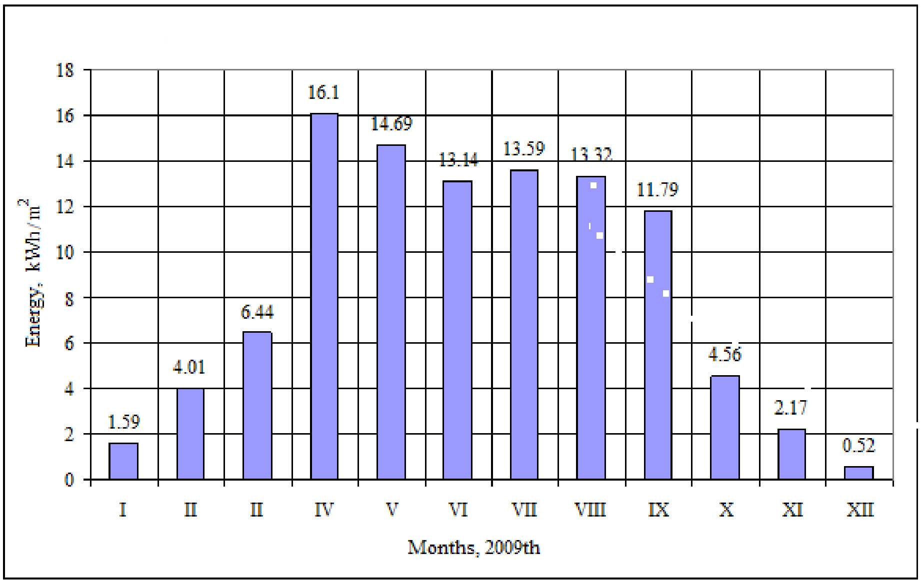



*Fig.9.* **The recorded output (the batteries are not loaded) energy levelsin 2009th, Total 101.9 kWh/m$^2$**

## Conclusion

1. Solar photo-electric power modules used for recording solar power recorder, which is similar to the load curve (equivalent to) the battery charging load curve, as a result, the device will record the battery retrieved the amount of energy.
2. Connected to a single crystal photo-electric module PVM10/12PF, solar power recorder, in 2009th year, calculated on a peak power of one kilowatt (kW$_p$), has registered 1,019 kWh of electricity, of which 826.3 kWh, or 81.1% recorded from April till November.
3. Taking into account the energy loss of battery and pieces of equipment to the consumer of energy for the amount assessed around 780 kWh of peak power per kilowatt.
4. If the solar plant with a peak power in kW installation costs 4000 EUR, then the cost of the pay back period, at constant electricity tariff, may be 70 years long.

5. Same unit price of solar cells can be up around 40% of the total project cost, therefore the world, emphasis is placed on battery to reduce the price by trying to reach: the sun using the following equipment with energy concentrators up to 1000 times, improving the production of silicon technology to reduce its prices in developing and the construction of thin film photoelectric cells and modules.

**References**


1. John W. Twidell and Anthony D. Weir.(1986). *Renewable energy resources*. London. E.& F.N. Spon, 392 pp.
2. Solar batteries. Solarhome, 2009. Available at: http://www.solarhome.ru/ru/pv/index.htm
3. Solar elements. Solarhome, 2009. Available at: http://www.solarhome.ru/basics/pv/techcells.htm
4. Solar batteries. Engineering, 2010. Available at: http://1kz.biz/battery/statyi_foto.shtml
5. The calculation of PV system, 2010. Available at: http://cxem.net/house/1-49.php
6. Energy efficiency of buildings, 2009. Available at: http://www.rea.riga.lv
7. Vents Dubrovskis, Solar sistems. 2008. Available at: http://www.ntz.lv/portals/bizness/raksts.html?xml_id=3555
8. Factory, 2009. Available at: http://www.ioffe.rssi.ru/main_menu/initiatives/Factory.pdf
9. Sun, 2008. Available at: http://pvlab.ioffe.ru/project/pdf/sun.pdf
10. The market analysis of photovoltaic modules used in the European Union, 2010. Available at: http://bds-ict.com/ru/?p=78
11. Solar PV, 2007. Available at: http://www.thg.ru/howto/solar_pc_i/solar_pc_i-02.html

# RESEARCH ON SOLAR ENERGY COLLECTOR WITH CELL POLYCARBONATE ABSORBER

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**Abstract.** *A flat plate solar collector with cell polycarbonate absorber and transparent cover has been made and its experimental investigation carried out. The collector consists of a wooden box, into which, a layer of heat insulation with a mirror film and 4 mm thick cell polycarbonate sheet, as the absorber, are placed. The coherence between collector's efficiency, heat carrier and ambient air temperature, as well as intensity of the solar radiation and heat power in the experimental investigation has been obtained. During the experimental examination the maximum temperature of the heat carrier reached 80̊C at the intensity of solar radiation about 0.8 kW/m$^2$ and ambient air temperature around 32̊C. The efficiency of the collector reached 33-60%, depending on the intensity of solar radiation and surrounding air temperature.*

**Keywords:** *solar collector, cell polycarbonate, power.*

## Introduction

The solar insulation, coming from the sun to the earth, perpendicularly to the atmosphere highest layers is about 1353 W/m$^2$, which is called the solar constant [1]. Going through the earth atmosphere up to 50% of direct solar radiation is absorbed by the layer of ozone, air and water vapour molecules, particles of dust, and turns into diffuse one. This part depends on the geographical and climatic conditions of the place. The intensity of direct solar radiation on the earth surface can reach 1 kW/m$^2$, but the amount of solar energy on the earth horizontal surface at our latitude can be up to 1000 kWh/m$^2$.

The energy of solar radiation is used for the production of heat, electric and mechanical energy. Passive and active solar heating systems are used. In passive systems the function of the absorber and cover is realised by the elements of the premises to be heated (windows, walls, floor), and the air circulation goes on in the way of convection. Active solar systems are solar collectors, used for water or air heating. For water heating flat plate and vacuum tube collectors widely are used.

In the majority of presently produced solar collectors, solar energy absorbers from non-ferrous metals (Cu, Al) are made. As a transparent cover hardened glass, which is relatively heavy and brittle, usually is chosen. Regardless of good thermo-technical parameters and long service time of these collectors, they are heavy (about 35 kg/m$^2$) and expensive, what hampers the wide utilization of them in Latvia. Therefore scientists in the entire globe are searching for new materials appropriate for the production of lighter, cheaper and more durable constructions of solar collectors. One of such materials is transparent cell polycarbonate (CPC) sheet, consisting of side by side placed squared canals. They can work at the wide range of temperature (– 40 ... +100̊C, in short-term up to +120̊C), have good solar radiation penetrability ($\tau > 0.8$), are light, flexible and mechanically durable. Therefore investigation in this direction is considered as perspective.

## Materials and methods

The cell polycarbonate collector is performed as a classic flat plate solar collector (Fig.1). It consists of a box, into which, a layer of heat insulation with a mirror film and 4 mm thick cell polycarbonate sheet, as the absorber, are placed. The front side of the collector box (directed to the sun) is covered by a 6 mm thick cell polycarbonate transparent sheet. The area of the absorber's working surface is 1.8 m$^2$, and its mass – about 27 kg. The volume of the heat carrier (water) into the absorber is about 5 litres. At the determination of the size of the collector's box, the coefficient of linear expansion (0.067 mm/(m·°C)) of the cell polycarbonate was taken into consideration. Accepting that the collector works at the temperature from –35°C up to +100°C, it was stated that the length of 2 m (at 20°C) long cell polycarbonate sheet will change by 18 mm. The collector box (frame) from wooden boards was made. They are mechanically durable, with good heat insulation ability and, as practise has shown, in outside conditions can work from 10 to 20 years.

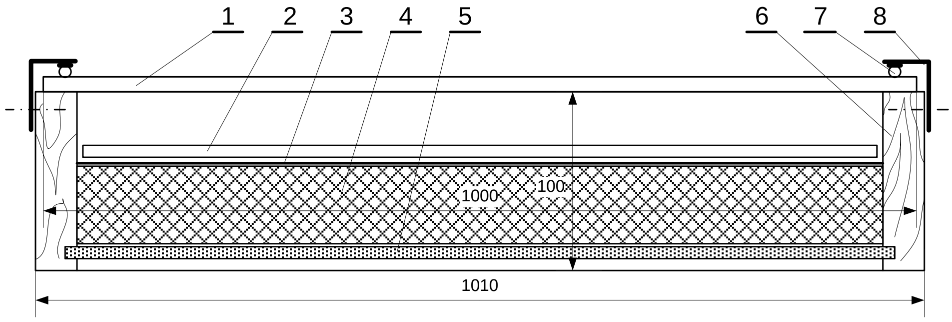


*Fig.1.* **Cross-section of the cell polycarbonate sheet collector:**
1– transparent cover (CPC, 6 mm), 2 – absorber (CPC, 4 mm), 3 – mirror film, 4 – heat insulation (rock wool), 5 – rear lid (board), 6 – frame (wooden board), 7 – rubber gland, 8 – set square

The absorber of the cell polycarbonate collector consists of heat carrier inflow 4 and outflow 1 tubes and a sheet of cell polycarbonate 3 (Fig.2). The tubes 1 and 4 are made of polycarbonate and have milled chinks, which length and width corresponds to the length and width of the polycarbonate sheet 3. The ends of the sheet are glued into the chinks, using junctions 2 and discs 5.

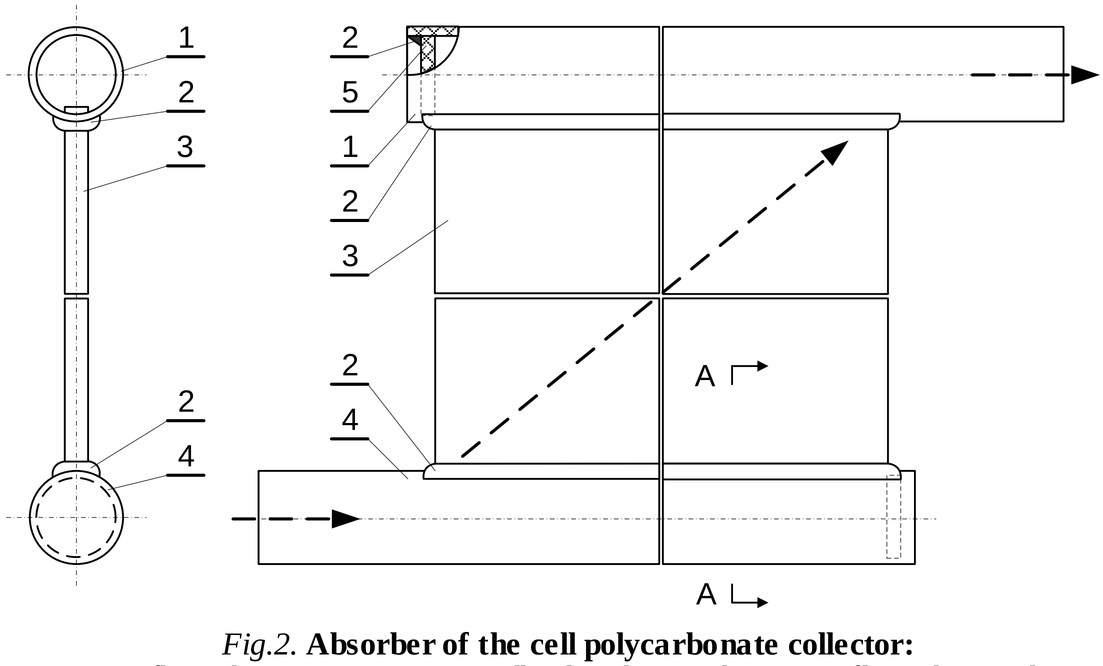


*Fig.2.* **Absorber of the cell polycarbonate collector:**
1 – outflow tube, 2 – junctions, 3 – cell polycarbonate sheet, 4 – inflow tube, 5 – disc

The solar radiation, striking the transparent cover, goes through it. The length of the solar electromagnetic waves on the earth surface is in the range of 0.4 to 2.4 µm. Therefore as a transparent cover ordinary or hardened glass panes are used, which coefficient of transparently is up to 90%. It means, the absorber, placed under the glass, absorbs up to 90% of striking it solar radiation energy. Solar radiation transforms into the heat energy in the absorber. A hot absorber irradiates heat energy, the frequency of which is in the range of infrared radiation (maximum about 8 μm); such waves do not go back from the absorber through the glass cover. It means the heat losses in the collector occur only by convection and conduction through the transparent cover.

A solar collector can work only together with the corresponding equipment. In point of fact, the main component of the solar collector system is a hot water basin 12 (Fig.3), to which a loop of the solar collector and a loop of hot water are connected. The collector's loop includes a heat exchanger 11, one way valve 9, circulation pump 8, expansion compensation vessel 5 with security valve 6, solar collector 3, heat carrier inflow valve 1, heat carrier and air outflow valve 4. All these components are connected with cupper tubes through which, when the circulation pump 8 is operating, liquid heat carrier is circulating and transporting the heat from the collector to the hot water basin 12. For an automatic control of the pump 8 operation a control device 7 with temperature sensors 2 and 10 is envisaged. When the temperature, measured by the sensor 2, becomes for some degrees higher as the temperature stated by the sensor 10, the pump 8 switches on, but when the temperature difference decreases, it switches off. The hot water loop consists from an expansion compensation vessel 14, valves 13 and 15. Through the valve 13 the hot water is delivered to consumers, but through the valve 15, the cold water flows into the tank 12.

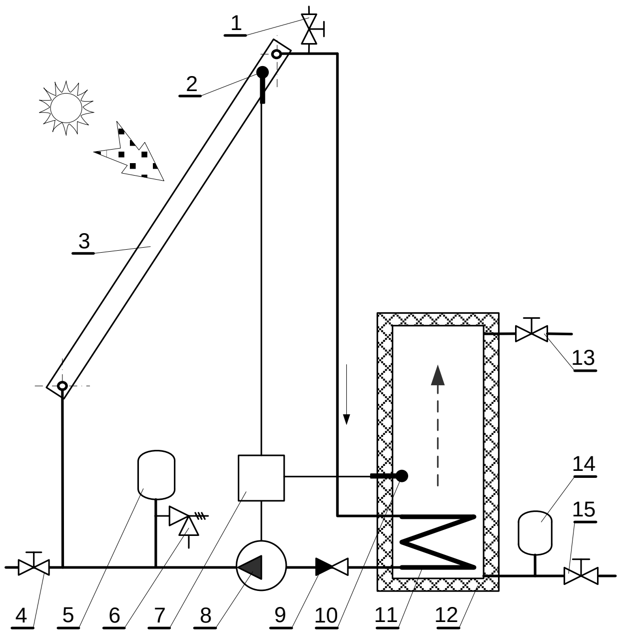


*Fig.3.* **Functional scheme of the solar collector equipment:**
1, 4, 15 – valves, 2, 10 – temperature sensors, 3 – solar collector, 5 – expansion compensation vessel, 6 – security valve, 7 – control device, 8 – circulation pump, 9 – one way valve, 11 – heat exchanger, 12 – hot water tank

The heat energy power of a flat plate solar collector can be calculated using Hottel-Uiller-Bliss equation [3]:

$$P_c = A[P_s \cdot \eta_o - K_l (T_h - T_o)], \qquad (1)$$

where $P_c$ – power of solar collector, W;

$A$ – collector's surface area, $m^2$;

$P_s$ – intensity of solar radiation, $W/m^2$;

$\eta_o$ – collector's optical coefficient;

$K_l$ – collector's heat loss coefficient, $W/(m^2 \cdot °C)$;

$T_h$ – heat carrier temperature, °C;

$T_o$ – surrounding air temperature, °C.

The collector's optical coefficient is calculated using formula (2):

$$\eta_o = \tau \cdot \alpha \,, \tag{2}$$

where $\tau$ – coefficient of solar radiation penetrability (0.6-0.95);

$\alpha$ – absorption coefficient of solar radiation (0.85-0.98).

The collector's optical coefficient does not depend on the sollar radiation intensity, as well as the temperature difference between the heat carrier and surrounding air. The coefficient of solar collector efficiency (3) is the ratio between the amounts of heat energy produced by the collector and received by the working surface of the collector. Divided both sides of the equation (1) by the intensity of solar radiation $P_s$, we will obtain:

$$\eta_c = \eta_o - K_l \frac{T_h - T_o}{P_s} \,. \tag{3}$$

The value of the coefficient of solar collector's efficiency (3) is dependent on:

- the meteorological parameters, like the intensity of the solar radiation and air temperature,
- constructive parameters of the collector such as the heat absorption ability of the absorber, the transparent cover penetrability of the solar radiation, the sickness of the heat insulation and its coefficient of the heat conductivity,
- such operational parameters of the collector as consumption of heat and temperature.

The numerical values of a flat plate solar collector optical and heat loss coefficients depend on the type of the collector and its construction (Table 1).

*Table 1.*

**Numerical values of optical and heat loss coefficients for different kind of solar collectors**

| Type of collector | Optical coefficient, $\eta_o$ | Heat loss coefficient, $K_l$, $W/(m^2 \cdot {}^\circ C)$ |
|---|---|---|
| Non selective and without a cover | 0.95 | 15 |
| Non selective with one glass cover | 0.85 | 7 |
| Non selective with two glass covers | 0.75 | 5 |
| Selective with one glass cover | 0.80 | 3.5 |
| Vacuum tube absorber | 0.75 | 2 |

When caring out the experimental investigation of solar collectors, it is possible to determine produced by them heat energy and its coefficient of efficiency knowing or experimentally obtaining the inflow and outflow heat carrier temperature, circulation pump operation intensity and the heat carrier heat capacity. In this case the power of a solar collector is calculated by formula [3]:

$$P_c = g \cdot C_c \cdot (T_{out} - T_{in}) \,, \tag{4}$$

where $g$ – consumption of heat energy, kg/s;

$C_c$ – heat capacity of heat carrier, J/(kg·°C), water $C_c = 4.19 \cdot 10^3$ J/(kg·°C);

$(T_{out} - T_{in})$ – difference between heat carrier outflow and inflow temperature, °C.

If the consumption of heat g is given in kilograms per hour (kg/h), the power of a solar collector in watts (W) can be calculated as:

$$P_c = \frac{g \cdot 4.19 \cdot 1000 \cdot (T_{out} - T_{in})}{3600} = 1.161 \cdot g \cdot (T_{out} - T_{in}) \,. \tag{5}$$

The coefficient of the efficiency for a certain solar collector with working area A by formula (6) can be figured [3]:

$$\eta_c = \frac{P_c}{P_s \cdot A} \,. \tag{6}$$

As the CPC collector was made at the end of the last year summer, only first experimental results have been obtained. The examination will be continued, as the objective of the research is to ascertain the efficiency of the collector as a function from the temperature difference between the collector's absorber and surrounding air. The obtained results will be compared with the same parameters of similar metal-glass (MG) collectors.
For the experimental investigation of the collector, a special stand has been used (Fig.4 and Fig.5). In point of fact, the stand is a platform with wheels, on which a 30 litres barrel 6, one way valve 5, heat carrier circulation pump 4, heat meter (M-CAL compact 0.6) 3 and solar collector 1 are placed (Fig.4).

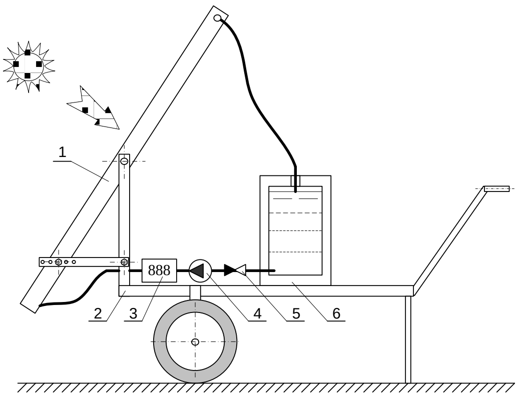


*Fig.4*. **Principal scheme of mobile stand for solar collectors' experimental investigation**


*Fig.5*. **Mobile stand for solar collectors' experimental investigation (look from the outside)**

Meteorological parameters during the investigation by the device MD-4 were measured (Fig.5, from left). As the used heat meter was not provided with an automatic data registration, the data for formulas (4) and (5) (pump productivity and temperatures $T_{in}$, $T_{out}$) during the examination after the accepted time interval were red. The intensity of the solar radiation $P_s$ and the surrounding air temperature $T_o$ automatically by the device MD-4 (logger HOBO H08) have been registered. In order to compare the cell polycarbonate collector's parameters with those of a metal-glass collector, like the coefficient of efficiency as a function from the difference of the heat carrier and surrounding air temperature, formulas (1) and (3) and data from Table 1 (for the cover of one pane of glass with $\eta_o$ = 0.85 and $K_l$ = 7) were used (Fig.6). During the experimental investigation the collector perpendicularly to the sun beams has been orientated.

## Results and discussion

The obtained experimental results are presented in Fig.6 and Fig.7. In Fig.6 the curves of water heating process on August 16, 2010, but in Fig.7 the comparison of efficiency of the CPC and metal-glass collector are given. Materials used for the manufacturing of the CPC collector (1.8 $m^2$) and its prices in Table 2 are shown.

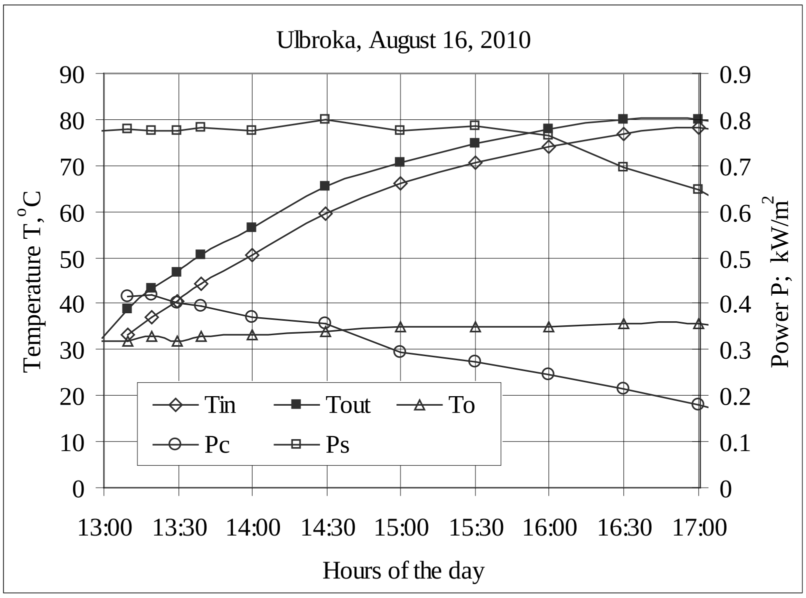


*Fig.6*. **Parameters of the CPC collector depending on the heating time: $T_{in}$, $T_{out}$ – heat career inflow and outflow temperatures of the absorber, °C; $T_o$ – surrounding air temperature, °C; $P_c$ – specific power of the collector, kW/m²; $P_s$ – intensity of solar radiation, kW/m²**

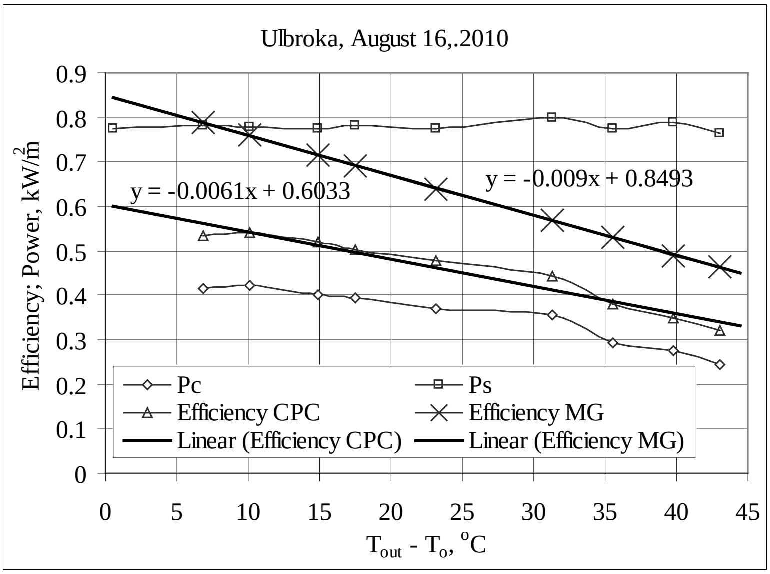


*Fig.7*. **Efficiency of CPC collector in comparison with the calculated efficiency of the metal-glass collector at the solar radiation intensity $P_s$**

As it is seen from Fig.6, at the solar radiation intensity about 780 W/m² the cell polycarbonate collector 36 litres of water (30 l in the hot water tank and 6 l into the collector's absorber) during 3 hours has heated by 43°C. During the heating time collector's coefficient of efficiency from 60% has decreased to 33% (Fig.7).

*Table 2.*

**Materials used for production of the CPC collector and its prices**

| N° | Material | Parameters of the material | Amount | Price, € |
|---|---|---|---|---|
| 1 | CPC sheet | Thickness 4 mm | 2 $m^2$ | 11.29 |
| 2 | CPC sheet | Thickness 6 mm | 2 $m^2$ | 18.36 |
| 3 | CPC section | U-shape 10 mm | 2.05 m | 4.49 |
| 4 | Wood-waste board OSB-3 | Thickness 3.8 mm | 2.05 $m^2$ | 10.78 |
| 5 | Wooden board | 30x100 mm | 6 m | 4.17 |
| 6 | Aluminium section | 20x20 mm | 6 m | 10.44 |
| 7 | Rockwool | Thickness 50 mm | 2 $m^2$ | 3.71 |
| 8 | Mirror film | Aluminium | 2 $m^2$ | 2.53 |
| 9 | Glue | Terostat | 78 ml | 2.85 |
| 10 | Thinner | Teroson | 100 ml | 0.90 |
| | | | **Total** | **69.52** |

In comparison with the metal-glass solar collector efficiency it is by 30% lower. Similar results are obtained by other researchers [4] and on the one hand it can be considered as the shortage of the CPC collectors. On the other hand, from Table 2 it is seen that the production of CPC collector is cheaper, only about 70 €, what is considerably lower than the price of metal-glass collector and its weight is only 13 kg/$m^2$.

## Conclusions

1. During the experimental examination the maximum temperature of the heat carrier reached 80°C at the intensity of solar radiation about 0.8 kW/$m^2$ and ambient air temperature about 32°C.
2. The efficiency of the cell polycarbonate collector was 33-60%, depending on the intensity of the solar radiation and surrounding air temperature. It is by 30% lower than of non-selective metal-glass collector, but its price is only about 40 €/$m^2$, which is much cheaper than of metal-glass collector.

**Acknowledgment**

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**References**

1. Дж. Твайделл, А.Уэйр. Возобновляемые источники энергии. М. Энергоиздат, 1990, 390 стр.
2. Д. Мак – Вейч. Применение солнечной энергии. Энергоиздат, 1981, 208 стр.
3. Н.В. Харченко. Индивидуальные солнечные установки. М. Энергоиздат, 1991, 208 стр.
4. А.В.Дорощенко, В.В.Костенюк. Перспективы развития солнечных коллекторов из полимерных материалов. Холодильная техника и технология, № 1 (117), Одесса, 2009.

**Anotācija.** *Izgatavots un eksperimentāli pārbaudīts saules enerģijas kolektors, kura absorberis un caurspīdīgais pārsegums izgatavoti no šūnu polikarbonāta loksnēm. Kolektora lietderības koeficients ir 33-60% robežās atkarībā no saules starojuma intensitātes un apkārtējā gaisa temperatūras.*

# THE TECHNOLOGICAL INVESTIGATIONS OF MANUFACTURING OF ENERGY CHIPS

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**Abstract.** *The methodology in Latvia forest industry provide to determine the quality of energy chips only in long- term storage places before selling. Due to the lack of hard empirical data about the quality parameters of energy chips in different phases of manufacturing process, this research paper consists of:*

- *the identification and analyses of the factors that influenced the values of energy chips quality features such as: bulk density, moisture content, ash content, higher and lower heating value according to actual moisture content and per dry mass of the chips;*
- *the methodology for determination the quality parameters of energy chips by analysis the wood moisture content and by choice the method of the manufacturing of energy chips.*

**Keywords**: *energy chips; technological investigations.*

## Ievads

The manufacturing of energy chips and transportation of assortiments to storage-s or to consumers is the process which includes the sequent technological phases: the choose of harvesting sites where the harvesting residues are planned to manufacture in energy chips [10,11,12], collection and storage of the harvesting residues in harvesting sites, chipping, loading, transportation, unloading and storage of energy chips.

To control the quality of energy chips and to manage the technological process of manufacturing, it is necessary to determine the moisture content of energy chips, ash content, bulk density and others factors that influenced the results in the controll points of the technological process.

Depends of dominant tree specie-s and forest types, the harvesting residues in harvesting sites mainly consists of branches and tree tops. The amount of the harvesting residues used in manufacturing of energy chips in deciduous forest stands reach 29% of amount of the round wood assortiments, in spruce forest stands 26%, in pine forest stands 14% [7,8,10].

At particular moisture content of energy chips the bulk density depends of the factors such as: branches, needles, bark, stem wood, heartwood and sapwood proportion in harvesting residues, the thickness of annual rings etc.

For the same tree species the bulk density could be with more or less deviation according to wood moisture content, forest type, forest stand age class, etc. For example, the bulk density of the alder wood (W=0% ) in rich deciduous forest type is 450kg/m$^3$ in wet deciduous forest type - 440kg/m$^3$ [2].

The methodology used in Latvia forest branch which determines the quality of energy chips only at the delivery places or storage places when loading of the ships are being, not providing the objective information about quality parameters of the delivered single loads.

As the result, the quality parameters of the energy chips loads could be reduced because of long -term storing. The quality of energy chips is dependent upon the source of the biomass and the techniques employed for comminution, handling and storage Chemical and biochemical reactions take place during the storage of chips. The reactions cause loss of dry matter, formation of fines, an increase in ash content, and a decrease of volatile materials. It was concluded that long-term storage of energy chips should be avoided [4, 5, 8, 9].

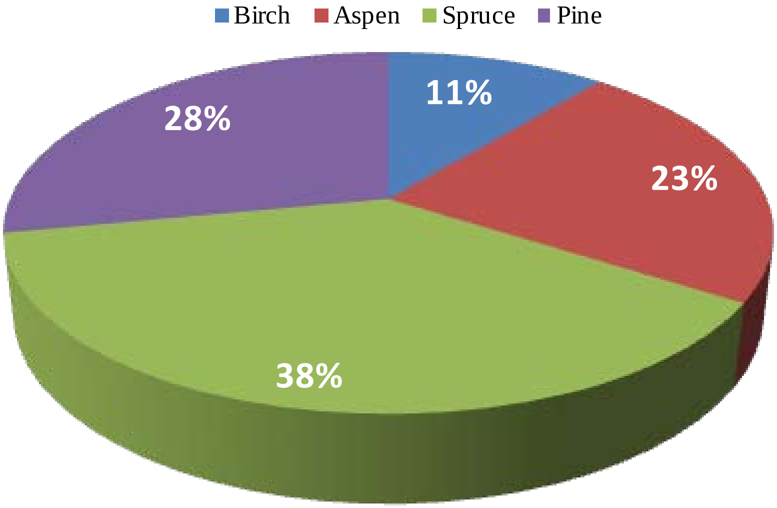


*Fig. 1.* **Dominant tree species in energy chips manufacturing places in 2010**

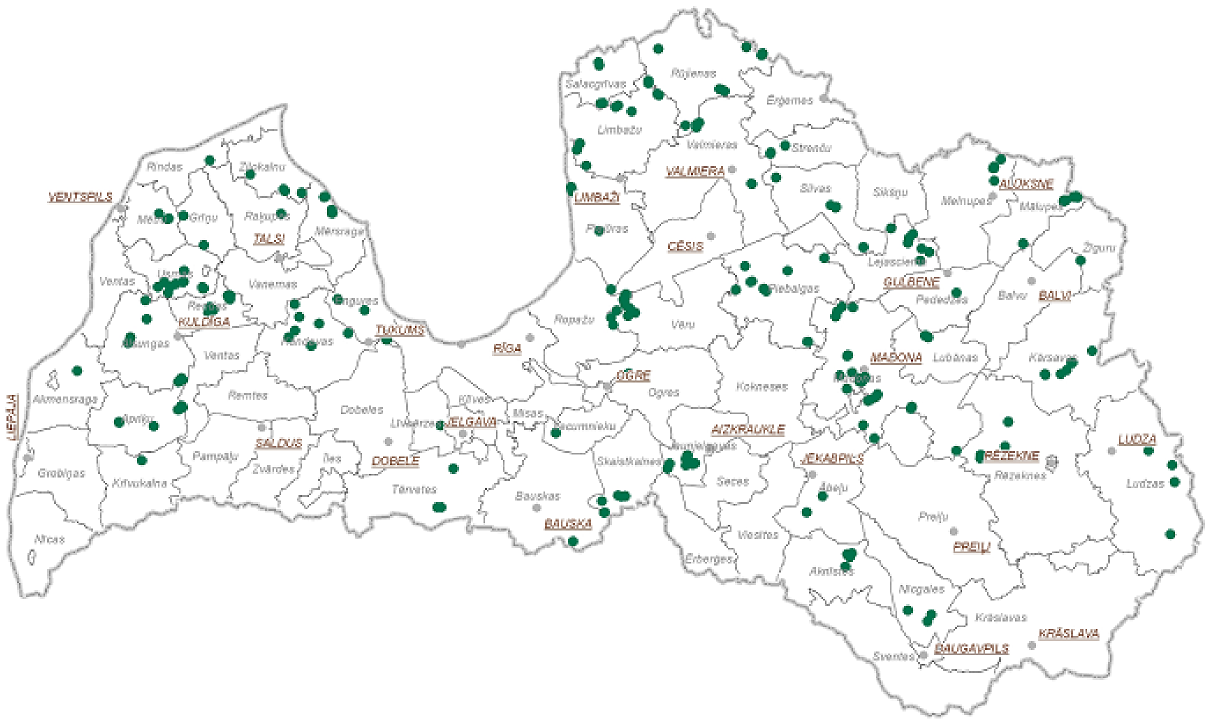


*Fig. 2.* **Dominant energy chips manufacturing places in 2010**

For objective assessment of the quality parameters of energy chips, adequate tasks have been handled:

1. to investigate the quality parameters of energy chips according to laboratory analyses according to standards: LVS CEN/TS 144774-2 (moisture content), LVS CEN/TS 14775 (ash content) un LVS CEN/TS 14918 (heating value) un LVS CEN/TS 15103 (bulk density) in the long –term energy chips storages for the period 01.2010. - 02.2011;
2. to investigate the quality parameters of moisture content of sample portions of energy chips in fixed long-term storage-s (longer 2 months) according to standard LVS CEN/TS

14778-2:2005 (sampling) and to determine the moisture zones (fig.10) at a cross section of a chip's pile;

3. unintentionally, in determined months, in different Latvia regions, in different forest types which is represented by single tree specie (for example in pine-spruce forest (formula:10 spruce)) to perform the chipping of the harvesting residues in harvesting sites 2-4 weeks after logging and to determine the quality of energy chips by testing of the samples according to standards: LVS CEN/TS 144774-2 (moisture content), LVS CEN/TS 14775 (ash content) un LVS CEN/TS 14918 (heating value) un LVS CEN/TS 15103 (bulk density) for the period 01.2010.- 02.2011. To compare the obtaining results to:
   3.1. the quality of the energy chips manufactured of the harvesting residues in the appropriate harvesting sites of forest types and wood species and stored in long–term storages( longer 6 months) for the corresponding period;
   3.2. the quality of energy chips stored in long–term storages( longer 2 months) for the corresponding period.
4. to perform the analysis of correlation of the factors: moisture content, bulk density, ash content and heating values of energy chips.

## The methods and materials

1. To achieve the objective, the analitical and experimental investigation have been performing based on technological process(2) (fig.3.) splitting it in main control points.

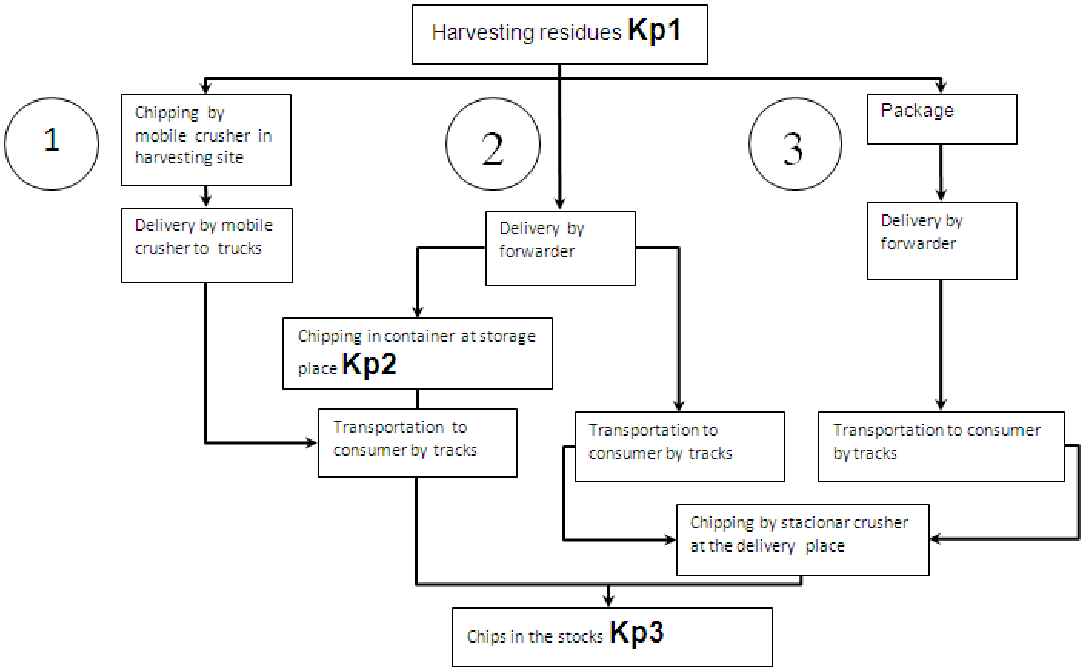


*Fig. 3.* **The scheme of the possible technological process of manufacturing of energy chips**

**1, 2, 3 –** the technological process**; Kp1, Kp2, Kp3** – the control points in the technological process for the energy chips quality control

2. Energy chips samples were taken in the control points of the technological process for investigation of the quality parameters according to standarts [13, 14, 15, 16, 17, 18].

## The results

1. The average parameters of energy chips bulk density have been determined **420-470kg/m$^3$** by wood moisture content(W=0% ) (fig.4.).

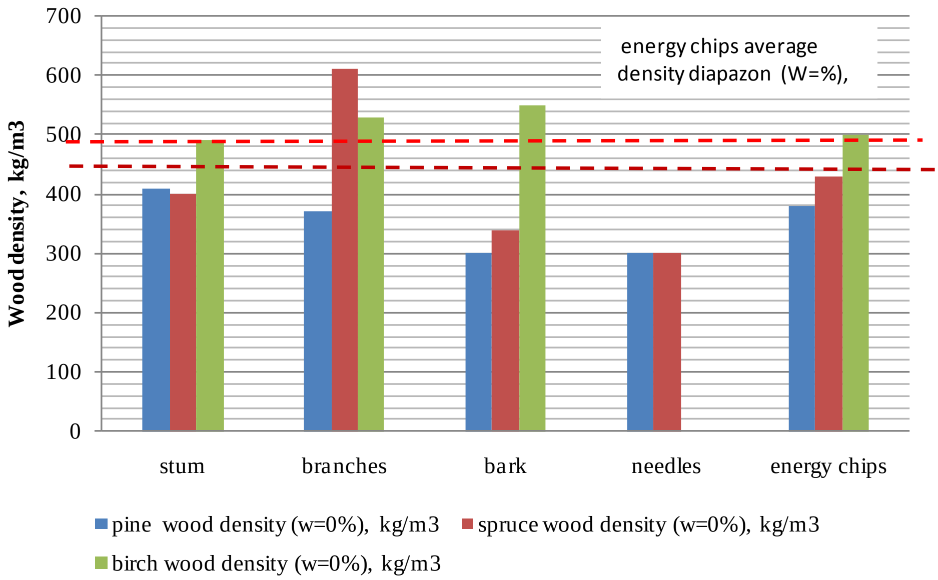


*Fig. 4.* **The average bulk density of energy chips and different parts of the tree**

2. Natural drying cannot bring the relative moisture content much more than 10 % below the original [12]. It is practically impossible to decrease the relative moisture content of harvesting residues bellow 30% (fig.5.).

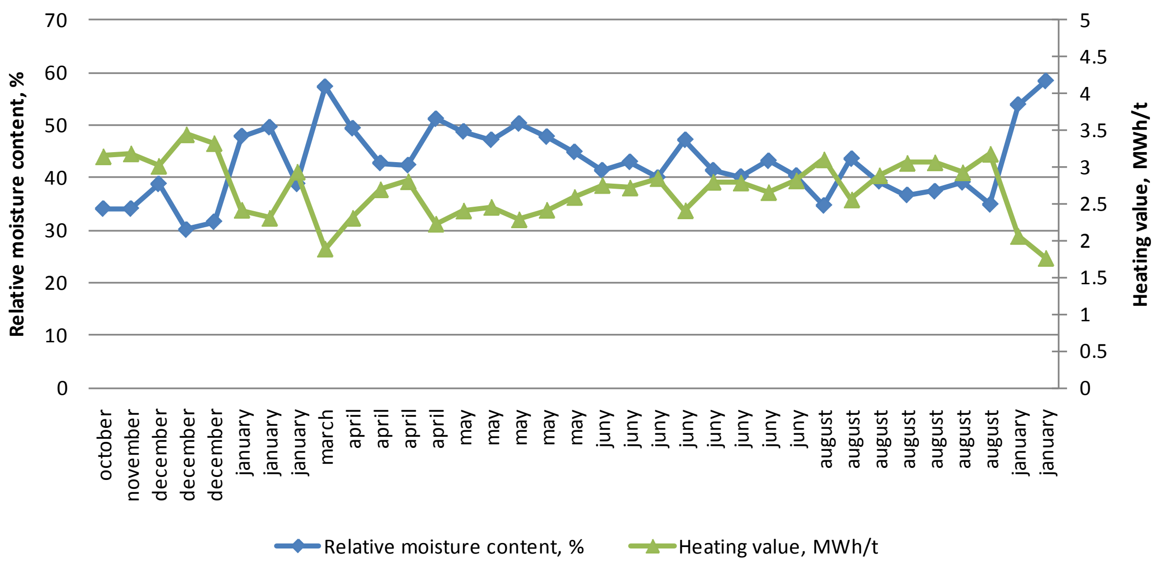


*Fig. 5.* **The dynamic of the relative moisture content and heating value parameters of energy chips for the period 2009-2010**

3. It is not advised to store the harvesting residues in athmosphere stocks for the period June-August. The optimal time for chipping is 2-4 weeks after logging when the moisture content of fresh wood (generally about 60%) is reduced till 30-35% (fig.6.). Prolonging the duration of the storage does not appear to have a positive effect.
By keeping harvesting residues in atmosphere stocks for prolonged term the relative moisture content in wood is increased, for example, in residues of some species like

spruce sapwood roti s created which aggravates parameters of heating value (fig.7.), but the number of measurements is unsufficient to make a general conclusion regarding impact wood fault on energy chops quality.

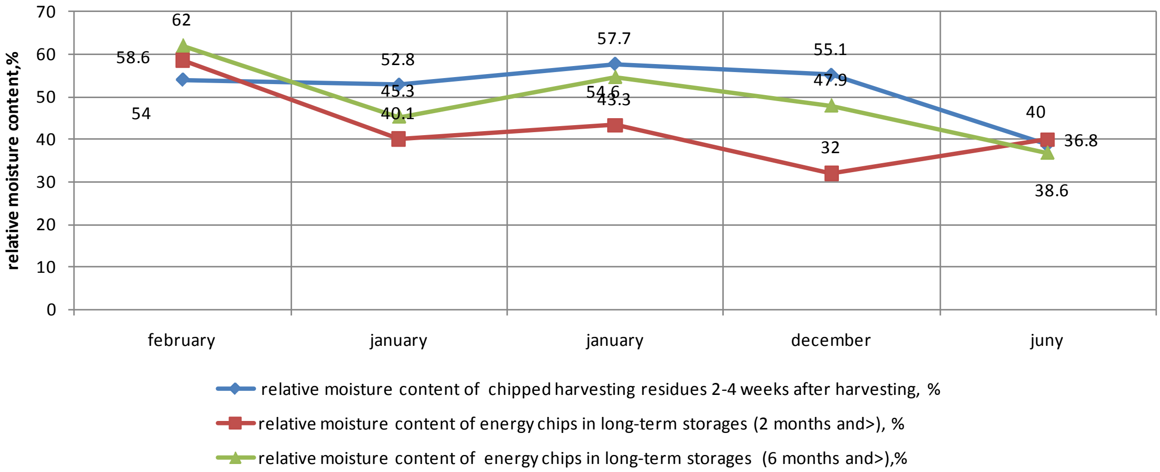


*Fig. 6.* **The selected technological process impact on relative moisture content of energy chips**

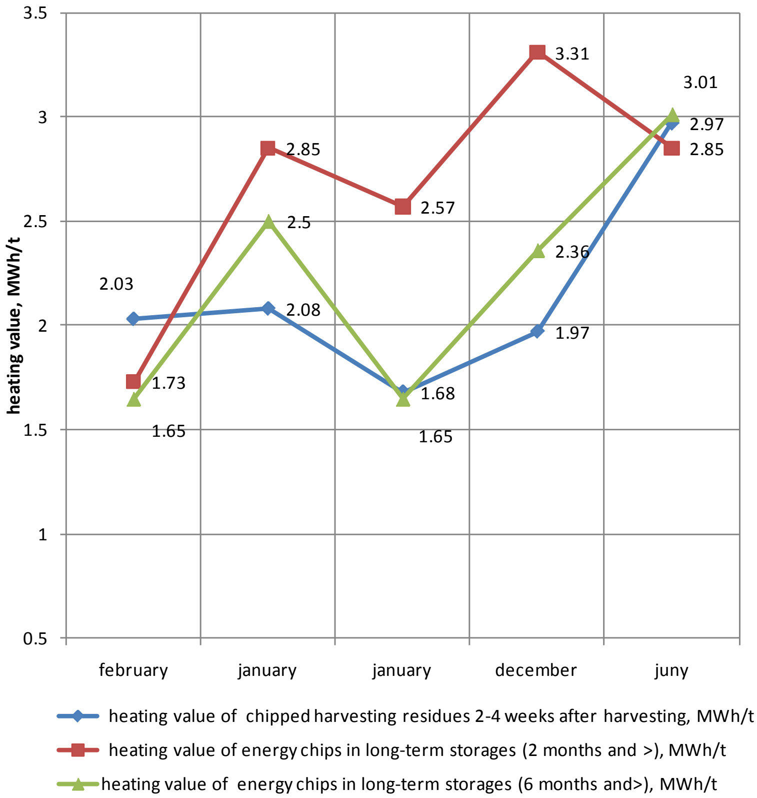


*Fig. 7.* **The selected technological process impact on heating value of energy chips**

4. The average relative wood moisture content of energy chips (42%) (fig.8.) and ash content (3.8%) (fig.9.) have been determined.

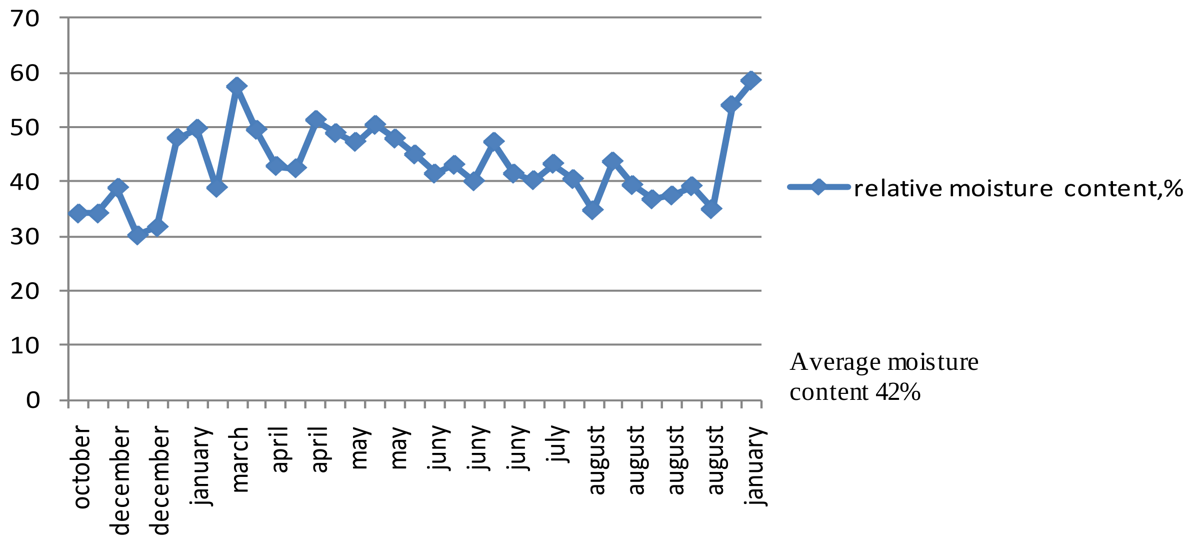


*Fig. 8.* **The dynamic of wood moisture content**

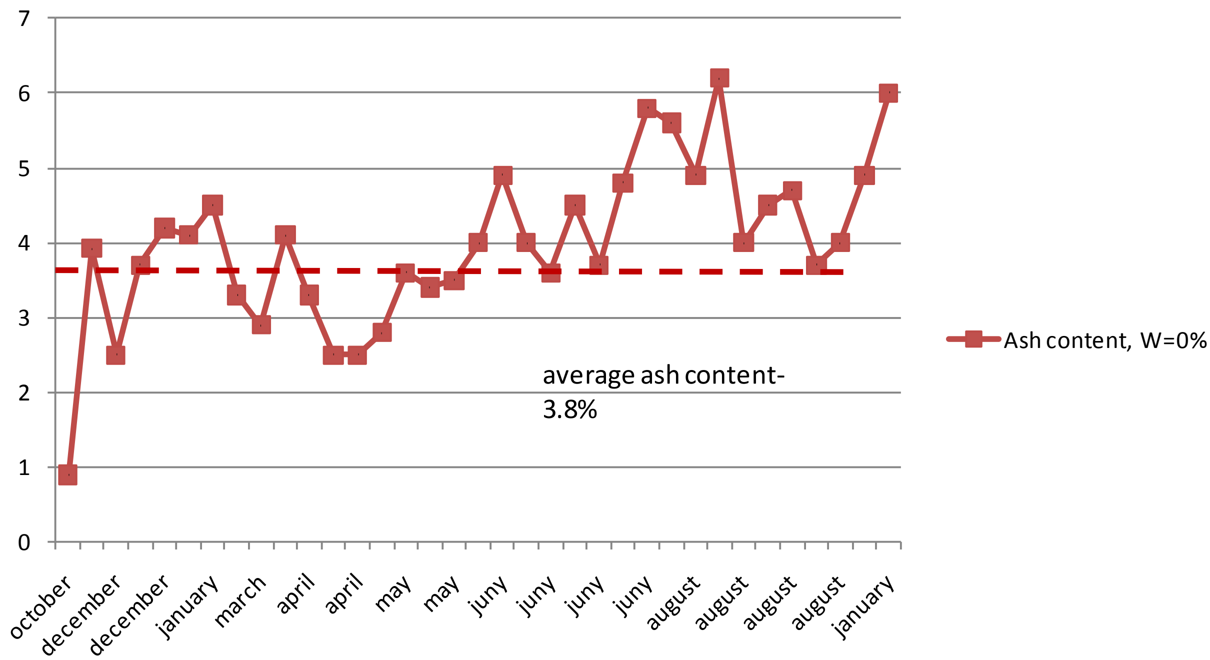


*Fig. 9.* **The dynamic of ash content**

5. The moisture zones and the wood relative moisture content in sampling places have been determinated in long-term energy chips storages (fig. 10.).

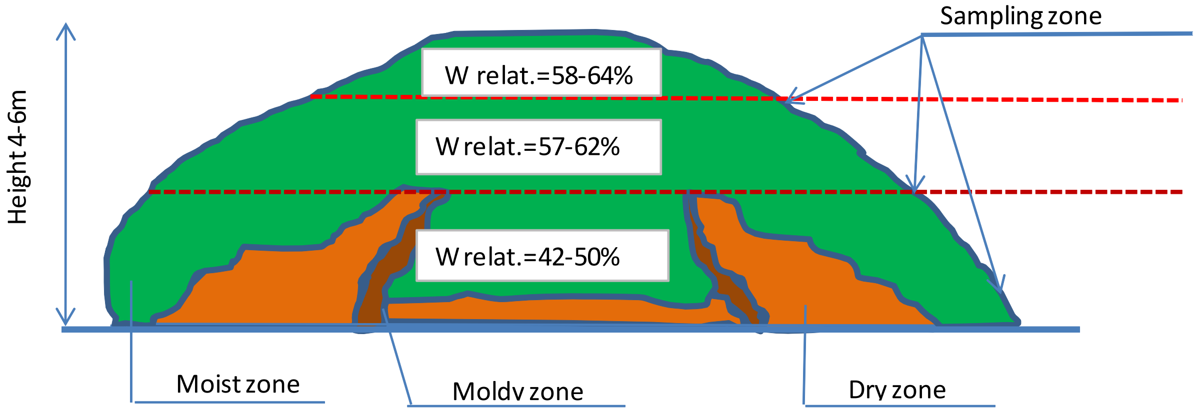


*Fig. 10.* **Moisture zones and relative wood moisture content in sampling places at a cross section of a energy chips pile (storing 10.2010-01.2011.; average moisture content 58.4%; amount 5003.71m$^3$ or 1696.44 t)**

6. The heating value changes of energy chips in 99.1 % cases can be explained by linear model of regression where the factor X – relative moisture content,%. The model of regression Y= -0.0573X+ 5.1568 (fig.11.).

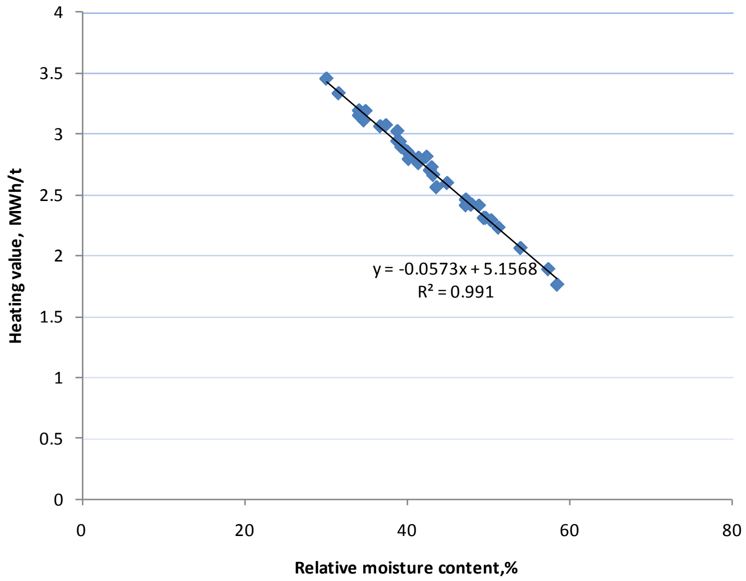


*Fig.11.* **The diagramm of correlation between the factrorial feature** ( relative wood moisture content, %) **and the feature of the result** (heating value, MWh/t)

7. The heating value changes of energy chips in 2 % cases can be explained by linear model of regression, where the factor X – ash content,%. The model of regression Y= -0.0544X+ 2.9135 (fig.12.).

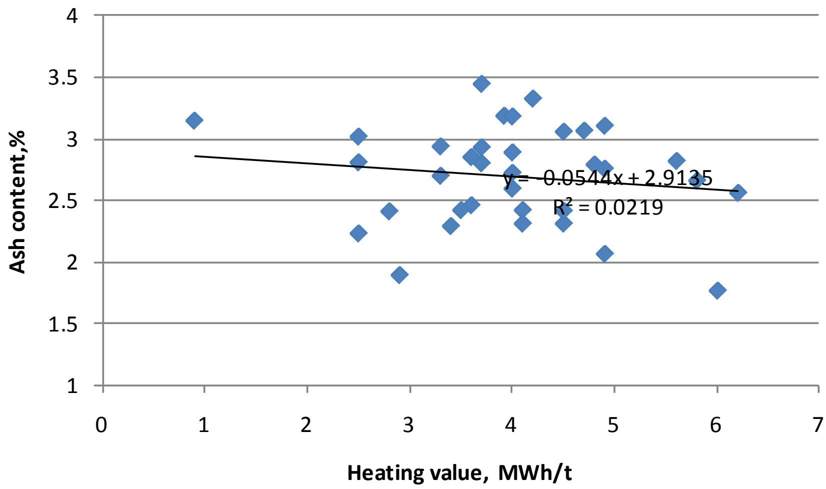


*Fig.12.* **The diagramm of correlation between the factrorial feature** ( ash content %) **and the feature of the result** (heating value, MWh/t)

8. The characteristic parameters represented the quality of energy chips manufacured in period 2010-2011 have been determinated (table 1).

*Table 1.*

**The results of the representative parameters of energy chips manufactured in 2010-2011**

| Standard | Parameter | Unit | Characteristic value | Variation |
|---|---|---|---|---|
| LVS CEN/TS 15103:2005 | Bulk density | kg/ loose $m^3$ | 320 | 290-440 |
| LVS CEN/TS 14775:2004 | Ash content, W=0% | % | 3.8 | 2.9-6.0 |
| LVS CEN/TS 14918:2005 | Hydrogen, W=0% | % | 6.1 | |
| | Oxygen, W=0% | % | 41 | |
| | Nitrogen, W=0% | % | 0.5 | |
| LVS CEN/TS 14918:2005 | Higher heating value per dry mass | MJ/kg | 20.3 | |
| | | MWh/t | 5.61 | 5.52-5.82 |
| | Lower heating value per dry mass | MJ/kg | 18.7 | |
| | | MWh/t | 5.19 | 5.18-5.277 |
| | Lower heating value according to moisure content of the chips | MJ/kg | 6.35 | |
| | | MWh/t | 2.394 | 1.763-3.098 |
| LVS CEN/TS 14774-2:2004 | Average relative moisture content | % | 42 | 30-58.4 |

## Conslussions

1. The quality parametrs of energy chips could be determined by testing the relative wood moisture content of harvesting residues (fig.13). In this way the storage costs and the impact on environment are decreased, the best solution for optimal technological process of energy chips manufacturing selection operatively could be accepted (fig.3.).

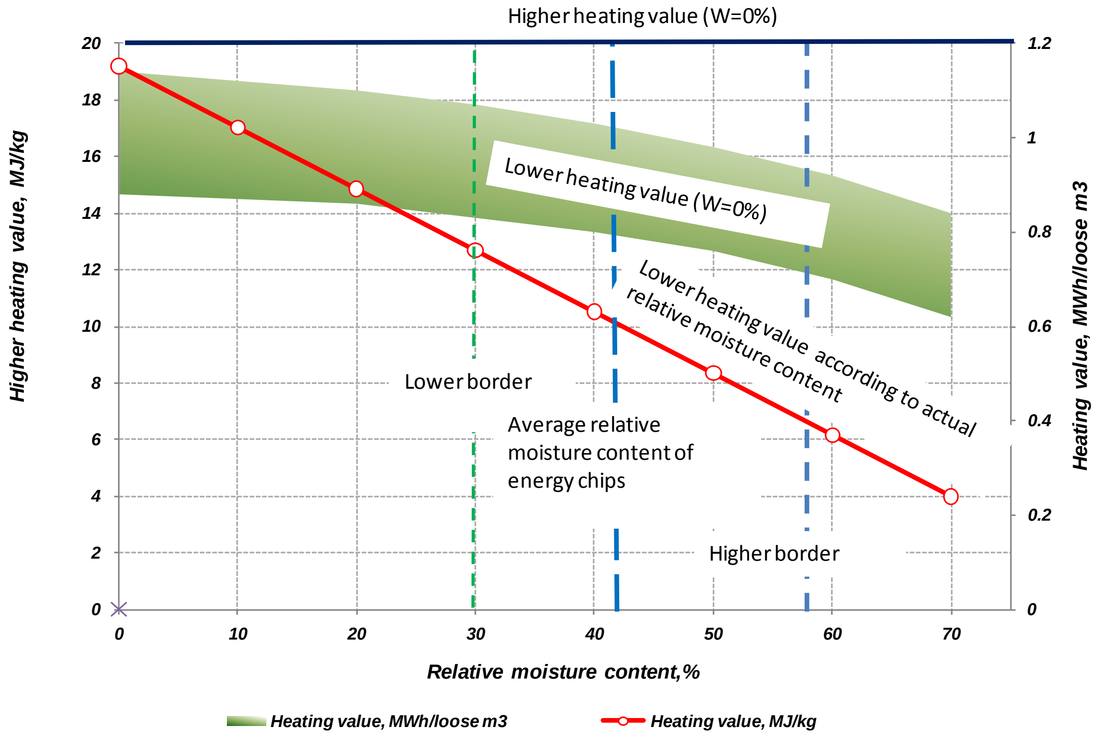


*Fig.13.* **The coherence diagramm between higher heating value and relative wood moisture content of energy chips in 2010 by average bulk density ( W= 0%) 420- 470 kg/m$^3$, average wood moisture content 42%, average ash content 3.8 and coherence 0.36 solid m$^3$=1 loose m$^3$**

2. The moisture content of fresh harvesting residues can vary from a minimum 40% to a maximum of 60%, depending on a number of the main factors, which generally include the species, the season and the tree portion. For example, moisture content of alder harvested in May is 45.6%, harvested in September – 40.1% [12]. The best period for chipping is when the wood relative moisture content is 35-40%. If in outumn-winter period it is impossible to ensure storaging of harvesting residues in storage less than 2 weeks, there is the risk that the higher zones of the stock is re-wetted and the relative wood moisture content increases up to 60%. In that case it is advised to choose the technological process (1) (fig.3.).

## Summary

Measurement methods based on the determination of dry weight, heating values and moisture content of energy chips used in long term energy chips storage places (piles in harbour) before selling give the final results characterized the quality of energy chips. By using only that methods, there are not possible to control the whole manufacturing process and to choose the best solution for decrease the risks to lose the quality of assortiment.

Accordingly, it is of great practical importance to establish a simple, effective and inexpensive methodology for determination the predict quality parameters of energy chip in the process of manufacturing..

This research paper focuses on the qualitative properties of energy chips. Energy chips often consists of material from various tree species with different proportions of wood, bark, foliage, twigs, needles, buds and even cones and different moisture content. Only by controlling the quality of energy chips in each phase of manufacturing it is possible to choose the correct technological solution.

## Bibliography


1. Brandel, G. 1990. Volume functions for individual trees, Swedish University of Agricultural Sciences, Dep. of Forest Yield Research, Report No. 26. (In Swedish; English summary.).
2. Bjorklund, T., Ferm, A. Pienikokoisen koivun ja harmaalepän biomassa ja tekniset ominaisuudet. Abstract: Biomass and technical properties of smallsized birch and grey alder // *Folia Forestalia*. 1982. № 500. P. 1-37.
3. Developing technology for large-scale production of forest chips. Helsinki. Wood Energy Technology Programme 1999-2003. Final report. Tekes. Technology Programme Report 6/2004.pp.53-62
4. Fagernäs, L., McKeough, P. & Kallio, M. 2004. Puupolttoaineiden esikäsittelyn kemialliset vaikutukset. Projektin loppuraportti
5. Flyktman, M. 2003. Polttoaineen kuivauksen kannattavuus laitoksilla. VTT Prosessit. Projektiraportti PRO2/T6510/02.
6. Hillebrand, K. & Nurmi, J. 2001. Hakkuutähteiden laadunhallinta. PUUT09. Puuenergian teknologiaohjelman vuosikirja. VTT Symposium 216:285–295
7. Hillebrand, K. & Nurmi, J. 2004. Energiapuun kuivatus ja varastointi – osaprojekti. Puuenergian teknologiaohjelman vuosikirja. VTT Symposium 231: 53–62.
8. Impola, R. 2001. Mekaanisen metsäteollisuuden sivutuotteiden polttoteknisten ominaisuuksien parantaminen. Osaraportti 2. Kuoren kosteuden alentaminen. VTT Energia. Tutkimusselostus ENE2/T0049/ 2001.
9. Kuoppamäki, R. 2001. Mekaanisen metsäteollisuuden sivutuotteiden polttoteknisten ominaisuuksien parantaminen. Osaraportti 3. Kuoren varastointi. VTT Energia. ENE2/T0019/2001.
10. Koksnes atliekas 2006: LVMI „Silava”. Pārskats par cirsmu atlieku apjoma un kvalitātes novērtēšanu. 2006.
11. Skogforsk&Silava 2006: T.Magnus, H.von Hofsten, H.Lundstrom, V.Lazdāns, A.Lazdiņš. Ciršanas atlieku kurināmā sagatavošana ar harvesteru izstrādātās kailcirtēs.2006.
12. http:/www. Biomasssaforestate.org/ilvasa/file/indaginesulla cippaturainItalia.pdf..
13. LVS CEN/TS 14778-2:2005 Paraugu ievākšana un sagatavošana.
14. LVS CEN/TS 15103:2005 Bēruma blīvums
15. LVS CEN/TS 14774-2:2004 Mitrums
16. LVS CEN/TS 14918:2004 Siltumspēja
17. LVS CEN/TS 15149-1:2006 Frakciju sastāvs
18. CEN/TS 14588:2003 Solid biofuels – Terminology, definitions and descriptions

# THE EFFECT OF STEAM EXPLOSION TREATMENT ON TECHNICAL HEMP FIBRES

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**Abstract.** *As hemp is a renewable resource with the high biomass yield it could be considered as potential abundant local biomass material for a wide range of applications. In this article hemp fibres architecture as a source of high strength cellulose are analysed. In experimental part steam explosion technology is applied to disintegrate technical hemp fibres to elementary fibres with the aim to find out the best way of procedure without usage to environment harmful chemical pre-treatments and looking forward to solve problems on further nano-level environment friendly hemp cellulose disintegration.*

**Keywords:** *auto-hydrolysis, cellulose, elementary fibres, hemp, steam explosion.*

## Introduction

Natural fibres as a renewable resource attract attention of scientists and practitioners and their applications are spreading in different industry branches. As cellulose is the most abundant biomass source from nature and has a very high theoretical strength 15 GPa and obtainable strength 8 GPa, an increasing number of research works are devoted to inventory local cellulose sources, understanding their specifics and potential applications. [1]
Rich in cellulose are bast fibers. Flax and hemp crops have been cultivated in Latvia from prehistoric times. Growing practice shows that biomass yield of hemp is high, and hemp improves the soil structure. [2], the tall plant stems of hemp suppress weeds effectively, and diseases and pests are rarely recorded. Thereby addition of pesticides is not needed. [3] It has also been reported that hemp produces several times more of the important cellulose source, fiber component, than other crops such as corn, kenaf [4], cotton. Therefore it is of interest to determine the potential for hemp fibres to find appropriate solutions and sustainable systems. Some newer industrial uses of plant cellulose have been developed and are found to be promising, one of them are cellulose nanoparticles usage as fillers to improve mechanical and barrier properties of biocomposites [5] that is rapid developing branch of biotechnology.
The fresh hemp stem consists of a hollow cylinder of 1-5 mm thick xylem covered by 10-50 μm cambium, 100-300 μm cortexes, 20-100 μm epidermis and 2-5 μm cuticles [6].
Hemp fibers are built from different hierarchical microstructures with a microfibrils as basic units (Figure 1, above). Microfibrils are embedded in a matrix of hemicelloses and/or lignin, and they form the different cell wall layers of an elementary fiber with an average diameter ranging from 10 to 50 μm [7].
Elementary fibers are bonded together with pectin and small amounts of lignin framing the next level of microstructure (Figure 1.) - technical fibers (filaments) with a diameters ranging from 50 to 100 μm [8]. Filaments are fixed together with a pectin-lignin matrix to form fibers bundles in a cortex of plant stems - bast fibres. A characteristic of the hemp fibers bundle is its high lignin content from 3.7 to 8% depending on the origin and variety of plant [9].
The cortex part of the hemp stems contains bundles of 100 to 300 primary and secondary single fibres with 4 to 6 sides. The single fibers length vary from 5 to 55 mm. Primary fibers nearest the stem surface are formed at the early growth stage during the phase of rapid

elongation and contribute to 92-95 % of the bast fibres located in cortex [11]. Cell wall thickness of primary fibers ~ 7-13 µm, length 20 mm. The secondary fibers near cambium layer are smaller (cell wall thickness 3-6 µm, length 2 mm) and placed only in the thick part of stem. The average area of the fiber cross-section is ~ 780 µm 2, lumen fraction 9% +/- 7 %. Therefore the load carrying of the single fibers are high (91 %) compared with wood fibers with larger lumens (small lumens has flax fibers too). [11]

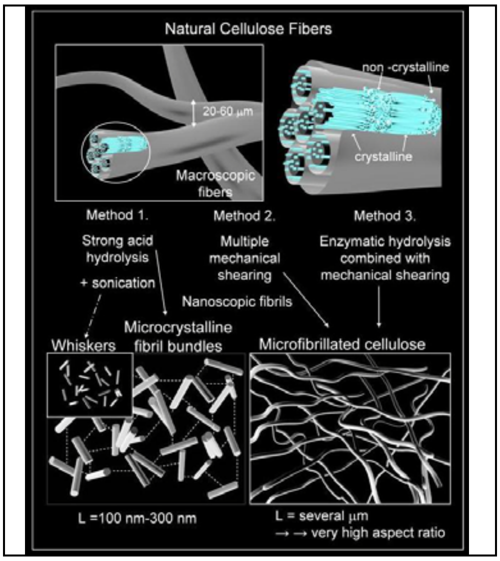


*Fig.1.* **Natural cellulose fibers structure** [10]

Microfibrils run roughly parallel to each other, following a steep helix around the cell [12]. Microfibrils are composed of crystalline and amorphous regions alternately and contain a large quantity of cellulose molecules. Individual cellulose microfibrils have diameters from 2 to 20 nm [13] and could be considered as a string of cellulose crystals linked along the microfibrils axis by disordered amorphous domains [14] as twists and kinks [15]. The cellulose amorphous regions are randomly oriented in spaghetti-like arrangement leading to a lower density compared to nanocrystaline regions [16].

Each type of cellulose has its own degree of polymerization and crystalline organization, which determine the fiber physical and mechanical properties. Preliminary investigations showed that degree of polymerization was 7000 in cellulose purified from raw hemp fibres [17]. The glucose monomers in cellulose form hydrogen bond both intermolecular within its own chain forming fibrils and intermolecular with neighboring chains forming microfibrils. These hydrogen bonds lead to formation of a linear crystalline structure with a high theoretical tensile strength of 15 GPa [18].

The properties of cellulose fibers are strongly influenced by many factors such as chemical composition, cellulose type, internal fiber structure, microfibrils angle, cell dimensions and defects, which differ from different parts of a plant as well as from different plants and varieties. The low overall angle of microfibrils in hemp fibers (4 degrees) explains the high stiffness in the range 50-80 Mpa (MFA in flax fibres 10 degrees) [11]. As a result technical hemp fibers are coarser, stiffer and more susceptible to damage in mechanical processing than technical flax fibers.

Most native celluloses are mixtures of cellulose $I_a$ and $I_ß$ [19]. Cellulose $I_a$ is a metastable form and can be converted into the $I_ß$ by an annealing treatment [20]. In these forms polysaccharide chains is similar although the hydrogen bonding pattern is different [21]. $I_ß$

form is present in the typical cellulose from annual plants. Some physical properties of cellulose fibers depend on the ratio between two allomorphs.

There are several different crystalline arrangements of cellulose which are denoted as cellulose I, II, III1, $III_2$, $IV_1$, and $IV_2$ and they can be inter-converted depending on chemical treatment and source [22]. Cellulose has outstanding properties at the crystal level. It has been reported that the crystal modulus of cellulose I may be as high as 138 GPa, cellulose II 88 GPa, cellulose III 73 GPa, and cellulose IV 75 GPa [23]. Hemp fibers and other plant fibers, including wood fibers mainly contain cellulose I [24].

Each natural fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a soft matrix composed of lignin and hemicellulose [25]. Hemicelluloses and to some extent pectin are the primary components of the binding substance of the elementary bast fibres, while lignin plays the part of stabilizer and screen for other fibrogenious substances [26]. The degree of polymerization in hemicellulose is much lower than in cellulose ranging from 20 to 300. By attached ferulic acid and *p*-coumaric residues, hemicellulose can form covalent bonds to lignin [27]. Hydrogen bonds are formed between xylan and cellulose. Due to this linking effect of hemicellulose, hemicellulose degradation leads to disintegration of the fibres into cellulose microfibrils resulting in lower fibre bundle strength [28]. Mainly the acid residues attached to hemicellulose make it highly hydrophilic and increase the fibres water uptake, which increases the risk of microbiological fibres degradation. It has been found that hemicellulose is thermally degraded at a lower temperature (150-180°C) than cellulose (200-230°C) by wet oxidation [29] and composite manufacturing [30]. The amorphous regions are susceptible to acid attack and, under controlled conditions, could be removed leaving crystalline regions intact. Since hemp belongs to the Angiosperm phylum, it contains hardwood lignin of coniferyl alcohol, sinapyl alcohol and a minor content of *p*-coumaryl alcohol [31].

To prepare harvested hemp to further processing different technologies could be used. During water retting or dew-retting the hemp bast is separated into large fibres bundles, after additional treatment is required to defibrillation the fibres bundles into single fibres and small fibres bundles. For this purpose degradation or disruption of the middle lamellae between the single fibres are necessary. Enzyme treatment [32] [33] [34], wet oxidation [35] [36] and NaOH treatment [37] [38] can degrade pectin and lignin in the middle lamellae between the single fibres. Physical defibrillation methods include steam explosion [39] [40] and ultrasound treatment [41].

As the content of cellulose in hemp fibres increased by steam explosion in retted hemp fibres from 73% to 85-90%, but in raw hemp fibres from 60-64% to 73-75% [11] it is obvious that retting has to be included before steam explosion. The results of other investigation shows that most lignin was removed when oxidative conditions were applied since it is decomposed to low molecular phenolic compounds and oxidized to carboxylic acids [42].

## Materials and methods

Disintegration of dew-retted hemp fibres of variety Bialobrzeckie grown in Agricultural Science Centre of Latgale by steam explosion was investigated.

Steam explosion auto-hydrolysis (also referred as steam explosion, steam explosion pulping, flash auto-hydrolysis or steam cracking) is principally a simple technique [42]. The biomass (wood or non-wood forest material, agricultural waste and fibre materials, waste from forestry, municipal and plantation management) for sustainable use is treated with saturated steam, usually at pressures up to 40 atmospheres. The treatment time varies from some seconds to some minutes.

After the treatment, within a split second, the biomass is decompressed (exploded) to one atmosphere. Empirically, the so-called severity parameter or the reaction ordinate $R_o$ can be expressed as [42]:

$$R_o = t * \exp [(T- 100)/ 14.75] \quad (1)$$

where: duration of treatment (t, minutes) and temperature (T, $^oC$) express the SEA severity against the base temperature $T_{base\ or\ reference}$ = 100 $^oC$. $R_o$ dimension is minutes but in practice using log $R_o$. In current article log$R_o$ fall in range from 2,36 to 3,42 (Table 1).

Similar SEA results may be achieved at different combinations of t and T. However, there is certainly a contribution from other factors such as moisture content of the sample, size of particles, etc.

Among the number of chemical and physical processes occurring during the SEA treatment, two are most important:

- a functional groups are cut off during the process and thereby acid molecules are formed in the system (for example, acetic groups in hemicellululoses provide formation of the acetic acid). These newly formed acids act as catalysts of hydrolysis of the treated material (auto-hydrolysis);
- after abrupt release of the pressure at the end of the SEA process, the difference of pressure in the tissues of the material and surroundings blasts the material providing an effective defibrillation of wood or other plant biomass.

Since the lignocellulose material, under conditions of steam explosion, can provide "self-sufficient" chemical and physical transformation, both the processes, hydrolysis and defibrillation, can be achieved just by the "tools" inherent in the system itself, without any additional reagents except steam. Further fractionation of the biomass products after SEA is rather simple.

In preparation stage raw fibers were first combed to remove shives and other contaminants, after three groups of samples for experiments were prepared: for control samples group primary hemp fibres were cut into the 2 mm long pieces, mass of one sample ~ 100 g. For another groups of samples alkali pre-treatment at temperature 80 °C for one hour with two different concentrations - 3% NaOH and 4% NaOH were carried out with following washing and drying under normal circumstances at room temperature (~20 °C). Experiment parameters and results are shown in Table 1.

*Table 1.*

**Experiment parameters**

| Sample weight, g | Moisture, % | | Evaporable fractions, % | STEX parameters | | | |
|---|---|---|---|---|---|---|---|
| | Before STEX | After STEX | | Time, s | Temperature, $^0C$ | Pressure, bar | log$R_0$ |
| ~ 6,1 | 65,1 | ~ 75 | 7,0 | 60 | 180 | 10 | 2,36 |
| ~ 6,1 | 65,1 | ~ 75 | 7,0 | 60 | 200 | 16 | 2,94 |
| ~ 6,1 | 65,1 | ~ 75 | 8,4 | 60 | 220 | 23 | 3,42 |

After drying, they were combed and chopped to a length of about 2 mm. The bleached fibers were subjected to disintegration by steam explosion during 60 seconds at high pressure in range from 10 to 23 bars and temperature 180-220 $^0C$.

## Results and discussion

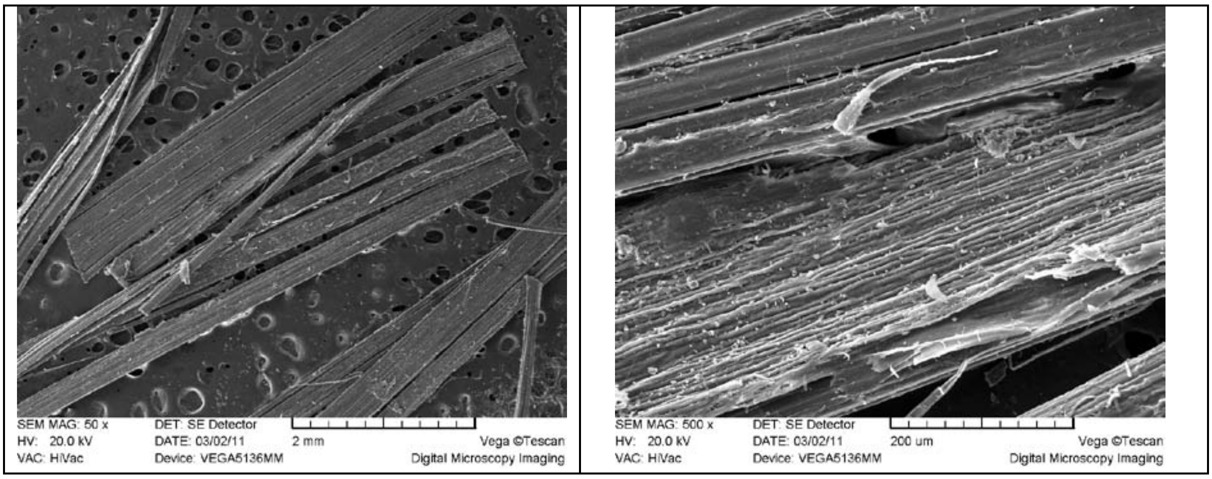


*Fig 2*. **SEM micrographs of control group sample before steam explosion**

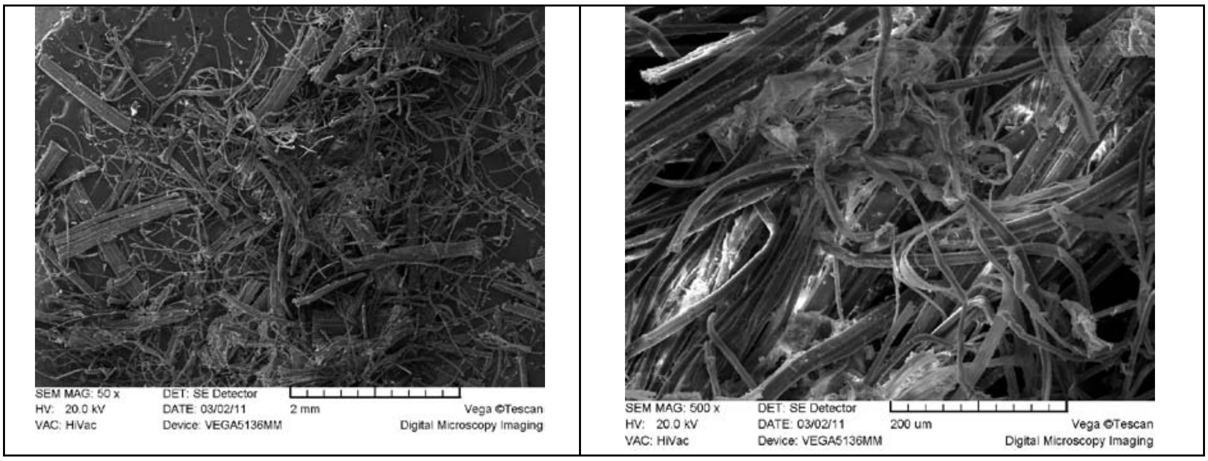


*Fig 3*. **SEM micrographs of control group sample after steam explosion**

Micrographs of control group samples subjected to steam explosion during 60 s at temperature 220 $^{0}$C and pressure 23 bars are presented in Fig. 3.

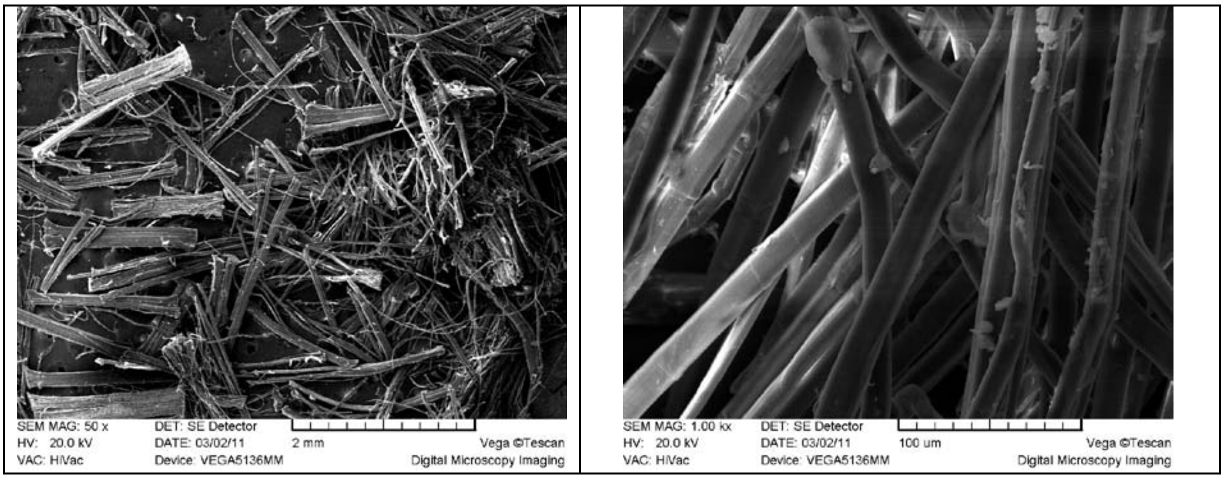


*Fig 4*. **SEM micrographs of alkali (NaOH 4 %) pre-treated group samples after steam explosion**

Comparison of samples micrographs before steam explosion in Figure 2 and Figure 3 shows that disruption of the middle lamellae between the single fibres are happen during steam explosion, only few pieces left undispersed (Fig. 3, left), average diameters of fibres 10-20 μm.
There are two families of nano-sized cellulose particles and corresponding technologies for their preparation are reported [16]: 1) cellulose nanocrystals (whiskers), 2) microfibrillated cellulose MFC (Figure 1). The raw fibers are first milled and then submitted to alkali (80 $^0$C, NaOH 4%) and bleaching treatments ($NaClO_2$/ acetate buffer, pH 4,8; 80 $^0$C) to eliminate lignin and hemicelluloses with the leaving cellulose moieties intact. Bleached fibers are subjected to hydrolyzing (acid hydrolysis treatment under controlled) or disintegration (mechanical shearing at high pressure) [16]. As show our experiments, steam explosion in the range of investigated parameters allow disintegrated retted hemp technical fibres to elementary fibres or at least to loosen bonds between elementary fibres without using alkali and/or acid treatments therefore prepared hemp fibres material with 85-90 % high cellulose content for further nano-scaled disintegration by other ecological methods.

## Conclusions

Hemp fibres are cellulose rich raw material with complicate inner structure, essentially a composite in which rigid cellulose microfibrils are embedded in a soft matrix composed of lignin-pectin and hemicellulose. For further processing degradation or disruption of the middle lamellae between the single fibres could be realized by physical defibrillation methods including steam explosion or chemical methods.
Steam explosion of untreated and alkali pre-treated hemp fibres show, that nor 3%, nor 4% alkali pre-treatment does not improve level of fibres disintegration therefore retted hemp fibres could be subjected to steam explosion without chemical pre-treatment.
Further investigations are needed to exploit/develop ecofriendly nanolevel disintegration possibilities.

## Acknowledgements

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### References

1. Lilholt, H., Lawther, J.M., 2000. Natural organic fibres. Elsevier. In: Kelly, A. and Zweben, C. (Ed.), comprehensive composite materials, vol. 1, pp. 303-325.
2. Bois W.F. Hemp as a raw material for the paper industry. Bedrijfsontwikkeling, 1982,13, 851-856
3. Robinson R. The great book of hemp. 1996, Park Street Press, Main; Roe P.J., Ansell M.P. Jute-reinforced polyester composites. J Mater Sci, 1985, 20, 4015-4020.
4. Werf H.M.G., Mathijssen E.W.J.M., Haverkort A.J. The potential of hemp for sustainable fibre production: a crop physiological appraisal. Annals of Applied Biology, 1996, 129, 109-123.
5. Fan M. Elementary hemp fibres and strength. BioResources 5(4), 2010, 2307-2322.
6. Garcia-Jaldon, C., Dupeyre, D., Vignon, M.R. Fibres from semi-retted hemp bundles by steam explosion treatment. Biomass Bioenergy, 1998, 14, 251-260.
7. Candilo M., Ranalli P. and Bozzi C. Preliminary results of tests facing with the controlled retting of hemp. Industrial crops and products, 2003, 11, 197-203.
8. Bhuvan M. Mohini P. and Sain M. Mechanical properties of thermally treated hemp fibres. J. Material research innovation, 2003, 7(4), 231-238.
9. Sedelnik N. Properties of hemp fibre cottonised by biological modification of hemp hackling noils. Fibres and textiles in Eastern Europe. January/March 2004, Vol. 12, No.1 (45).
10. http://i243.photobucket.com/.

11. Thygesen A. Properties of hemp fibre polymer composites -An optimisation of fibre properties using novel defibration methods and fibres characterisation, PhD thesis, The Royal Agricultural and Veterinary University of Denmark, ISBN 87-550-3440-3.
12. Bos H.L. and Donald A.M. In situ ESEM study of the deformation of elementary flax fibres. J. Material Science,1999, 34, 3029-3034.
13. Lu J., Askeland P., Drzal L.T. Surface modification of microfibrillated cellulose for epoxy composite applications. Polymer, 2008, 49, 1285-1296.
14. Azizi Samir M.A.S., Alloin F., Dufresne A. Review of recent research into cellulosic whiskers, their properties and their applications in nanocomposite field. Biomacromolecules, 2005, 6, 612-626.
15. Montari S., Roumani M., Heux L., Vignon M. R. Topochemistry of carbaxylated cellulose nanocrystals resulting from TEMP-mediated oxidation. Maxromolecules, 2005, 38, 1665-1671.
16. Siqueira G., Bras J. And Dufresne A. Cellulosic bionanocomposites: a review of preparation, properties, applications. Polimers 2010, 2, p. 728-765. ISSN 2073-4360.
17. Thygesen, A., Madsen, F.T., Lilholt, H, Felby, C., Thomsen, A.B., 2002. Changes in chemical composition, degree of crystallisation and polymerisation of cellulose in hemp fibres caused by pre-treatment. In: Lilholt, H., Madsen, B., Toftegaard, H., Cendre, E., Megnis, M., Mikkelsen, L.P., Sørensen, B.F. (Ed.), Sustainable natural and polymeric composites - science and technology.
18. Lilholt, H., Lawther, J.M., 2000. Natural organic fibres. Elsevier. In: Kelly, A. and Zweben, C. (Ed.), Comprehensive composite materials, vol. 1, pp. 303-325.
19. Atalla R.H., VanderHart L.D. Native cellulose: A composite of two distinct crystaline forms. Science, 1984, 223, 283-285.
20. Sahena I. M., Brown R.M.J. Cellulose biosynthesis: current views and envolwing concepts. Ann. Bot., 2005, 96, 9-21.
21. Souza Lima M.M., Borsali R.M.J. Rodlike cellulose microcrystals: structure, properties and applications. Macromol. Rapid.Commun, 2004, 25, 771-787.
22. Dufresne A. Polymer nanocomposites from biological sources. In: Encyclopdia of nanosciences and nanotechnology, 3nd ed, Nalwa H.S.,ed.American Scientific Publisher, Valencia, C.A., USA.
23. Nishino T. Natural fibre resources. In: Green Composites, ed: C.Baillie, 2004, Woodhead Publishing Ltd., England.
24. Fan M.Characterization and performance of elementary hemp fibres: factors influencing tensile strength. BioResources 5(4), 2307-2322), 2010.
25. Gravitis J. Nano level structures in wood cell wall composites. Cellulose Chemistry and Technology, 2006, 40(5), 291-298.
26. Szalkowski Z.: Podstawy chemicznej technologii surowcov I wlokeien lykowych, Warszawa, 1967.
27. Bjerre AB, Schmidt AS. Development of chemical and biological processes for production of bioethanol: Optimization of the wet oxidation process and characterization of products. 1997, Riso-R-967(EN), Riso National Laboratory: pp 5-9.
28. Morvan C, Jauneau A, Flaman A, Millet J, Demarty M. Degradation of flax polysaccharides with purified endo-polygalacturonase. Carbohydrate Polymers, 1990,13, 149-163.
29. Bjerre AB, Olesen AB, Fernqvist T, Plöger A, Schmidt AS. Pretreatment of wheat straw using combined wet oxidation and alkaline hydrolysis resulting in convertible cellulose and hemicellulose. Biotechnol Bioeng, 1996, 49, 568-577.
30. Madsen, B., 2004. Properties of plant fibre yarn polymer composites – An experimental study. Ph.D. thesis, BYG-DTU, Technical University of Denmark, ISBN 87-7877-145-5.
31. Thygesen A., Geoffrey Daniel, Hans Lilholt, Thomsen A.B. Hemp fiber microstructure and use of fungal defibration to obtain fibers for composite materials. Journal of Natural fibers, 2005, 2(4), 19-37.
32. Thygesen A., Thomsen A.B., Skammelsen Schmidt A., Jorgensen H., Ahring B.K., Olsson L. Production of cellulose and hemicellulose-degrading enzymes by filamentous fungi cultivated on wet-oxidised wheat straw. Enzyme Microbial Technology, 2003, 32 (5), 606-615.
33. Madsen F.T., Burgert I., Jungnikl K., Felby C., Thomsen A.B. Effect of enzyme treatment and steam explosion on tensile properties of single hemp fiber. 12th International Symposium on Wood and Pulping Chemistry (ISWPC), 2003, Madison, P80.
34. Brühlmann F., Leupin M., Erismann K.H., Fiechter A. Enzymatic degumming of ramie bast fibers. Journal of Biotechnology, 2000,76, 43-50.
35. Thomsen A.B., Rasmussen S., Bohn V., Nielsen K.V., Thygesen A., Hemp raw materials: The effect of cultivar, growth conditions and pretreatment on the chemical composition of the fibres. Riso National Laboratory. Report No.: R-1507.
36. Mwaikambo LY, Ansell MP. The effect of chemical treatment on the properties of hemp, sisal, jute and kapok for composite reinforcement. Die Angewandte Makromolekylare Chemie, 1999, 272, 108-116.

37. Wang H.M., Postle R., Kessler R.W., Kessler W. Removing pectin and lignin during chemical processing of hemp for textile applications. Textile Research Journal, , 2003, 73, 664-669.
38. Garcia-Jaldon C., Dupeyre D., Vignon M.R. Fibres from semi-retted hemp bundles by steam explosion treatment. Biomass & Bioenergy, , 1998, 14, 251-260.
39. Madsen et al., 2003; Vignon M.R., Garcia-Jaldon C., Dupeyre D. Steam explosion of the woody hemp chénevotte. International Journal of Biological Macromolecules, 1995, 17, 395-404.
40. Zimmer H, Kloss D. Ultraschallaufschluss von Hanf. Ziele-Technologie-Anwendung-Resultate-Qualitätsmanagement. Proceedings of the Bioresource Hemp '95 Symposium; Frankfurt, Germany. Nova-Institute.
41. Klinke H.B., Ahring B.K., Schmidt A.S., Thomsen A.B. Characterization of degradation products from alkaline wet oxidation of wheat straw. Bioresour Technol, 2002, 82. 15-26.
42. Gravitis J., Dobele G., Abolins J., Tupciauskas R. & Veveris A. Non-sulphur lignin studies under biorefinery concept and evaluation of energy consumption by steam explosion. Presentation, Paris, January, 2011.

# BIOMASS YIELD OF DIFFERENT PLANTS FOR BIOGAS PRODUCTION

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**Abstract.** *In order to investigate yield potential of plants probably suitable for biogas production preliminary field trials were carried out at Research and Study farm "Vecauce" in 2010 using eight annual plant species: maize, winter oil-seed rape, oil radish, sunflower, foxtail millet, millet, hemp and amaranth. All species (except oil radish) were represented with several varieties, and some species were harvested at 2-3 development stages. Obtained fresh biomass yield was from 33.05 (millet 'Rudes') till 74.60 (amaranth 'Raudonukai') t ha$^{-1}$, but dry matter yield – from 6.98 (amaranth 'Margiai') till 22.05 (winter oil-seed rape 'Excalibur' at GS 85) t ha$^{-1}$. It was self-evident that biomass yield substantially depended on used species, but also variety influence within the species was relevant. Our data clearly demonstrated substantial ($p<0.05$) harvest time influence by harvesting winter oil-seed rape and maize at three different times; the highest yield was obtained for rape at GS 85, but for maize – in early October. Studies are only at the initial stage and have to be continued.*

**Keywords:** *biomass plants, species, varieties, harvest timing, yield.*

## Introduction

Suitability of plants' biomass for biogas production is widely investigated in other European countries. As biogas production from agricultural substrates in Latvia has been started only since 2008, we have lack of knowledge about the possibly suitable plants, their varieties, and best growing methods. Plants were investigated mainly for forage production before, but possibility to grow some of them was forgotten at all. Researchers from Western Europe have mentioned two main factors for choice of plant species or materials for biogas production: specific outcome of methane from 1 kg of organic dry matter, and biomass yield from 1 ha.

Large part of biogas production success is related to growing technology including choice of proper species and varieties, harvest timing, chopping and ensiling of biomass. Maize (*Zea mays* L.) is considered as the very suitable plant for using as biogas substrate, but success can not be always guarantied growing only one plant species. Energy crop rotations are practiced in European countries; it means that one energy crop followed by another provides obtaining biomass twice a year, suppress weed growth and save costs. Two plant species can be grown simultaneously, for example maize and sunflower or maize and millet. Such method increases nutrients content and stabilizes crop yield during dry seasons.

The aim of our research was to clear possibility to grow eight different plant species, including untraditional species, for biomass production in Latvian conditions, to compare their biomass yield level, and to start to clarify the main yield determining factors.

## Materials and methods

In order to investigate yield potential of plants probably suitable for biogas production in Latvia field trials of different importance were carried out at Research and Study farm "Vecauce" (latitude: N 56º 28´, longitude: E 22º 53´) of Latvia University of Agriculture in 2010. Three trial blocks were established using eight annual plant species: maize (*Zea mays*) (1$^{st}$ block; 4 replications, 3 harvest dates, four hybrids: 'Tango', 'Celido', 'Ronaldinio', 'Fernandez'), winter oil-seed rape (*Brassica napus*) (2$^{nd}$ block, 4 replications, 3 harvest dates, two varieties: line 'Ovation', hybrid – 'Excalibur'), and preliminary trial in 3$^{rd}$ block with 6 plant species (was not replicated): oil radish (*Raphanus sativus*), sunflower (*Helianthus*

*annuus*), foxtail millet (F. millet further in the text) *Setaria italica*, hemp (*Cannabis sativa*), millet (*Panicum miliaceum*), amaranth (*Amaranthus*). All species were represented with several varieties (except oil radish – one variety 'Gausiai' was used): sunflower – 'Alussa', 'Alyssa' and 'Pacific'; F. millet – 'Rudukes' and 'Aukses'; hemp – 'Bialobrezskie', 'Felina 32', 'Epsilon 68', 'Benico', 'Santhica', 'Uso 31', 'Futura 75' and 'Fedora 17'; millet – 'Gelsves', 'Juosves' and 'Rudes'; amaranth – 'Geltonukai', 'Raudonukai' and 'Margiai'.
Soil in the trials' site was soil-gleyic loam with pH KCl = 6.7 to 7.2; content of available for plants K was 146 (winter oil-seed rape – 2$^{nd}$ block) to 190 (maize and other species: 1$^{st}$ and 3$^{rd}$ block) mg kg$^{-1}$ and P – 121 (winter oil-seed rape – 2$^{nd}$ block) to 232 (maize and other species: 1$^{st}$ and 3$^{rd}$ block) mg kg$^{-1}$; humus content 27 to 30 g kg$^{-1}$. Traditional soil tillage with mouldboard ploughing in autumn or month before sowing (winter oil-seed rape) was used in all trials' blocks. Sowing was done according to the described design given in Table 1. Crops were fertilized using a complex mineral fertilizer at the rate of N 18 kg ha$^{-1}$, P 34 kg ha$^{-1}$, K 75 kg ha$^{-1}$ before sowing. Top-dressing with nitrogen fertilizer was done twice for maize and winter oilseed rape (70 + 70 kg N ha$^{-1}$), hemp and sunflower (70 + 60 kg N ha$^{-1}$), and 70 kg N ha$^{-1}$ for other crops. Sowing rates and dates of all crops are shown in Table 1.

*Table 1.*

**Sowing rate and sowing date of crops**

| Type | Sowing date | Sowing rate |
|---|---|---|
| Maize | 06.05.2010 | 83300 kernels ha$^{-1}$ |
| Winter oilseed rape | 18.08.2009. | line - 80 seeds m$^{-2}$<br>hybrid - 50 seeds m$^{-2}$ |
| Sunflower | 19.05.2010. | 83300 seeds ha$^{-1}$ |
| Oil radish | 17.05.2010 | 30 kg ha$^{-1}$ |
| Setaria italica | 17.05.2010 | 15 kg ha$^{-1}$ |
| Hemp | 17.05.2010 | 70 kg ha$^{-1}$ |
| Millet | 17.05.2010 | 25 kg ha$^{-1}$ |
| Amaranth | 17.05.2010 | 17 kg ha$^{-1}$ |

Weeds were controlled using herbicides in winter oilseed rape (GS – full emergence) and maize (at 3-5 leaf stage) trials. Butisan star s.c. (metasachlor, 333 g L$^{-1}$, + kvinmerac, 83 g L$^{-1}$) 2.5 L ha$^{-1}$ was applied for oilseed rape, and Maisters OD 61 s.c. (foramsulfuron, 30 g L-$^{1}$, + natrium metil-jodosulfuron, 1 g L$^{-1}$) 1.5 L ha$^{-1}$ + Estet 600 e.c. (2.4 – D, 600 g L$^{-1}$) 0.5 L ha$^{-1}$ was applied for maize. Mechanical weeding was used for 3$^{rd}$ block because of limited availability of herbicides registered for specific species. Insects were controlled by insecticide Fastak 50 e.c. (alfa-cipermetrin, 50 g L$^{-1}$) 0.3 L ha$^{-1}$ only in winter oilseed rape.
Crops were harvested at different development stages to determine yield (t ha$^{-1}$): maize was harvested by special harvester for trials (HALDRUP) with automatic sampler, but other species were harvested by VARI system harvester and average samples for detecting dry matter content (%) and other quality parameters were taken by hand and after that – chopped and dried. Maize (1$^{st}$ trial block) was harvested on 3 September, 17 September, and 4 October. In 2$^{nd}$ block winter oilseed rape biomass was harvested at GS 65 (21 May), GS 79 (21 June), and GS 85 (5 July). Seed and straw yield was determined after harvest (combine harvester HEGE-140) at GS 90-92. Harvest times in the 3$^{rd}$ block: oil radish - at GS 85; sunflower – at GS 80-83; *Setaria italica* – at GS 75 and GS 85; millet – at GS 75 and GS 85; amaranth – at GS 85; hemp – at 05.08.
Dry matter (DM) content was detected by drying samples up to constant weight at 105 °C and organic dry matter (ODM or VS) was calculated after ashing samples at 550 °C. DM and

ODM yield (t $ha^{-1}$) was calculated. Crude protein was detected by Kjeldahl method (LVS EN ISO 5983-2: 2009), sulphur content – CS-500 analyzers method, and fat content by ISO 6492: 1999 method.
ANOVA procedures and descriptive statistics were used for processing the experimental data.
Vegetation period of 2010 characterizes with similar to long-term average temperature and precipitation observations in May and June, but very warm and moist July and August. September was behind warmth conditions observed in long-term period.

## Results and discussion

As so different plant species were used wide range of fresh biomass yields were obtained per all three trial blocks: the highest average fresh biomass yield (62.02 t $ha^{-1}$) was obtained from rape; it was by 23.56 t $ha^{-1}$ higher if compared to average yield of millet (38.46 t $ha^{-1}$) (Fig. 1). Range of average ODM content at harvest of all species per all harvest dates was also wide (from 111.7 g $kg^{-1}$ (sunflower 'Alussa' harvested at GS 83) to 335.2 g $kg^{-1}$ (foxtail millet 'Rudukes' harvested at GS 85). For good quality silage making DM content of plant is very important: if biomass is too wet – additional drying before ensiling can be needed; in other case losses during ensiling can be great. Lower ODM content was noted for sunflower, amaranth and rape at first harvest time, higher values for hemp, millet, foxtail millet, rape and maize at last harvest dates.
ODM yield of investigated plant species varied within a wide range: from 5.81 t $ha^{-1}$ (amaranth 'Margiai' harvested at GS 85) to 21.79 t $ha^{-1}$ (maize 'Fernandez' harvested at 4 October) and 22.05 t $ha^{-1}$ (winter oil-seed rape 'Excalibur' at GS 85, Fig. 4). It was evident that harvest timing affected the obtained yield amount. The average ODM yields of all species are shown in Figure 1.

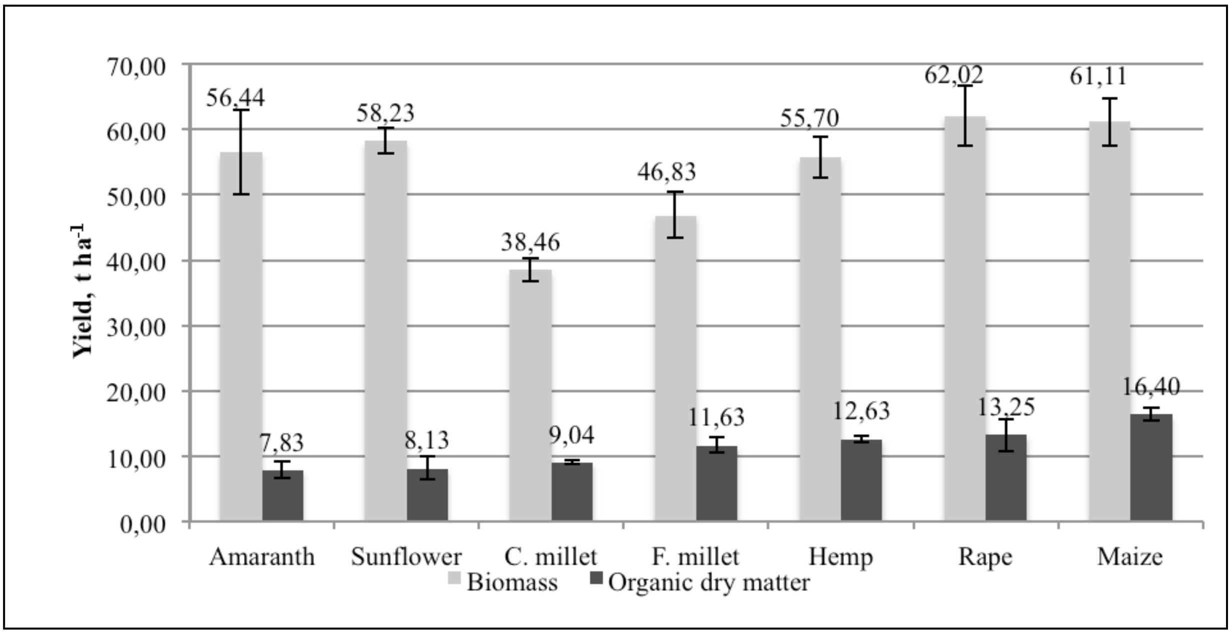


*Fig. 1.* **Average fresh biomass and organic dry matter yield of all species (average from all varieties and harvest dates)**

The ODM yield is an important factor influencing biogas and methane yield per unit area. Maize is the main crop used as biogas substrate in Europe due to its very high yield potential from 1 ha [1]. Our investigation showed very high fresh biomass yield of rape (Fig. 1), but maize hybrids achieved highest average ODM yield (16.40 t $ha^{-1}$). Sunflower and amaranth showed 2nd and 3rd highest fresh biomass yields respectively, but at the same time their

average ODM yields was lowest: amaranth – 7.83 t $ha^{-1}$ followed by sunflower 8.13 t $ha^{-1}$. In our research sunflower demonstrated the highest average fat (122.4 g $kg^{-1}$) and protein (104.8 g $kg^{-1}$) content from investigated species. Some authors [1, 2] mentioned that sunflower theoretically can be suitable plant for biogas production due to its high fat content, but empirical research did not approved it. Other researchers, e.g., P. Vindis et al. [3] reported that the highest bio-methane production was achieved using exactly the sunflower substrate (283 NL $kg^{-1}$ VS), followed by maize (187 NL $kg^{-1}$ VS). Also A. Adamovics et al. [4] mentioned high output of methane from sunflower; potential bio-methane yield from unit area is mentioned 2627 $Nm^3$ $ha^{-1}$ for sunflower in agroecological conditions of Latvia.
Amaranth is a crop widely investigated in other countries, also some data on performance of millet and foxtail millet is possible to find. A. Svirskis [5] had mentioned that amaranth, millet, foxtail millet, and some other plant species can be successfully grown for food and fodder in Lithuania's agro-climatic conditions on organic and conventional farms. Two year field trial was carried out during 2006-2007 in Lithuania. The year 2006 was very dry, while 2007 was normal and the yield was higher. Conditions in our investigations in 2010 were even more favorable (very warm season with surplus precipitation) for amaranth and millet, and obtained yield exceeded results in Lithuania (Table 2). Such results propose to continue research with these crops.

*Table 2.*

**Fresh biomass and dry matter yield of amaranth, millet, and foxtail millet in comparison with data obtained in Lithuania, t $ha^{-1}$**

| Species | Varieties | 2006 Lithuania Svirskis, 2009 [5] | | 2007 Lithuania Svirskis, 2009 [5] | | 2010 Latvia | |
|---|---|---|---|---|---|---|---|
| | | FM yield | DM yield | FM yield | DM yield | FM yield | DM yield |
| Amaranth | Geltonukai | 34.4 | 4.41 | 27.0 | 7.47 | 50.3 | 7.98 |
| Millet | Rudes | 13.7 | 2.31 | 16.5 | 4.90 | 33.0 | 9.39 |
| Millet | Gelsves | 15.0 | 2.88 | 19.2 | 6.01 | 40.4 | 8.54 |
| Millet | Juosves | 13.3 | 2.04 | 22.1 | 6.80 | 34.1 | 9.90 |
| F.millet | Rudukes | 11.3 | 1.74 | 15.6 | 7,61 | 52.4 | 11.28 |
| F.millet | Aukses | 13.7 | 2.05 | 17.6 | 6,94 | 48.4 | 10.33 |

P. Vindis et al. [6] reported methane production from amaranth substrate 125 NL $kg^{-1}$ VS. Amaranth (on average145 mg $kg^{-1}$) and millet (on average137 mg $kg^{-1}$) were confirmed as sulphur-richest species in our trial. High content of sulphur can increase hydrogen sulphide concentration in the biogas. Hydrogen sulphide is formed in the biogas plant by the transformation of sulphur-containing protein. Hydrogen sulphide and other sulphur containing compounds must be removed from biogas before it is burned; otherwise there is a risk of corrosion damage to the co-generation unit [7]. Amaranth also demonstrated the highest ash content (139.90 – 167.74 g $kg^{-1}$) in DM from investigated crops. J. Viglasky and J. Huska [8] reported similar ash content (10.17 to 22%) of amaranth grown at the Slovak Agricultural University in Nitra. Results of their ash analysis showed that the ash residue contains 1 mg $kg^{-1}$of cadmium; 5.05 mg $kg^{-1}$ of cobalt; 11.28 mg $kg^{-1}$of copper; 4.9 mg $kg^{-1}$of nickel and 34.3 mg $kg^{-1}$of zinc. Results of the analyses have proved that this plant grown on a polluted field has a high tendency to absorb heavy metals from the soil. It means that amaranth can play an important role as a raw material source for industrial biofuel production as well as for environmental protection in this century. B. Pisarikova et al. [9] reported a significant dependence of nutritional value of the above ground biomass of amaranth on the plant growth stage. During plant growth, the nutritional value decreased, which was presented especially by a significant linear decrease of the crude protein content and a significant increase of crude fiber. We have not yet investigated the changes of amaranth chemical composition during maturing.

Hemp (*Cannabis sativa*) grown in Latvia is mainly well-known as oil and fibre plant. Research of hemp as prospective biomass plant for biomass production is only in the initial stage. The ODM yield of hemp ranged from 10.70 t ha$^{-1}$ ('Benico') to 14.20 t ha$^{-1}$ ('Futura 75') (Fig. 2). Swedish scientists [10] did not find significant difference in the specific methane outcome depending on harvest timing (stage of maturity). Harvesting samples on 10 July, 30 July, 4 September and 19 October, 0.25, 0.27, 0.26, 0.23 Nm$^3$ methane per kg VS respectively was obtained. At the same time biomass yield for the four different harvest times was: 3.6, 6.9, 14.2 and 14.3 t ha$^{-1}$ of total DM respectively. The energy yield in the form of methane per hectare was highest at harvest in September and October: 122 and 111 GJ per hectare respectively. The harvest time showed to have little effect on the specific methane yield but a large effect on the biomass yield and thus the methane yield per hectare. A. Adamovics et al. [4] from investigations in Latvia reported similar methane outcome from hemp: 294±2 L kg$^{-1}$ VS. Potential bio-methane yield from hemp is calculated 3113 Nm$^3$ ha$^{-1}$ [4]. We have challenge for future to investigate the best harvest time for hemp to obtain the highest methane yield per ha.

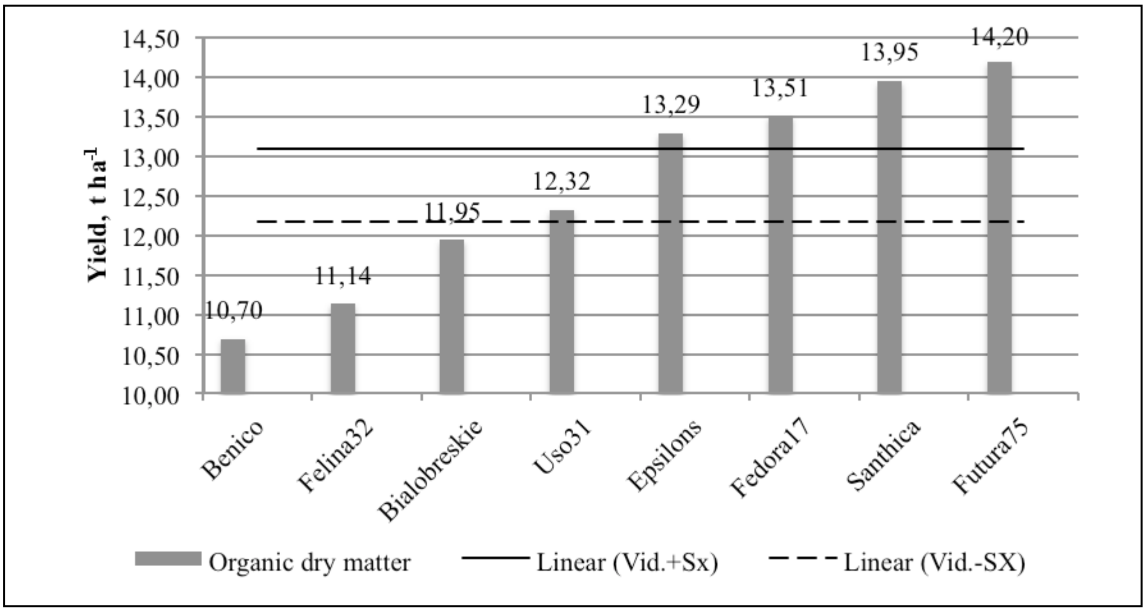


*Fig. 2.* **Organic dry matter yield of hemp depending on used variety.**

For obtaining high ODM yields maize has to be harvested as late as possible in Latvian conditions; this is quite well demonstrated in our previously published papers [11, 12, 13]. Also results of current investigation showed that ODM yield increased significantly ($p<0.05$) during maize development till October. Speaking of other species, only for millet (Fig. 3) marked relevance was not noticed between yields harvested at different dates: ODM yield of variety 'Gelsves' ranged from 7.76 t ha$^{-1}$ (GS 75) to 9.96 t ha$^{-1}$ (GS 85) due to maturing, but other two varieties yielded more in earlier stage of maturity.

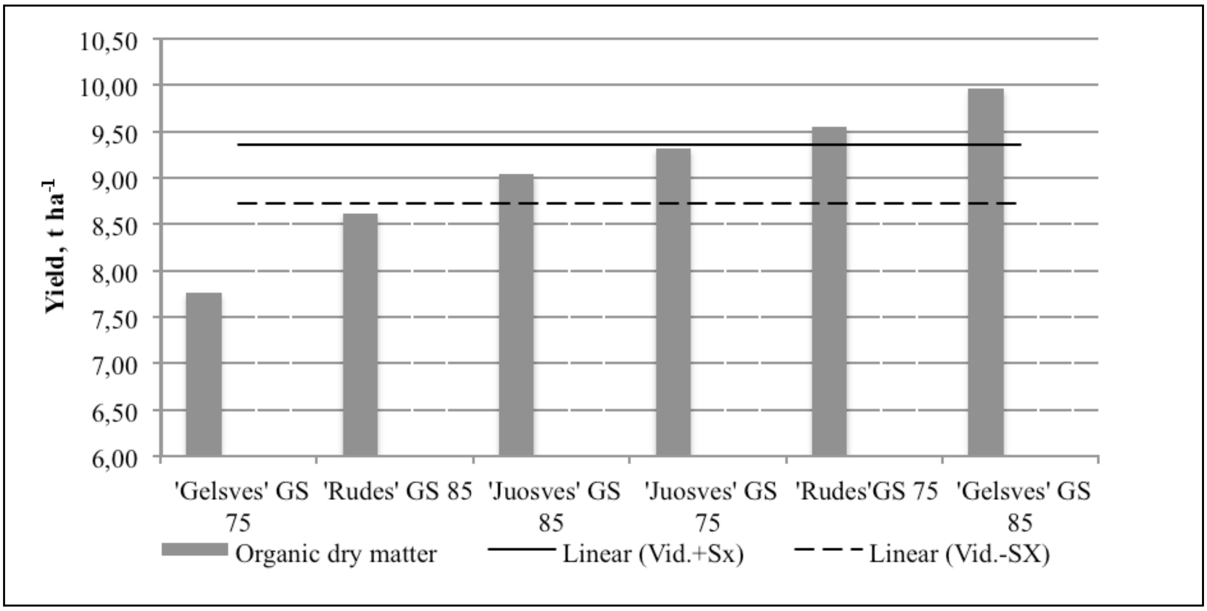


*Fig. 3.* **Organic dry matter yields of millet at different harvest times**

Oilseed radish is well-known crop used for green manure in Latvia. It is crop best known for its deep tap root, quick emergence and rapid growth. It is primarily used to break up soil compaction, capture residual nitrogen, and suppress weeds, increase water infiltration, and increase soil biology [14]. Seeds of oilseed radish can contain up to 48% oil unsuitable for human consumption, but promising as a source of biofuel [15]. This could hence make an interesting biodiesel candidate. Oilseed radish is still unrecognized as bio energy crop; in our investigation we obtained fresh biomass yield 57.8 t $ha^{-1}$ with DM content 167 g $kg^{-1}$ and DM yield was 9.66 t $ha^{-1}$. Potential of this plant biomass for biogas production is challenge to investigate during current research also due to its possibility to form high biomass very quickly (~40-50 days).

Oilseed rape is very interesting crop from different aspects of bio-energy production. It is highly productive biomass crop. Our research showed the highest average fresh biomass yield of rape and the $2^{nd}$ highest average ODM yield (Fig. 1) from eight investigated species. Significant ($p<0.05$) harvesting time impact on biomass yield (Fig. 4) was noted; higher fresh biomass yield was determiner in $2^{nd}$ harvesting time (at GS 79), but it decreased in $3^{rd}$ harvesting time (at GS 85). Increased ODM content at later harvesting times was observed and it reached 31% for ‘Excalibur’ and 29% for ‘Ovation’ at the GS 85 (Fig. 4). Also ODM yield was highest at the last harvesting date (GS 85).

Winter oilseed rape is mainly grown for oil production purposes. Varieties used for food and fodder are low in glucosinolates and erucic acid. *Brassica* crop species produce a higher quality fuel if compared to other oilseed species due to their relatively low specific qualities in oil [16].

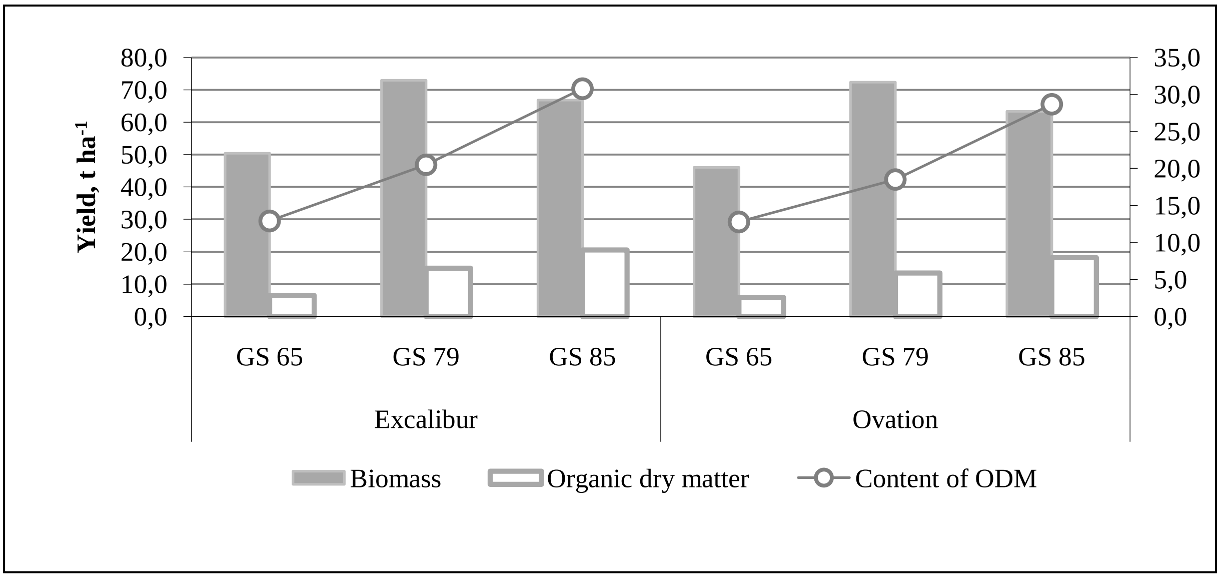


*Fig.4.* **Fresh biomass and ODM yield of winter oil-seed rape and ODM content according to different harvest times and varieties**

Economic seed yields of 3-4 t ha$^{-1}$ are normally produced in Europe [17], we observed 2.5-3.5 t ha$^{-1}$ (at favorable agro-ecological conditions – more than 4 t ha$^{-1}$) in central region of Latvia [18]. High seed yields were obtained also in our experiment, and hybrid variety 'Excalibur' (5.43 t ha$^{-1}$) gave significantly ($p<0.001$) higher yield than line variety 'Ovation' (4.53 t ha$^{-1}$). Superior straw yield was obtained also from 'Excalibur' – 9.1 t ha$^{-1}$ (DM content 92%), but that of 'Ovation' was 7.9 t ha$^{-1}$ (DM content 91%). Currently there is no market for oilseed rape straw in Latvia, and almost all of it is chopped and incorporated into soil. Oilseed rape straw is lignocellulose containing agricultural residue that could be used for energy production. Thus oilseed rape seed yield is supplemented with raw materials which can be processed in energy – heat or bioethanol. Lignocellulose is the most abundant organic material on earth and therefore is a promising raw material for bio energy production [19]. Both biogas and ethanol can be produced from the lignocellulosic raw materials. Practically *Brassica rapa* is used for biogas production and *Brassica napus* is used as raw material for biodiesel and bioethanol [20]. Results showed considerable energy potential from oilseed rape using seeds for biodiesel production, and straw material for bioethanol and biogas production according to A. Petersson et al. [21].

A further investigation on different ways of oilseed rape usage for energy production purposes has to be developed in Latvia.

## Conclusions

All eight investigated crops gave comparatively high biomass yields, but average organic DM yields above 10 t ha$^{-1}$ were obtained from maize (16.40 t ha$^{-1}$), winter oilseed rape (13.25 t ha$^{-1}$), hemp (12.63 t ha$^{-1}$) and foxtail millet (11.63 t ha$^{-1}$). Very good meteorological conditions of 2010 for Southern origin plants should be also taken into account using trial data. It was demonstrated that biomass yield substantially depended from used species, but also variety influence within the species was relevant. Harvesting of more matured crop mainly caused significant ODM yield increase (maize, winter oilseed rape); deviation from such tendency was observed for millet. Studies are only at the initial stage and have to be continued, investigating in detail effect of variety and harvesting time on yield amount as well as bio-methane outcome from different species.

**Acknowledgement**

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**References**

1. Amon, T., Amon, B., Kryvoruchko, V., Machmuller, A., Hopfner-Six, K., Bodiroza, V., Hrbk, R., Friedel, J., Potsch, E., Wagentristl, H., Schriener, M., Zollitsch, W. Methane production through anaerobic digestion of various energy crops grown in sustainable crop rotations. Bioresource Technology, No. 98, 2007, p. 3204-3212.
2. Schittenhelm, S. Chemical composition and methane yield of maize hybrids with contrasting maturity. European Journal of Agronomy, No. 29, 2008, p. 72-79.
3. Vindis, P., Mursec, B., Rozman, C., Cus, F. A multi-criteria assessment of energy crops for biogas production. Journal of Mechanical Engineering, 2009.
4. Adamovics, A., Dubrovskis, V., Plume, I. Biomethane yield from energy plants in Latvia. Proceedings of the 18th European Biomass Conference “From research to industry and markets”, Florence: Eta-Florence Renewable Energies, 2010, p. 484-486.
5. Svirskis, A. Prospects for Non-Traditional Plant Species Cultivated for Forage in Lithuania. 2009, Published in internet: http://notulaebotanicae.ro/nbha/article/viewFile/3123/2962
6. Vindis, P., Mursec, B., Rozman, C., Janzekovic, M., Cus, F. Mini digester and biogas production from plant biomass. J. Achiev. Mater. Manuf. Eng., 35/2, 2009, p. 191-196.
7. Koller, J. Treatment of Biogas for Use as Energy. Acta Polytechnica, Vol. 50, 2010.
8. Viglasky, J., Huska, J. Amaranth phytomass for energy and multifunctional uses. Project manuscript; Conference Proceedings; Bio-energy Enlarged Perspectives 10-11 October 2003, Budapest.
9. Pisarikova, B., Peterka, J., Trckova, M., Moudry, J., Zraly, Z., Herzig, I. Chemical Composition of the Above-ground Biomass of Amaranthus cruentus and A. hypochondriacus. ActaVeterinaria, Brno, Vol. 75, Issue 1, 2006, p. 133-138.
10. Kreuger, E., Escobar, F., Svensson, S-E., and Björnsson, L. Biogas production from hemp – evaluation of the effect of harvest time on methane yield. Presented in Poster Session PT01 – Bioenergy 11th IWA World Congress on Anaerobic Digestion, 23-27 September 2007, Brisbane, Australia
11. Gaile, Z., Bartuševics, J. Will maize become an important crop for biogas production in Latvia? Grassland Science in Europe, Vol. 14, 2009, p. 372 - 375.
12. Bartuševics, J., Gaile, Z. Influence of maize hybrid and harvest time on yield and substrate composition for biogas production. Research for Rural Development – 2009, Jelgava, LLU, p. 44 - 49.
13. Gaile, Z. The Role of Maize Harvest Timing for High-quality Silage Production. LLU Raksti, No. 25, 2010, p. 116-128. (in Latvian).
14. Arlauskiene, A., Maikšteniene, S. The effect of catch crop nitrogen on soil properties and spring barley yield. Latvian Journal of Agronomy, No. 10, 2008, p. 78-82.
15. No, S. Y. Inedible vegetable oils and their derivatives for alternative diesel fuels in CI engines: a review. Renewable and Sustainable Energy Reviews, No. 15, 2011, p. 131–149.
16. Kalniņš, A. Possibilities of production and utilization of bio-fuels in Latvia. Rīga, 2005, 167 p. (in Latvian).
17. Rathke, G.-W., Behrens, T., Diepenbrock, W. Integrated nitrogen management strategies to improve seed yield, oil content and nitrogen efficiency of winter oilseed rape (*Brassica napus* L.): a review. Agriculture, Ecosystems and Environment, No.117, 2006, p. 80–108.
18. Balodis, O., Gaile, Z., Bankina, B. Developments of winter oilseed-rape growing experience in Central Latvia farms. Proceedings of 10th Congress of the European Society for Agronomy. Italian Journal of Agronomy, No. 3, 2008, p. 503-504.
19. Ofori, A., Becker, H. C. Breeding of *Brassica rapa* for Biogas Production: Heterosis and Combining Ability of Biomass Yield. Bioenergy Research, No. 1, 2008, p. 98–104.
20. Dopako, R., Vega-Nieva, D. J., Ortiz, L. Herbaceous energy crops: reviewing their productivity for bioenergy production. Published in internet: http://193.146.36.56/ence/publicaciones/Valencia_OC7.3.pdf
21. Petersson, A, Thomsen, M. H., Hauggaard-Nielsen, H., Thomsen, A. B. Potential bioethanol and biogas production using lignocellulosic biomass from winter rye, oilseed rape and faba bean. Biomass and Bioenergy No.31, 2007, p. 812–819.

# UNTRADITIONAL SOLUTIONS FOR THE USAGE OF GREENHOUSE EFFECT

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**Abstract.** *The heat solar energy traditionally is used in greenhouses for ensuring optimal plant vegetation regime in our climatic conditions. Glass verandas built during last centuries at the south side of living houses and summer cottages are appreciated as original use of solar energy. Veranda as light and warm room was used for different household needs and also for social activities.*
*Up-to-date materials and technologies proposes wide spectrum of innovative activities for greenhouses and conservatories. The variable amount of solar energy is possible to smooth out by using accumulation system. In the paper results from vegetable drying experiments are presented. In the research used products – carrots, dry matter of the product at the start 8.5%, chopped product – 9.9%, after desiccation – equilibrium moisture content 10 -11%. The experimental device placed in the room is simulating the processes, which would occur if we use greenhouse for product drying, accordingly making changes in the design of conventional greenhouses by separating drying section from growing section, supplying warm heated in the greenhouse upper layer air from the bottom by forcing it with axial ventilator, and accordingly choosing appropriate accumulation system for energy storage in case when outside air temperature drop occurs.*

**Keywords**: *greenhouses, heat energy accumulation, drying.*

## Introduction

The heat solar energy traditionally is used in greenhouses for ensuring optimal plant vegetation regime in our climatic conditions. Glass verandas built during last centuries at the south side of living houses and summer cottages are appreciated as original use of solar energy. Veranda as light and warm room was used for different household needs and also for social activities [1, 2].

Up-to-date greenhouses are equipped with effective ventilation, extra lightning and heating systems, what ensure optimal plant vegetation regimes and extend greenhouses' life time, but simultaneously using big amount of energy sources. As interest of dried products is rising, the new energy effective technologies for product drying are looked for. Nowadays drying processes are characterized with high intensity, but also with high energy consumption and low energy efficiency [3, 4, 5].

By analogy of the nature processes, for example seed drying in variable environment conditions, possibilities of the drying of biological products in variable temperature conditions are being evaluated.

Great increase of the volume of biological agriculture production – mainly in small farms, conservation of biologically high value production with minimal drying processes expenses and usage of local energy sources at the moment attracts increasing interest [6].

In south countries solar heat has been used for a long time for different product drying. It is easier and more convenient to keep dried products comparing to preserved products [1].

The aim of our research is to evaluate efficiency of desiccation processes in greenhouses made from modern materials with minimal changes in ventilation and heating systems, minimizing heat losses and equalizing variable solar heat flow applying heat accumulation system

## Materials and methods

If we want to use solar energy stored in the greenhouse, we need to know the temper of the solar radiance. In the Table 1 the amount of energy gained from the solar collector is presented, the data is taken from the Ulbroka Research Institute of Agricultural Machinery solar collector experiments. It is seen that, it is possible to use the solar collector from April to September because of the amount of gained energy 53.3 – 89.3 kWh $m^{-2}$, speaking about green houses, the similar situation occurs – during April to October it is possible to dry products in the greenhouse without additional energy use, but if we want to dry products during the rest season, then it is needed to provide additional energy amount, for example by burning biomass.

*Table 1.*

**Amount of energy gained from solar collector kWh $m^{-2}$, coefficient of performance 44.3%**

| **Month** | **Amount of energy gained from solar collector kWh $m^{-2}$** |
|---|---|
| March | 42.8 |
| April | 55.8 |
| May | 71.7 |
| June | 89.3 |
| July | 88.5 |
| August | 71.2 |
| September | 53.3 |
| October | 25.5 |
| **Total** | **498.1** |

Speaking about heat energy variations during the 24 hour cycle, in Figure 1 it is very well seen, that temperature is the highest from 11.30am to 3pm, at the same time air humidity is the lowest. It is very important to add, that the highest humidity level is from 4am to 6am. Speaking about drying process, the 90% humidity level during morning time will influence the overall humidity level in the greenhouse, for this reason it is advisable to stop the drying process, id est to stop the ventilation processes during night time.

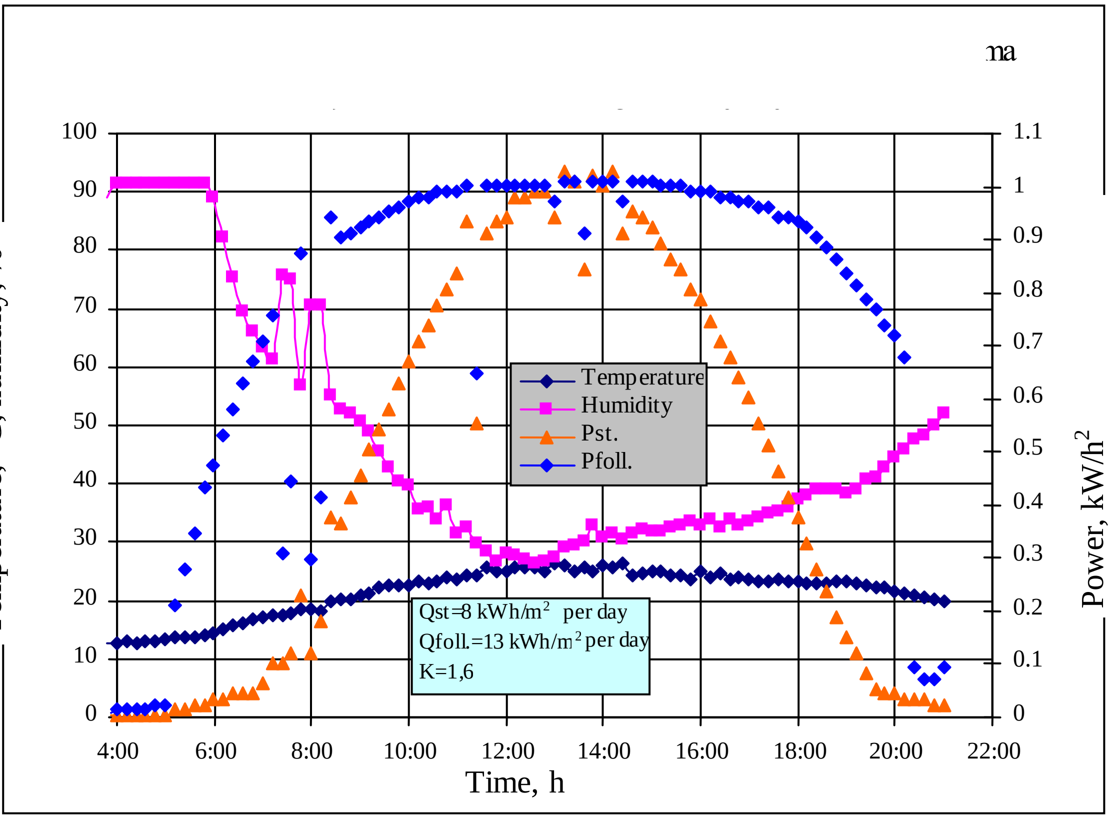


*Fig. 1.* **With MD-4 registered air temperature, humidity and Solar radiation power of two different solar collectors – stationary and following; Ulbroka 30th June 2006**

Speaking about possibilities to accumulate the heat energy, it is necessary to mention, that there are many different ways of energy accumulation. It is possible to accumulate heat energy by solid or liquid matter, using different materials. In the table below, some examples of heat accumulation are presented.

*Table 2.*

**Characteristics of the HAS**

| Character of HAS | Stone chip | Water | Sodium sulphate | Paraffin |
|---|---|---|---|---|
| HAS mass for accumulation of 1 GJ heat energy at ΔT=20°C, kg | 60000 | 11900 | 3300 | 3750 |
| HAS mass as the ratio to water mass, kg/kg | 5 | 1 | 0.28 | 0.32 |
| HAS volume for accumulation of 1 GJ heat energy at ΔT=20°C, $m^3$ | 49.6 | 11.9 | 2.26 | 4.77 |
| HAS volume as the ratio to water volume, $m^3/m^3$ | 4.2 | 1 | 0.19 | 0.4 |

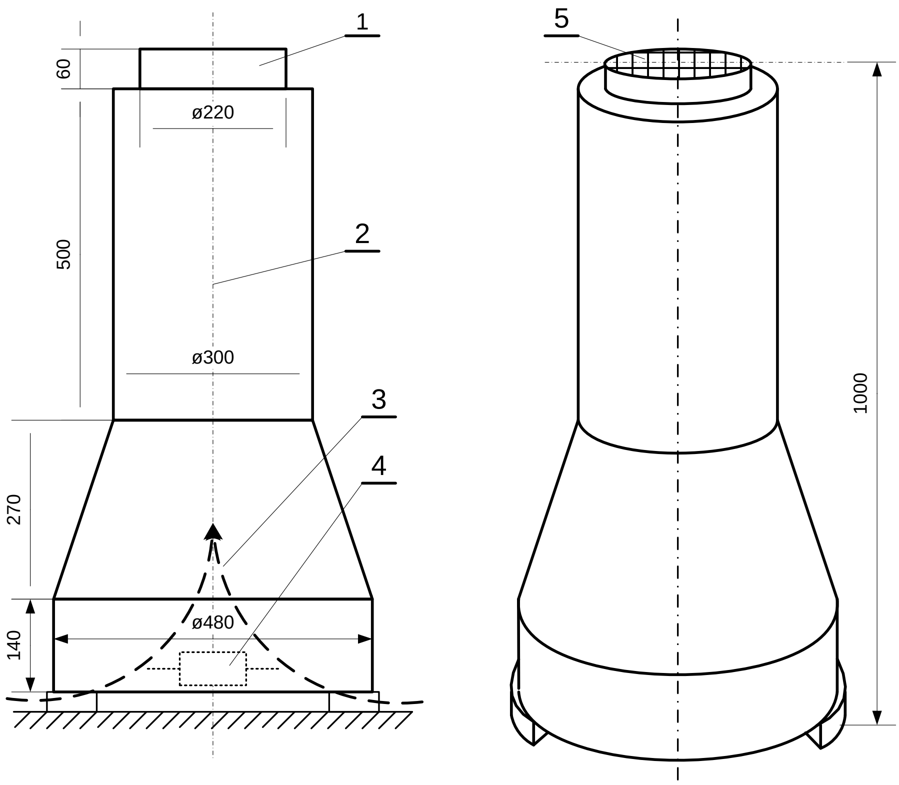


*Fig. 2*. **The scheme of the experimental device**
1 – outflow air temperature; 2 – inflow air temperature; 3 – inflow air; 4 – heating element; 5 – bolter with product

In Figure 2 the scheme of equipment used in our desiccation experiments is shown. The diameter of the bolter 5 is 20 cm, area of the bolt 0.031m$^2$. This device was used for determination of changes in mass of different products at minimal air flow at temperature 36 – 38°C (convectional heat flow due to warm air rise to the top) in device, comparing with results of drying process in the room at the same surrounding air temperature 36– 38°C . The experimental device placed in the room is simulating the processes, which would occur if we use greenhouse for product drying, accordingly making changes in the design of conventional greenhouses by separating drying section from growing section, supplying warm heated in the greenhouse upper layer air from the bottom by forcing it with axial ventilator, and accordingly choosing appropriate accumulation system for energy storage in case when outside air temperature drop occurs.

In the research used products – carrots, dry matter of the product at the start 8.5%, chopped product – 9.9%, after desiccation – equilibrium moisture content 10 -11%.

The product was chopped before drying, the thickness chips was 1-2 mm, the length 15-20-25-30 mm, the width 4-5 mm, the thickness of layer 25-30 mm, at periodical 20-24 h cycle at air temperature 36 – 38°C and surrounding air temperature 14 -15°C. The balance of the product was as follows: at the start 200g of product was taken, and at the end 25g left, that means – the mass of separated water was 175 g.

## Results and discussion

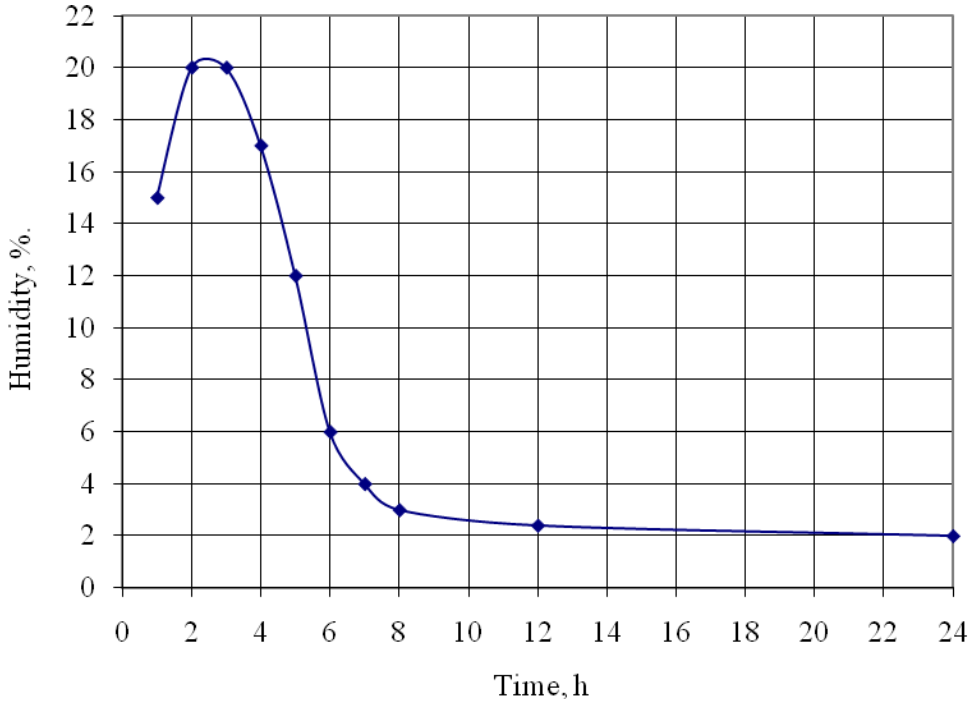


*Fig. 3.* **The mass changes of the drying product during 24 hour drying cycle with convectional air flow**

In Figure 3 results from drying process in the experimental device are shown. As it is seen 70 to 75% of water is separated during the first 3 – 4 hours drying period. The intensive drying process is because of convection air flow, which occurs due to warm air rise to the top.
In Table 3 changes of product mass changes are shown, when in the room there is no air flow and surrounding air temperature is 36 – 38°C. Comparing results from different drying process (Figure 3 and Table 3), it is seen that higher intensity is achieved during drying process at intensive air flow. Analyzing experimental data of the drying process without air flow it is seen, that in this case process goes on more softly, during first 4 hours equal amount of moisture is drained.

*Table 3.*

**The mass changes of the drying product during 24 hour drying cycle with intensive air flow**

| Time period, h | Humidity,% |
|---|---|
| 0 - 1 | 6 |
| 3 | 6 |
| 3 | 6 |
| 4 | 6 |
| 5 | 3 |
| -24 | 72 |

## Conclusions

1. During periodical drying process in greenhouses at the temperature 36 - 38°C and cycle duration 20-24 hours it is possible to get the product with humidity level 10-12 %.
2. Small and average area greenhouses are possible to transform to space for different product drying processes at a quite low expenses.
3. Currently available new generation Solar collectors, water accumulation tanks, heat pumps, water heating boilers with costs for about 3.5 to 5 thousands Ls, comparing with small and average size greenhouse expenses from 1 to 2 thousands.
4. More simple and available heat accumulation method at the moment is greenhouse, were solid stone material is used for greenhouse basement were air flow channels are implemented using low energy consuming fans.

## Acknowledgment

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### References

1. Харченко Н.В. , Индивидуальные солнечные установки, 1991., Москва, Энергоатомиздат, с. 208
2. Abolins J., Ernests J. Heat energy in manufacturing and households. 1986. Rīga:”Zinātne”, pp 123. (in Latvian)
3. How does energy occur? 2010. Available at: www.zalaenergija.lv (in Latvian)
4. Greenhouse prices. 2010. Available at: http://www.hothouses.lv/ceni.php (in Latvian)
5. Warm air generator. 2010. Available at: http://www.grandeg.lv/?l=3&item_id=162 (in Latvian)
6. Upītis A., Kristapsons M., Ziemelis I., Šķēle A. Local energy sources in energy supply system of agricultural district. 2009. In: proceedings of 8 th International Scientific Conference “Engineering for Rural Development”. May 28-29. 2009. Jelgava. Latvia, p.361-364.

# ANALYSIS OF REED RESOURCE DYNAMICS IN WATER BODIES OF EASTERN LATVIA

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**Abstract.** *The paper shows the results obtained during the research of reed dynamics revealing that in Eastern Latvia 20 lakes and pisciculture farms are potentially important for the reed extraction. In 2008, the reed resources there covered a territory of approximately 2300 ha. The ortophoto images of potentially important water bodies made in 1997, 2005 and 2008 were analyzed using the computer program ArcMap. The reed growth develops differently in every water body, but in general the eutrophication of water bodies and the enlargement of reed-covered areas can be observed. The most rapidly the reed occupies new territories in pisciculture farms and shallow lakes. The analysis of reed resource dynamics show that reed-covered areas in this region are expanding every year. The main factors that influence the distribution of reed growths refer to human activities, climatic conditions, hydrological regime in water bodies and natural processes of eutrophication.*

**Keywords:** *Common reed, biomas energy, dynamics of reed resources .*

## Introduction

In Latvia there is no special interest in reeds. They grow on lake and river coasts and in almost every pisciculture farm. Currently, insignificant amounts of reed are used in building. The reeds die off every year and decompose on the coasts of lakes and pisciculture farms creating the emission of $CH_4$ in atmosphere. Nevertheless, as the costs of fossil energy resources are growing, the interest in possibilities of using the local biomass in power supply is also increasing. The previous studies show that reeds can be used as raw material in fuel production. [7,8,9]. Uncertainty about reed stability and capacities of renovation is one of the reasons why reed resources are not used adequately. To evaluate the accessibility of reed resources in future and the influence of using reeds on ecosystems, it is necessary to study the current situation of reed growths and their changes when reeds are not cleared away, in order to obtain data that would allow understanding changes in reed growths after reed extraction. Reeds grow in places where fluctuations of water level are not wider than 50 cm. [2] In many countries the reed *Phragmites australis*, the most widespread reed in Latvia, is considered to be an invasive species. Reeds form big mono-specific growths that supersede other plants and endanger the biological diversity in biocenosis. There are special reed monitoring and control activities in USA, Canada and Western Europe. To stop the reed invasion, such methods as mechanical removal, drainage, cultivation with discs, granulation, burning, abatement by herbicides and biological control, are used. [3]

In Latvia there is no monitoring system of reed growths. Eutrophication processes are taking place in natural lakes and in artificial water bodies of Latvia, but the intensity of these processes is not clarified. The intensity and the areas of reed invasion in Latvia are not explored yet, there is no information about dynamics of reed growths. To evaluate the reeds as renewable resources, their amount and tendencies of development, the changes of reed-covered areas were analyzed in lakes that are potentially important for reed extraction.

## Research object

Reeds (*Phragmites australis*) are perennial caulescent plants of grass family. The height can reach 4 m. The stalk is bare, steep, firm and thick (diameter 0.7-1.2 cm). The growths are usually large, monodominant on the coasts of water bodies and sea, in wetland forests, marshes and moist meadows. Decumbent rootstocks (the length of vegetative nurslings

reaches 10-15 cm) can rapidly occupy new territories. This plant is characteristic for plant communities in forested fens and overgrown shallow waters (Cl. Phragmitetea, All. Phragmition) and for other plant communities of this class. [1]
The research is made on the dispersion intensity of reeds growing wild in lakes and pisciculture farms of Latgale region.

## Materials and methods

The research on reed dynamics is made in natural and artificial water bodies of Latgale region that are potentially important for the extraction of reed biomass and encompass the whole Latgale region. The research is made in water bodies that are important for reed extraction [10]: Lubana lake, Gumelis, Raznas lake, Feimanu lake, Rusonas lake, Birzkalna lake, Cirisa lake, Kvapanu ponds and Naglu ponds. The changes of reed growths were observed during the period of 1997 – 2010, using ortophoto images of 1997, 2005, 2008 and 2010 (see the images 1 and 2). The analysis of images was made using the method of distant survey in computer program ARC GIS. During the summer periods, the reed-covered areas were identified in each of the above mentioned lakes.

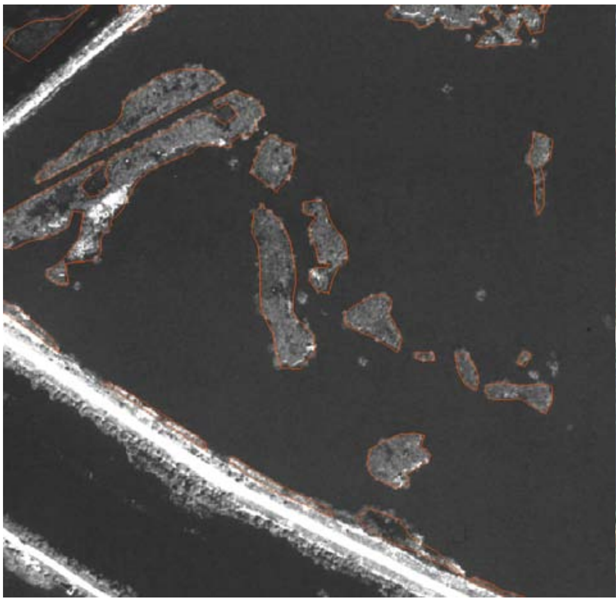

*Fig. 1.* **Reed growths in Kvapanu ponds Ortophoto of 1997**

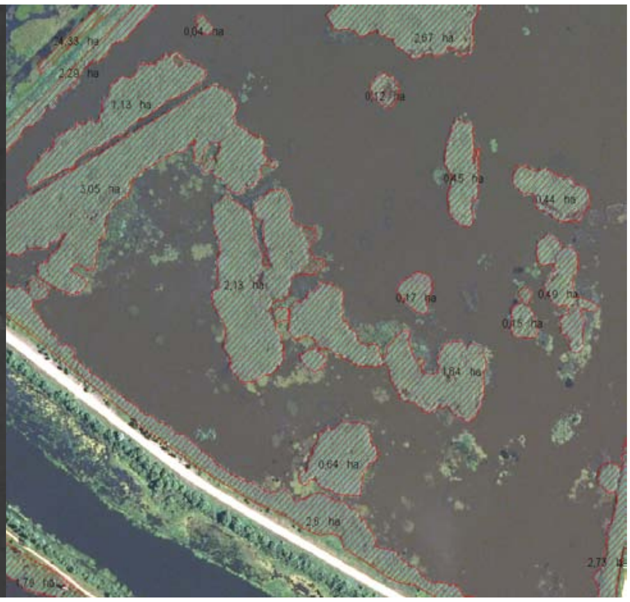

*Fig. 2.* **Reed growths in Kvapanu ponds Ortophoto of 2008**

## Results and discussion

Lakes cover 1,5% of the territory of Latvia or 1000 km$^2$. 2256 lakes are larger than 1 ha. 16 lakes are larger than 10 km$^2$ and cover 45% of the total surface of lakes in Latvia. The lakes of Latvia are characterized by eutrophication that often has a negative impact on lake biotopes. The remains of decomposing aquatic plants create the undesirable emission of $CH_4$ in atmosphere. The reed *(Phragmites Australis)* is one of the most widespread aquatic plants, it occupies larger or smaller areas in all water bodies of Latvia.
Lubanas lake is the largest lake of Latvia. It is the richest in reed resources as well. A rapid enlargement of reed-covered areas can be observed in this lake as reeds occupy new territories in the coastal zone. The lake is comparatively shallow therefore in Lubanas lake, as well as in Kvapanu and Idenas ponds, it is possible to observe the enlargement of reed clumps and their merger in more shallow places that are distant from the coast. The ortophotos of 1997 show reed clumps that are growing separately close to each other,

whereas ortophotos of 2008 often reveal that these clumps have already merged and are forming joint growths (image 3).
Using the ortophotos of 1997 it was calculated that the read-covered area in Lubanas lake was 440 ha or 5,36% of the total mirror surface of the lake. The ortophotos of 2005 showed 678 ha of reeds. In average, within one year the reed-covered area had expanded by 29,25 ha or by 0,36% of the total lake surface. The ortophotos of 2008 revealed reed growths of 734 ha, that is 8,94% of the total lake surface. The changes of reed growths are demonstrated in image 5.

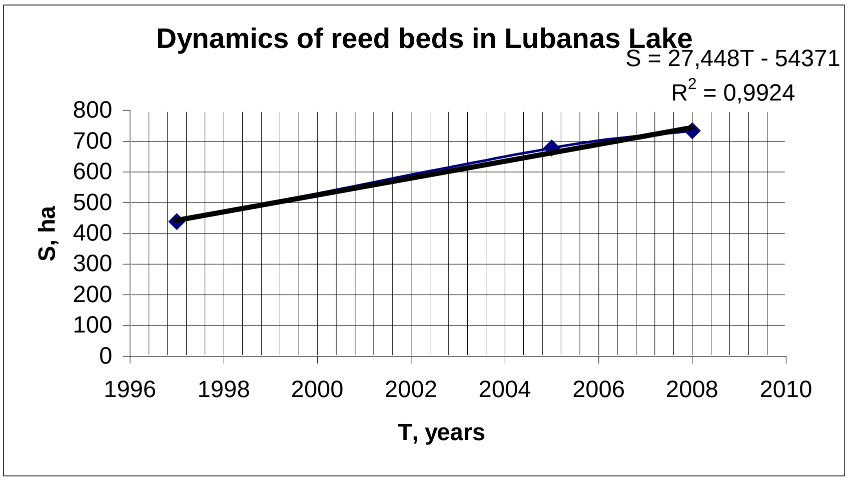


*Fig. 3.* **Changes of reed growths in Lubana lake 1997 – 2008**

Kvapanu ponds is one of the biggest pisciculture farms in Latvia. It is composed of 6 ponds with the total surface of 610 ha. The studies of reed dynamics show that the reed-covered areas in Kvapanu ponds are rapidly expanding. The analysis of ortophotos 1997 reveal that reeds cover 74 ha or 12,1% of the total mirror surface of the ponds. In 2005, 120 ha were covered by reed. In 2008, it was already a territory of 160 ha or 26,4% of the total surface of the ponds (Image 4). Every year 1,21 ha (0,21% of the total surface of the ponds) overgrow.

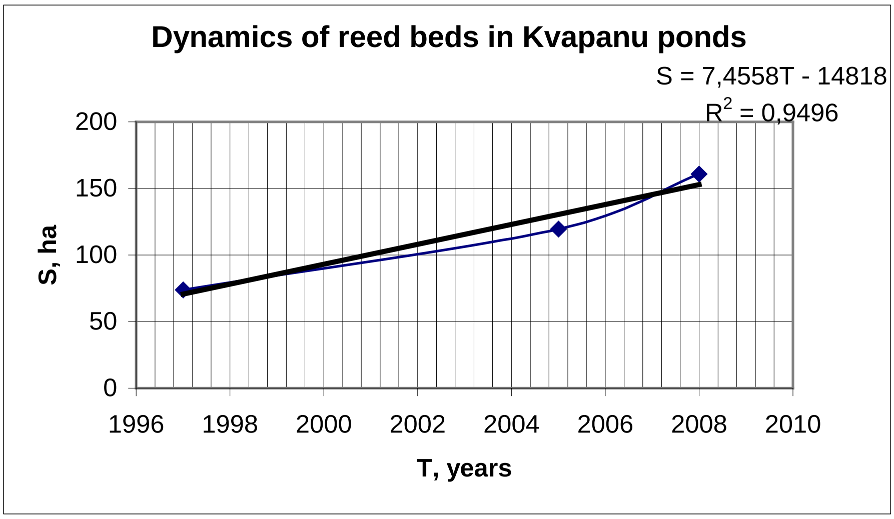


*Fig. 4.* **Dinamics of reed growths in Kvapanu ponds**

In 1997, there were counted 269 separate reed growths with the surface of 0,01 – 6,38 ha. In 2008, as the reeds were expanding and the areas were merging, only 106 separate growths were counted. The largest growth covered already 21,2 ha. The reed growths in Kvapanu ponds are presented in image 5. If the reed growths of 1997 and 2008 are compared, a rapid enlargement can be observed.

Gumelis is a specific shallow lake located in the Northern part of Lubanas lake. It is artificially created separating it from Lubanas lake as the result of hydro-ameliorative activities when the Northern dike was built-up. The total surface of Gumelis that in summer season is under water, covers approximately 220 ha. When the water level in Aiviekste river rises, Gumelis and proximal flood-land meadows are regularly flooded. Reed-covered areas in Gumelis are comparatively small. However, a rapid enlargement of reed-covered areas can be observed. This enlargement is one of the rapidest of all the water bodies that are being studied. Analyzing ortophoto images of 1997, in Gumelis there were found 18 ha of reed growths (8,2% of the total mirror surface of the water body). Ortophoto images of 2005 showed 33 ha of reeds (15% of the total surface). In 2008, the reeds covered 50 ha (22,7% of the total surface of the water body) (Image 6).

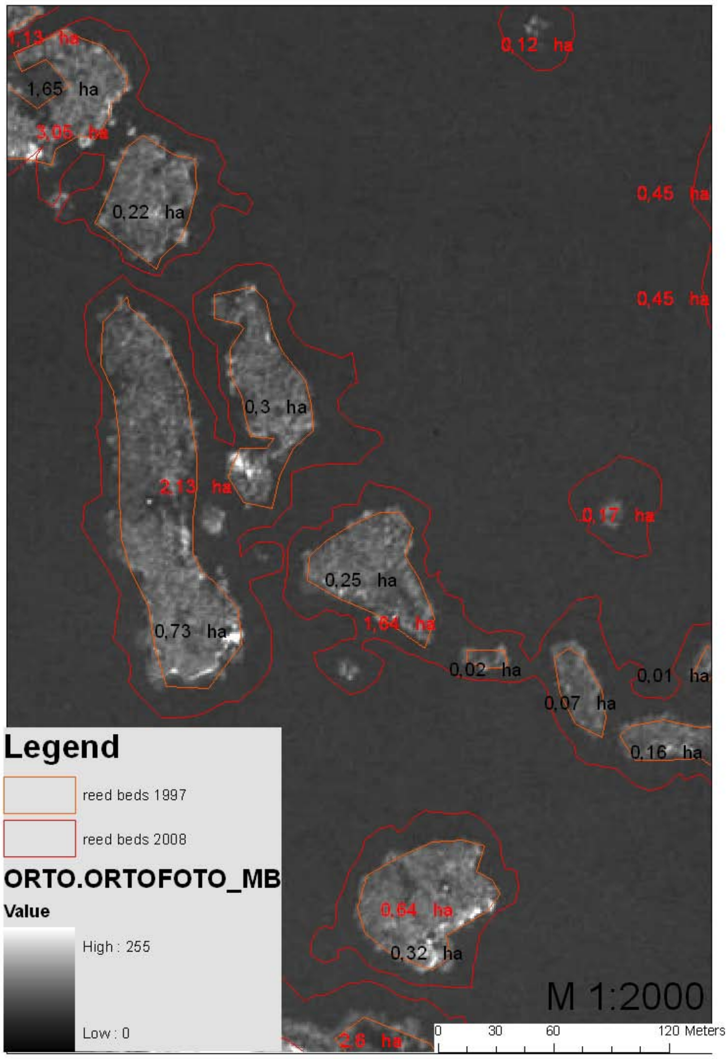


*Fig. 5.* **Reed growths in Kvapanu ponds**

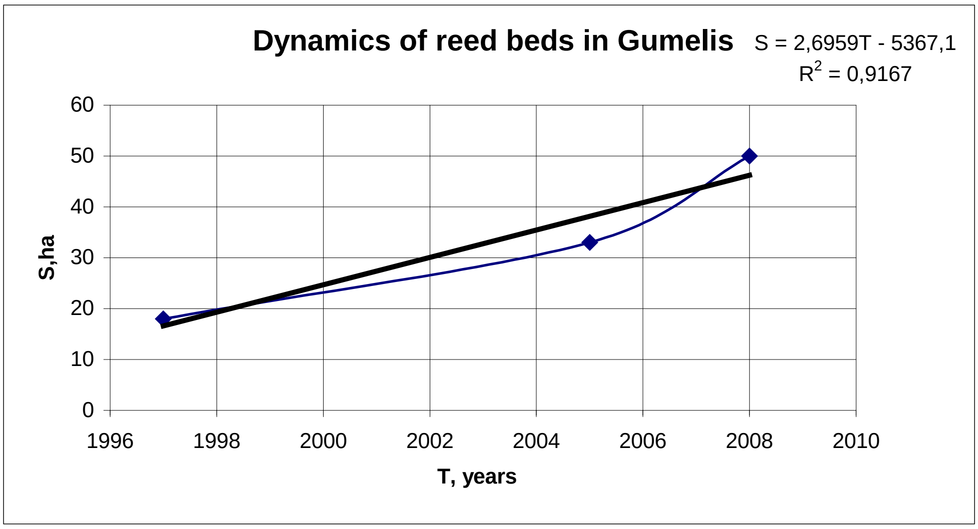


*Fig. 6.* **Dynamics of reed growths in Gumelis 1997 – 2008**

On average, the reed-covered surface is expanding annually by 2,9 ha or 1,3% of the total surface of the lake. Naglu ponds are an important complex used for the fish breeding. The total mirror surface of the ponds is approximately 960 ha. (In the research only 11 ponds, located between Rezekne river and Canal, were analyzed). Unlike in Kvapanu ponds, in Naglu ponds there is an active fish farming, that is why the ponds are regularly drained and flooded again as the result of technological process of fish farming. Therefore why such a rapid enlargement of reed-covered areas as in Kvapanu ponds, cannot be observed. In 1997, ortophoto images of pisciculture farm showed the reed growths of 47 ha, while in 2005 the reed growths were already 54 ha and in 2008 - 62 ha (see image 7). In 1997 they covered 4,9% of the total mirror surface, in 2005 - 5,6% and in 2008 – 6,5%. It can be seen that the enlargement of reed-covered area is insignificant if compared with Kvapanu ponds. However the general tendency remains and the reed-covered areas are expanding.

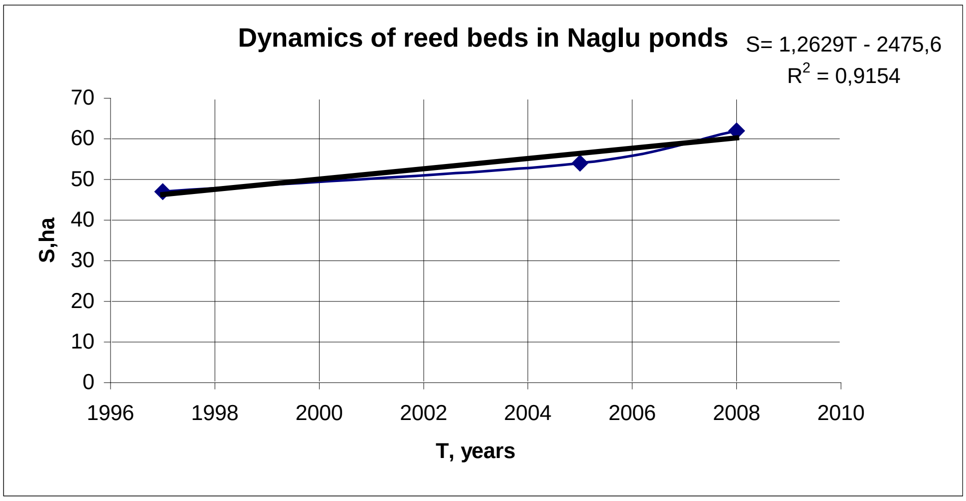


*Fig. 7.* **Dynamics of reed growths in Naglu ponds 1997-2008**

Raznas lake is the second largest lake in Latvia with significant reed growths on the coast. Ortophoto analysis of 1997 showed that reed growths covered 256 ha of Razna lake (4,4% of the total mirror surface of the lake). In 2005, the growth had expanded and covered already

277 ha (4,8% of the total surface), while in 2008 they covered 290 ha (5% of the total surface). The changes of reed-covered areas are presented in image 8.

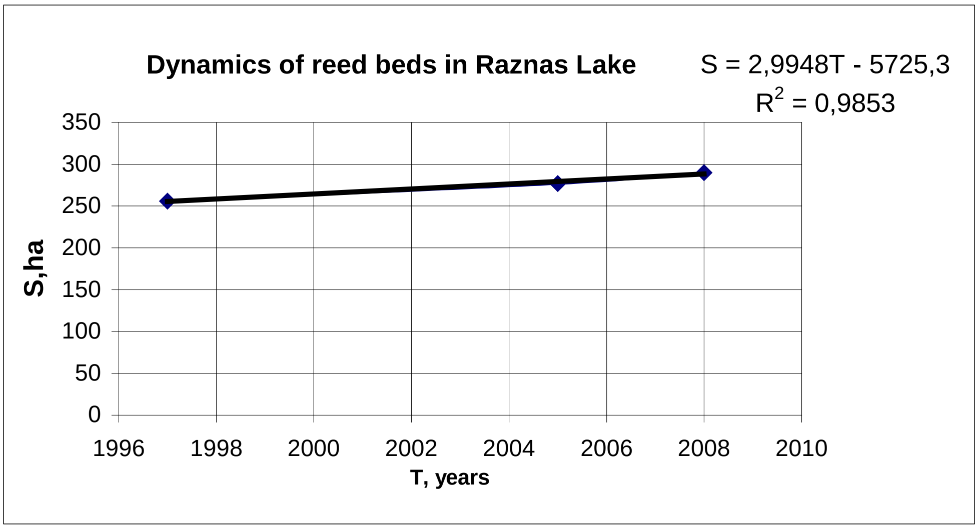


*Fig. 8.* **Dynamics of reed growths in Raznas Lake 1997 – 2008**

The reed-covered surface of Raznas lake is expanding annually by approximately 3 ha.
Feimanu lake is located in the bloc of Rusonas lakes and it is quite shallow. If compared with the lakes and pisciculture farms situated in the bloc of Lubana, the reeds are dispersing much slower in Feimanu lake. In 1997, ortophotos showed reeds on 82 ha. In 2005, they covered 83 ha, while in 2008 they covered 85 ha (see image 9).

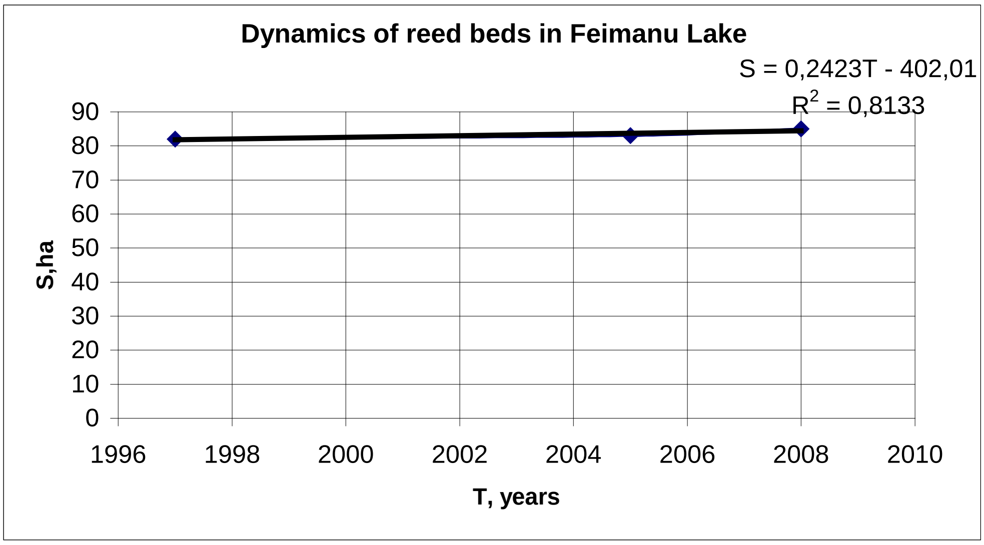


*Fig. 9.* **Dynamics of reed growths in Feimanu Lake 1997 – 2008**

In 1997, the total overgrowth of Feimanu Lake covered 13,1% of the mirror surface. In 2005, the reed-covered surface was 13,3% and in 2008 – 13,6%. It can be seen that the enlargement is comparatively insignificant: in 11 year period the reeds have occupied only 0,5% of the total lake surface.
Rusons is one of the largest lakes in Latgale region. It is one of the richest in resources as well. The reed-covered areas have expanded more rapidly than in Feimanu Lake. In 1997, ortophotos showed that reeds covered 212 ha, in 2005 – 218 ha, in 2008 – 261 ha and in

2010 – already 279 ha (see image 10). The total overgrowth of the lake has enlarged by 2,9% of the total surface: from 8,9% in 1997 to 11,8% in 2010.

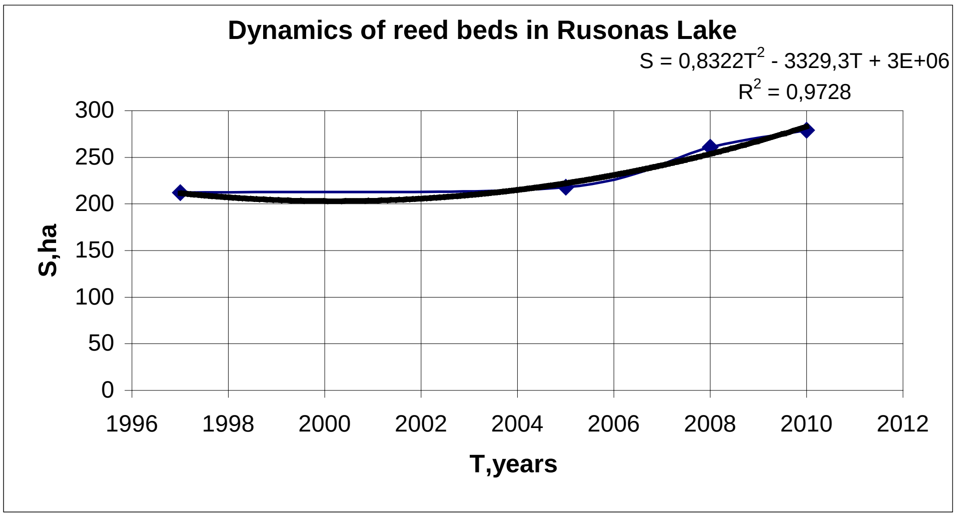


*Fig. 10.* **Dynamics of reed growths in Rusonas Lake 1997 – 2010**

Birzkalna lake is comparatively shallow and it is located in the bloc of Rusonas lakes. The total surface of this lake is 272,2 ha, average depth – 2,7 m, maximal depth – 3,9 m. It is a running-water lake. Reed-covered areas are comparatively small. In 1997, the reeds covered 25 ha (9,2% of the total lake surface), while in 2010 they had occupied 30 ha (10,9% of the total lake surface) (see image 11). The total overgrowth of the lake had enlarged by 1,7%.

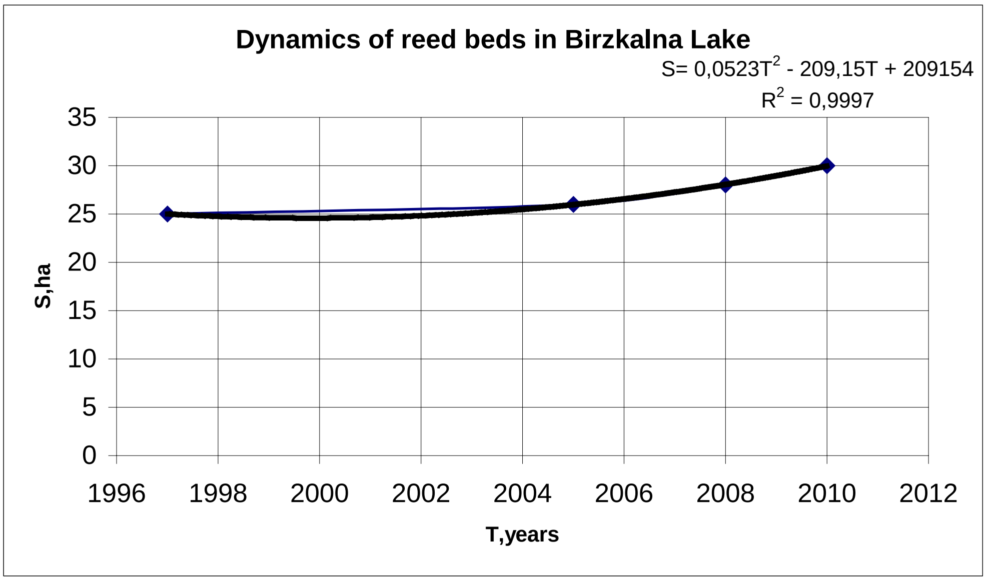


*Fig. 11.* **Dynamics of reed growths in Birzkalna Lake 1997 – 2010**

A comparatively small enlargement of reed-covered area can be observed in Cirisa Lake as well. The total lake surface is 630,6 ha, average depth – 4,1 m, maximal depth – 10 m. It is a running-water lake. Ortophoto analysis of 1997 showed that reeds covered 61 ha of Cirisa Lake (9,7% of the total lake surface). In 2005, reeds covered 63 ha (10% of the total surface), in 2008 – 66% (10,5% of the total surface), in 2008 – 66 ha (10,5%) and in 2010 – 67 ha (10,6%) (see image 12).

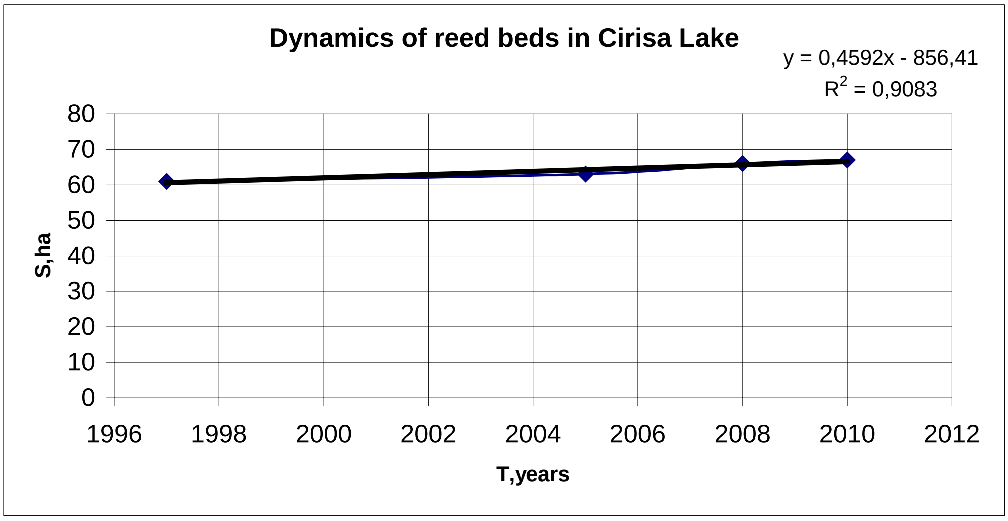


*Fig. 12.* **Dynamics of reed growths in Cirisa lake 1997 – 2010**

Like in other lakes of this bloc, the total overgrowth of the lake is comparatively small. During 13 years it has enlarged by 0,9% from 9,7% in 1997 to 10,6% in 2010.
In all the lakes that were studied, the enlargement of reed-covered areas was observed but it should be mentioned that the intensity of this enlargement was different (see image 13).

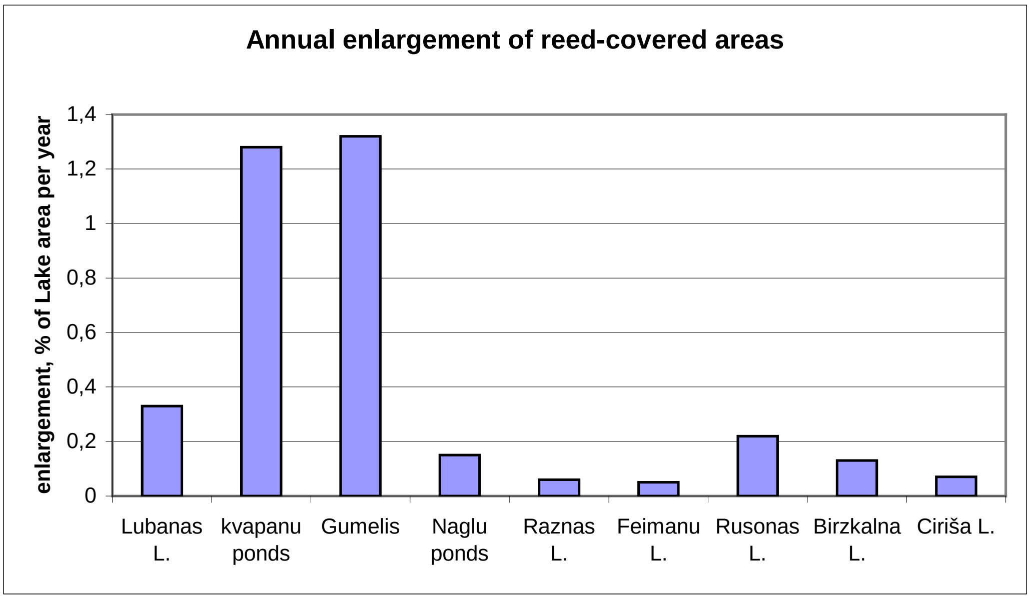


*Fig. 13.* **Annual enlargement of reed-covered areas**

If compared with the lakes located nearby, the rapidest enlargement of reed-covered areas could be observed in Rusonas lake where the total surface of reed growths had expanded by 64 ha during 13 years (see image 14) that is 2,9% of the total lake surface or 0,22% per year. The smallest enlargement of reed-covered areas was observed in Feimanu lake where in 11 year period the reeds have expanded only by 3 ha or 0,5% of the total lake surface. In Birzkalna lake and Cirisa lake the enlargement has been a little bit faster. In Birzkalna lake the reed growths have expanded by 5 ha (1,7% of the total lake surface) during 13 years, while in Cirisa lake they have expanded by 6 ha (0,9% of the total lake surface).

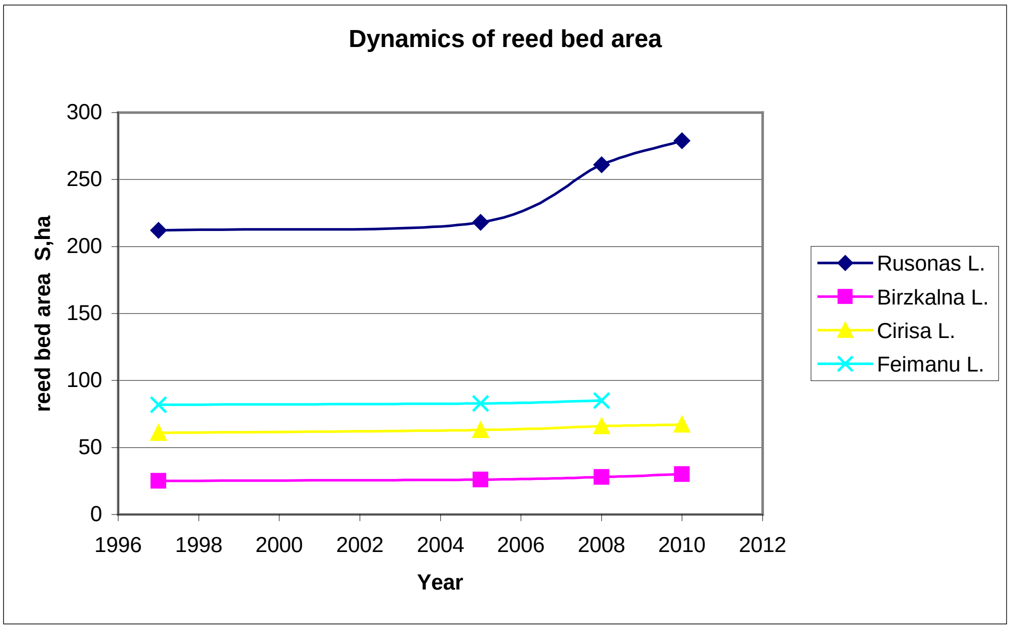


*Fig. 14.* **Enlargement of reed growths in Rusonas and proximal lakes**

In the water bodies located in the bloc of Lubanas, the reeds have expanded much faster (see images 15 and 16). During 11 years the reeds in Lubanas lake have expanded by 294 ha (3,6% of the total lake surface). The rapidest enlargement of reed-covered areas was observed in Gumelis and in Kvapanu ponds. During 11 years the reed growths in Kvapanu ponds have enlarged more than twice, the ponds are overgrowing quickly. In 2008, the reeds covered already 26,2% of the total surface of the ponds.

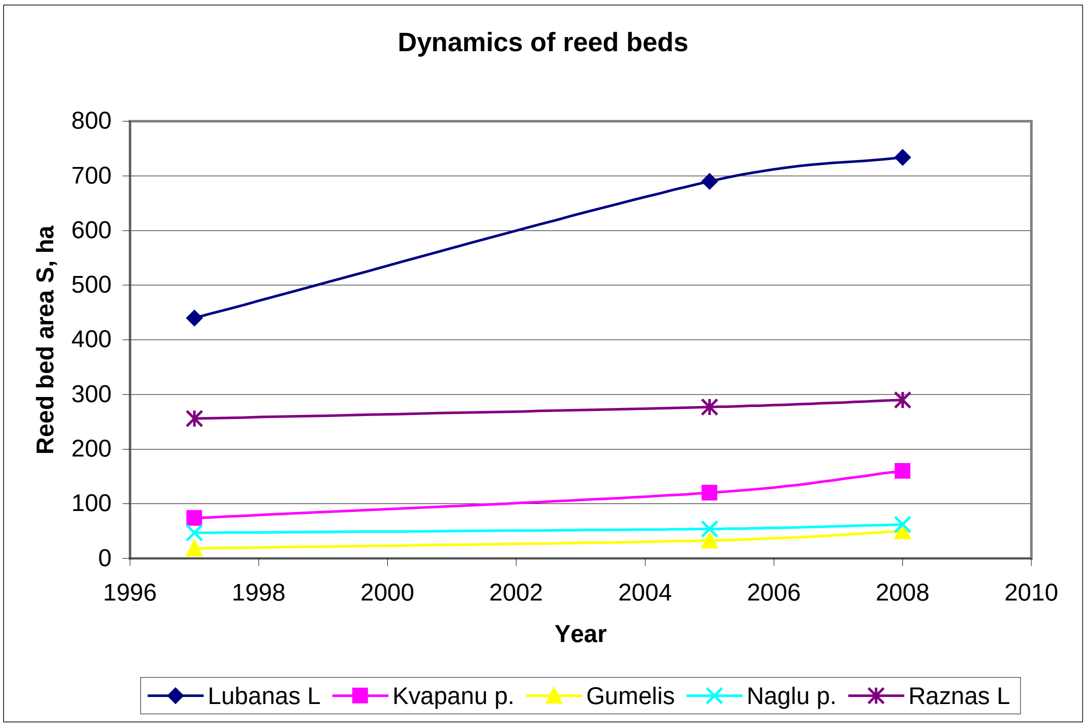


*Fig. 15.* **Enlargement of reed growths in the lakes of the bloc of Lubana**

During the given period, the reed-covered areas in Gumelis have expanded by 38 ha (18% of the total surface of the water body). The total overgrowth covers 22,7% of the total surface. If this tendency continues, Kvapanu ponds and Gumelus due to their shallowness will completely overgrow and paludify in 60 years.

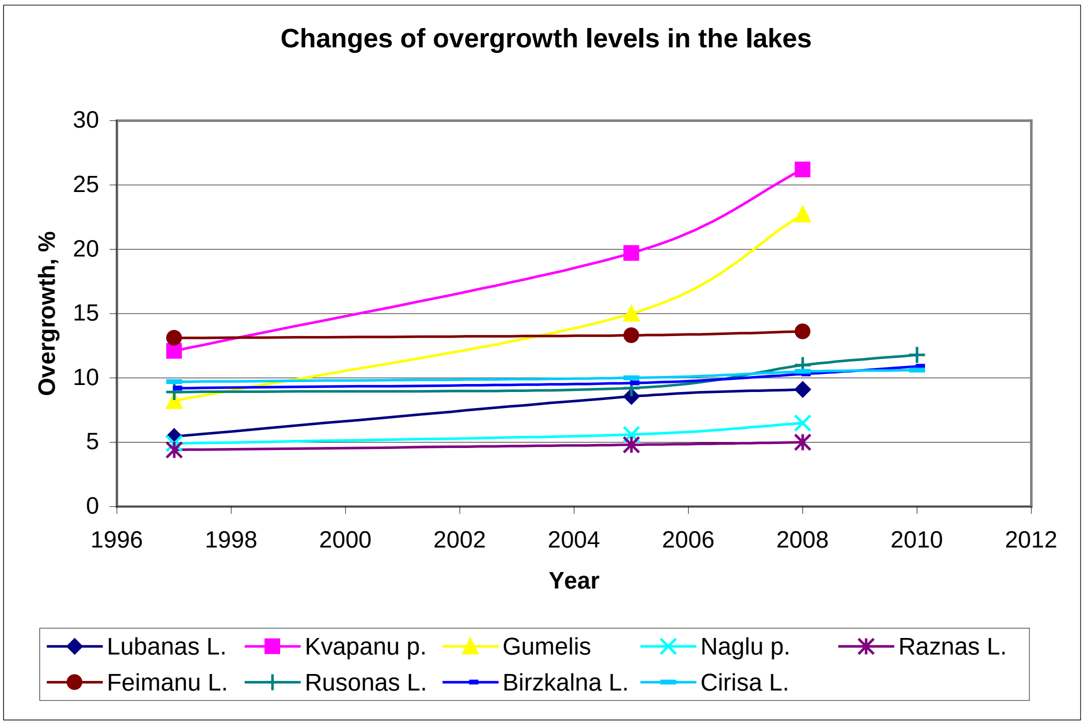


*Fig. 16.* **Changes of overgrowth levels in the lakes**

The changes in Naglu ponds are comparatively small. The total reed-covered area have expanded by 15 ha or by 1,6% of the total surface. The fast limitation of reeds could be the explained by the commercial activities in the ponds where the water level is periodically lowered and then raised again dwarfing the dispersion of reeds in new territories.

The reed-covered areas in Raznas lake have enlarged comparatively slowly. During 11 years they have expanded by 34 ha (0,6% of the total lake surface).

## Conclusions

1. In all the lakes and water bodies that are studied, the reed-covered area is expanding every year, the lakes are gradually overgrowing. The intensity of reed dispersion differs in every water body.
2. The annual enlargement of reed-covered areas ranges from 0,05% to 1,5% of the total surface of water bodies. The rapidest enlargement of reed-covered areas is observed in Gumelis and in Kvapanu ponds. If this intensity of dispersion maintains, in 60 years Kvapanu ponds and Gumelis will completely overgrow.
3. The reeds are forming large monodominant growths that supersede other species of plants and reduce the biological diversity in lakes and artificial water bodies. Separate reed growths and clumps merge and form one-piece reed areas. The reeds of shallow water bodies are expanding not only in the coastal zone but in the whole aquatorium. The capacities of reeds to occupy new territories depend on the depth of the water body.
4. The richest reed resources are concentrated in Lubanas lake, Kvapanu ponds, Raznas lake and Rusonas lake that are the most perspective for the reed extraction.
5. Since 1997, the total enlargement of reed-covered areas in the 9 lakes that are studied, covers 542 ha. It indicates a stable augmentation of reed resources.

## Acknowledgements

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EIROPAS SOCIĀLAIS FONDS

## References

1. http://www.latvijasdaba.lv/augi/phragmites-australis-cav-trin-ex-steud/](10.02.2010)
2. http://www.issg.org/database/species/ecology.asp?fr=1&si=301
3. Back,C.L, Holomuzki J.R „Long-term spread and control of invasive, common reed in Sheldon Marsh, Lake Erie"Ohio Journal of Science, Volume 108, Dec. 2008, p.-108-112 – http://www.freepatentsonline.com/article/Ohio-Journal-Science/214526722.html (10.02.2010)
4. Blossey, B. 2002. Biological Control of non-indigenous plants. Cornell University: http://www.invasiveplants.net/phragmites/problem.htm (10.02.2010).
5. Schwarzlander m, Hafliger P. „Shoot Flies, Gall Midges, and Shoot and Rhizome Mining Moths Associated with Common Reed in Europe and Their Potential for Biological Control" Proceedings of the X International Symposium ons Biological Control of Weeds 4-14 July 1999, Montana State University, Bozeman, Montana, USA, p.397-420 http://www.invasive.org/publications/xsymposium/proceed/05pg397.pdf (10.02.2010)
6. Afonin, A.N.; S.L. Greene; N.I. Dzyubenko, A.N. Frolov (eds.). 2008. Interactive Agricultural Ecological Atlas of Russia and Neighboring Countries. Economic Plants and their Diseases, Pests and Weeds[Online]. Available at: http://www.agroatlas.ru.(10.02.2010)
7. Čubars E., Noviks G. (2009). Evaluation of Reed Resources in the Lubanas Lake and substantiation of their use in energy production. Environment. Technology. Resources. Proceedings of the 7th International Scientific and Practical conference June 25-27, 2009 Vol.1. Rēzekne, 66.-74. (2009).
8. Komulainen M., Simi P., Reed energy-Possibilities of using the common Reed for energy generation in southern Finland, reports from Turku University of applied sciences 67, Turku, 19.-20. (2008).
9. Lindh T., Paappanen T., Kallio E. Production of reed canary grass and straw as blended fuel in Finland [Electronic source] -http://www.vtt.fi/inf/julkaisut/muut/2005/vtt_reed_canary1.pdf- (15.01.2010).
10. Čubars E. "Research of Reed Resource Energy Efficiency and Territorial Location for Sustainable Bio Energy Production and Development of Infrastructure in Latgale Region, RTU zinātniskie raksti. 14. sēr., Ilgtspējīga telpiskā attīstība. - 1. sēj. (2010), 67.-71. lpp. [Online]. Available at: https://ortus.rtu.lv/science/lv/publications/8939.

# III

# ENVIRONMENTAL TECHNOLOGIES

# TANNINS OF DECIDUOUS TREES BARK AS A POTENTIAL SOURCE FOR OBTAINING ECOLOGICALLY SAFE WOOD ADHESIVES

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**Abstract.** *The bark of deciduous trees grown in Latvia: grey alder, black alder, ash tree and goat willow were sequentially extracted using solvents of increasing polarity. The data about total content of both lipophilic and hydrophilic compounds were obtained using sequentially extraction with hexane and ethanol. The highest yields of hydrophilic extractives were found for grey alder and ash tree barks (25.7% and 25.8%, respectively). Hydrophilic extract from the both alder species contained high amount (up to 12% on bark dry mass) of condensed tannins (CT) or oligomeric proanthocyanidins, whereas CT content of extract from ach tree was negligible. The main component of ethanol-water extract from alder bark was identified using $^{13}C$ NMR and MALDI–TOF MS spectroscopy as* a *mixture of A- and B-type oligomeric procyanidins with the epicatechin units polymerization degree of 2-7. Ecologically friendly wood adhesives were obtained on the condensed tannin basis.*

**Keywords***: bark of deciduous trees, condensed tannins, proanthocyanidins, wood adhesive, free radical scavenging activity.*

## Introduction

The bark of deciduous tree species is scarcely explored as a source for obtaining of valuable extractives products. Grey alder, black alder, ash tree and goat willow cover, respectively, 6.8; 2.6; 3.4 and 0.7% of Latvian forest area. The composition of their bark extractives was not yet studied systematically. High portion (about 30%) of proanthocyanidins, better known as condensed tannins (CT) in polyphenolic pool of alder bark [1] makes it a prospective raw material for not only for medicine and veterinary but also for industrial application. Such condensed tannins as „quebracho" are produced commercially from wood and bark of *Schinopsis sp.* trees and are often used as a raw material for the production of tannin-formaldehyde wood adhesives [2]. Phenol–formaldehyde based wood adhesives still today dominant in European markets. However, toxic formaldehyde emission and necessity to diminish petrochemicals consumption stimulate the search of alternative environmentally safe adhesives. The antimicrobial properties of condensed tannins [3] make their application in wood composites and adhesives industry very attractive.

Proanthocyanidins are mixtures of oligomers and polymers composed of flavan-3-ol units linked mainly through C4-C8 or C4-C6 linkage (B-type) as well as the flavan-3-ol units can also be linked by an additional ether bond between C2-O-C7 (A-type). The size of proanthocyanidins molecule is described by the degree of polymerization (DP) [4].

The aim of the present work was screening of some widely spread in Latvia and Europe deciduous tree species: grey alder (*Alnus incana*), black alder (*Alnus glutinosa*), ash tree (*Fraxinus excelsior*), and goat willow (*Salix caprea*) as a potential source for CT obtaining and their testing in composition of formaldehyde free wood adhesives.

## Materials and methods

The bark of deciduous trees samples were collected from the forest in the East-South part of Latvia. Samples were sequentially extracted with solid-liquid fluidized bed extractors IKA using solvents of increasing polarity: hexane, ethyl acetate and, finally, aqueous ethanol (1:1, v/v). The ethanol was removed under vaccuum and the remaining aqueous solutions were frozen and freeze-dried. The total amount of extractives was determined gravimetrically. Total phenolics content was determined by the Folin-Ciocalteu method [5] using gallic acid (Sigma-Aldrich) as a reference compound and condensed tannins content was measured by buthanol–HCl method using procyanidin dimer B2 (Extrasynthese) as a reference compound [6]. The condensed tannins were purified from non-tannin phenolics using Sephadex LH-20 [6]. $^{13}$C-NMR (Bruker Advance 300 spectrometer, 75 MHz) and TOF-MS (QSTAR Elite System Hybrid Quadrupole-TOF/MS) spectroscopies were used for characterization of proanthocyanidins isolated from alder bark.

Condensed tannins from grey alder bark were tested for their potential antioxidant activities using a 1,1-Diphenyl-2-picrylhydrazil (DPPH$^{\bullet}$) (Sigma-Aldrich) assay. Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) (Sigma-Aldrich) was used as a reference standard. Test was performed spectrofotometrically [7], the inhibition percentage (IP) of DPPH$^{\bullet}$ was calculated as:

$$IP = \frac{(A_B - A_A)}{A_B} \times 100\%,$$

where $A_B$ is absorbance at 517 nm in blank probe (antioxidant was omitted) and $A_A$ is absorbance in the sample after 15 min. The IP values were plotted as a function of the antioxidant concentration. From the graphs the antioxidant concentration needed to obtain 50% IP was determined and defined as $IC_{50}$. According to the definition, higher antioxidant activity results in lower value of $IC_{50}$.

The condensed tannins based adhesives were obtained by mixing of aqueous tannin solution (pH 7) with 50% (w/v) aqueous polyethylenimine (PEI) solution (Sigma-Aldrich) at 22°C. The tannin adhesives were characterized by differential scanning calorimetry (DSC) using a Metter Toledo DSC 828 apparatus [8].

The resulting adhesives were tested for obtaining of plywood panels. Plywood panel samples were made using tree plies of birch (thickness of 2 mm each), and 170 g/m$^2$ of adhesive. The panels were pressed for 10 minutes at 140°C and pressure of 2 MPa. The samples obtained were conditioned in a climate room (25°C and 65% humidity) for 24 h. Then the quality of plywood panel gluing was evaluated by the statistic bending (modulus of elasticity) and the bonding shear tests, carried out according to EN314 -1:2005 [9].

## Results and discussion

The highest yield of hydrophilic extract was found for bark of grey alder and ash tree and lowest for goat willow (Figure 1). Grey alder bark is notable among investigated tree species not only by the highest total yield of hydrophilic extracts (36% from o.d. bark) but also by the high content of polyphenolics in them (13-17% from o.d. bark).

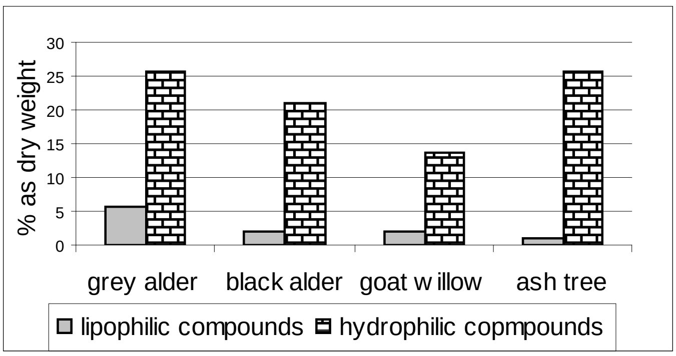


*Fig.1.* **The yield of lipophilic and hydrophilic extractives (% of oven dry bark)**

The butanol-HCl assay has greatest strength on confirmation of presence of a polymeric interflavan structure [6]. Hydrolyzable tannins do not react in this assay. The condensed tannins (proanthocyanidins) contents in the ethanol-water extracts of *Alnus incana* and *Alnus glutinosa* were 43.44% and 34.27%, respectively. The hydrophilic extract from ash tree bark, unlike the grey alder and black alder bark, did not show positive reaction in butanol-HCl assay. This indicates the negligible CT content in *F. excelsior* bark. Purified proanthocyanidins from grey alder bark were analyzed by $^{13}$C-NMR spectroscopy. The NMR signals assignment was made based on the literature data [10].

The structural diversity of the linkage (A and B type) and stereoisomer of catechin and epicatechin units is apparent from the $^{13}$C-NMR spectrum (Figure 3). Specifically, C5, C7, and C8a carbons of procyanidins appear in the region 160-150 ppm. Peak at 144.4 belong to C3' and C4' of procyanidins units. The cluster of peaks between 110 and 90 ppm is assigned to C8, C6, C6", C8" and C 2' of procyanidins. The region between 90 and 70 ppm is sensitive to the stereochemistry of the C ring. The ratio of the 2,3-cis to 2,3-trans isomers could be determined through the distinct differences in their respective C2 chemical shifts. C2 gives a resonance at 75.3 ppm for the *cis* form and 79 ppm for the *trans* form, the *cis* isomer is dominant. C3 of both *cis* and *trans* isomers occurs at 71.5 ppm. The C4 atoms showed a peak between 37-29 ppm. The chemical shift of the ketal carbon (C2) formed as a result of additional bond observed at 100.9 ppm. The results suggested the presence of another interflavan linkage (2C-O-7C). The 13C NMR spectrum showed that procyanidins units are connected mostly by C4-C8 or C4-C6 interflavonoid bonds. Judging by a special diagnostic feature peak at 100.9 ppm related to ketal carbon signal, proanthocyanidins contain doubly linked flavanyl units in the molecule (2C-O-7C) typical for A-type procyanidins (Figure 4).

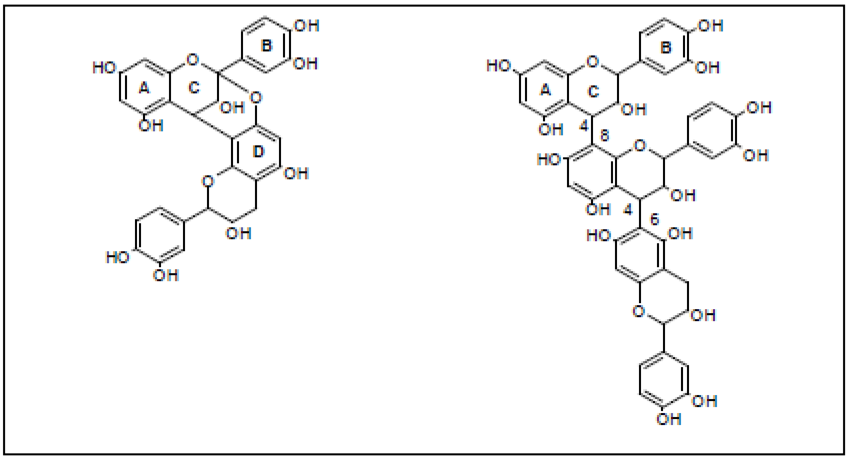

*Fig.2.* **Grey alder bark A-type procyanidine and C4-C8 and C4-C6 interflavanoid bonds containing procyanidine (B-type)**

The TOF-MS spectrum of proanthocyanidins showed that the molecular mass of proanthocyanidins polymers is not higher than 2018 Da (Figure 4).

This value corresponds to the flavan-3-ol heptamer. Detection of the molecular ion $[M-H]^-$ with mass of 575 Da confirmed the presence of A-type procyanidin in the composition of grey alder CT, whereas regular fragmentation in the range 288 – 2017 Da gave evidence that oligomeric procyanidins composed by epicatechin units. Using TOF-MS electron spray negative ionization and NMR spectroscopy the grey alder bark condensed tannins were for the first time identified as a mixture of A- and B-type oligomeric procyanidins with the epicatechin units polymerization degree of 7 (Figures 3 and 4).

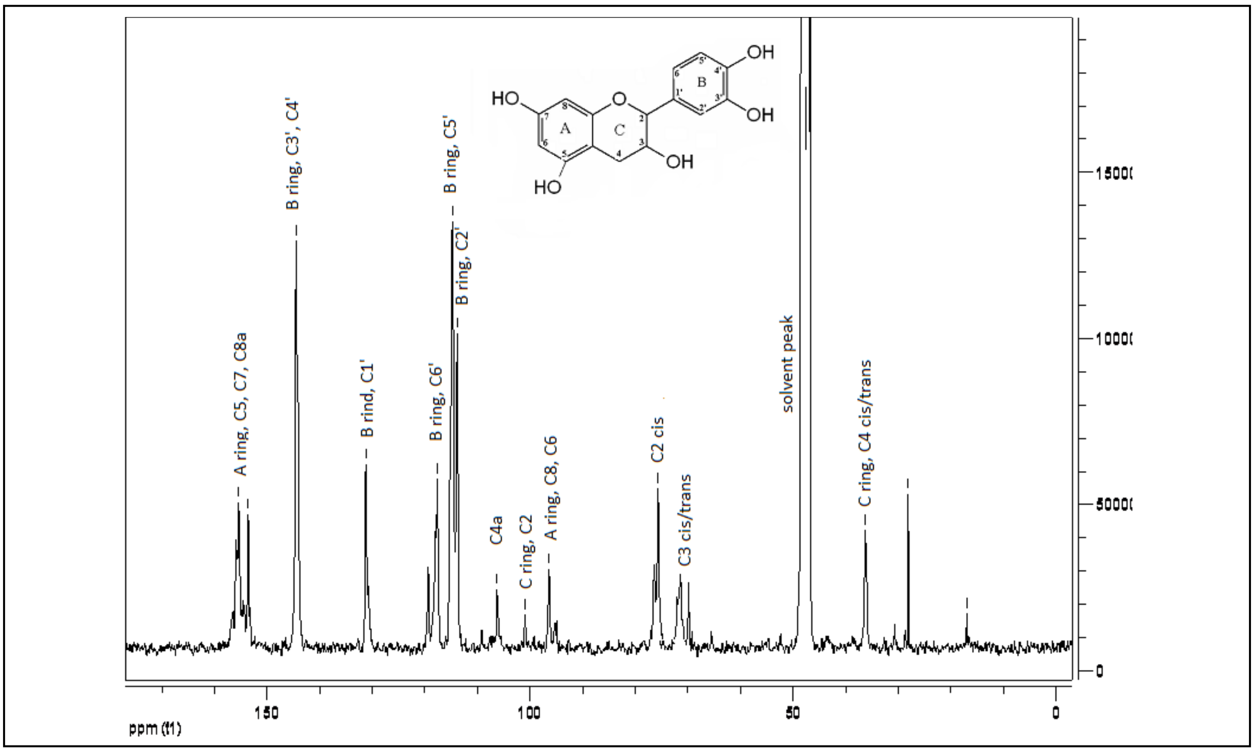


*Fig.3.* **[13] C-NMR spectrum of proanthocyanidins from grey alder bark**

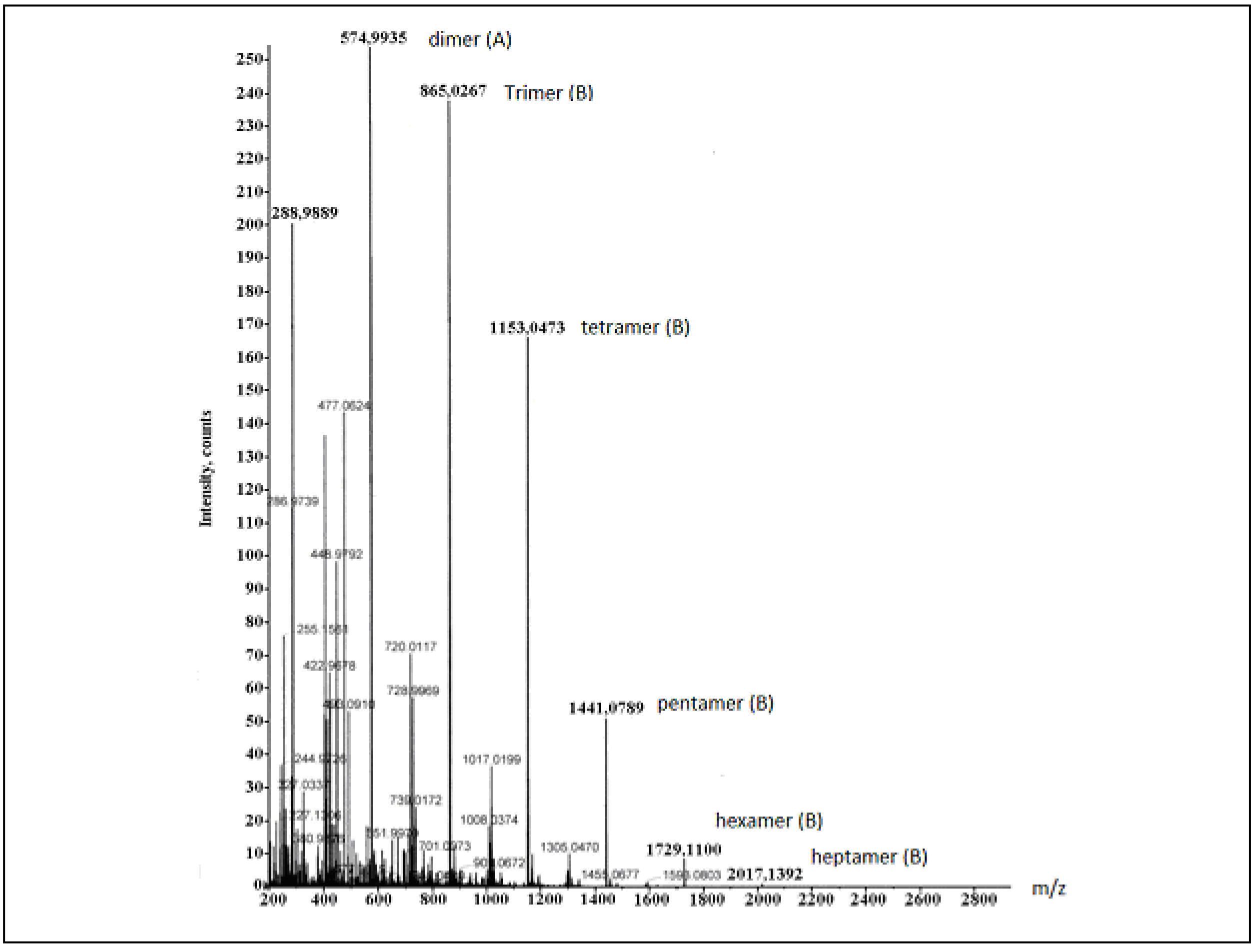


*Fig.4.* **MS spectrum of proanthocyanidins from alder bark**

The test with stable organic radical DPPH• has been used for characterization of antioxidant activity of EtOH extract from alder bark as well as of the proanthocyanidins isolated from it. . Proanthocyanidins from *Alnus incana* bark showed the higher radical scavenging activity as compared with the reference standard Trolox. The $IC_{50}$ values of proanthocyanidins, EtOH extract and Trolox were 3.1, 9.0 and 4.7 mg/l, respectively. The proanthocyanidins concentration necessary for 50% DPPH• inhibition was 1.5 times lower than that for the standard (Trolox).

Novel formaldehyde-free adhesives for wood material were obtained on the basis of rich-in-tannins EtOH extract from grey alder bark and aqueous PEI solutions.

The physico-mechanical characteristics of the tannin-PEI gels were investigated using DSC and the results obtained showed a large heat absorption peak at ~120°C, which indicated that the gel hardening proceeds in the temperature range 100-140°C. Therefore, the temperature of 140°C was chosen for manufacture of plywood composite (Figure 5) from birch veneer by hot pressing.


*Fig.5.* **Plywood samples for tension shear test in accordance with the standard EN 314**

*Table 1.*

**Result of the test of glue and tannin-PEI adhesives on shear strength**

| **Mean values** | **Tannin based adhesive** | | **PF resin adhesive** | |
|---|---|---|---|---|
| | longitudinal | transverse | longitudinal | transverse |
| MR ($KN/mm^2$) | 21.9±0.7 | 0.49±0.05 | 13.6±0.8 | 0.36±0.03 |

The results of the gluing quality tests of plywood composite (Table 1) showed that the mechanical properties of plywood glued using the CT-PEI based adhesives were higher than those for plywood glued using standard PF glues.

## Conclusions

- The major components of aqueous ethanol extracts from *Alnus sp.* trees growing in Latvia are condensed tannins (up to 0.36 g/g of hydrophilic extractives or 12.6 % on bark dry mass). High portion of CT in polyphenolic pool of alder bark makes it a prospective raw material for industrial application.
- The grey alder bark condensed tannins were for the first time identified as a mixture of A- and B-type oligomeric procyanidins with the epicatechin units polymerization degree of 2-7.
- The antioxidant activity in the of grey alder proanthocyanidin in the test with DPPH· free radical was 1.5 times higher than that for the standard (Trolox).

- The rich-in-tannins EtOH extract have the high prospects for obtaining formaldehyde-free adhesives for wood materials. The synthesized tannins-based adhesive provided 1.4 times increase in bending strength, in comparison with conventional phenol-formaldehyde resins.


**Acknowledgement**

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**References**


1. Teliševa G., Dižbite T., Bikovens O., Krasiļnikova J. Baltalkšņa miza ka izejviela bioloģiski aktīvu poilifenolu, ķīmikāliju un sorbentu iegūšanai. Rakstu krājums „Lapu koku audzēšanas un racionālas izmantošanas pamatojums, jauni produkti un tehnoloģijas", Rīga, LV KĶI, 2009, 170-174 lpp.
2. Tondi, G., Pizzi, A.Tannin-based ragid foams: Characterization and modification. Ind. Grops Prod., 29, 2009, p. 356.
3. Scalbert, A. Antimicrobial properties of tannins. Phytochem., 30, 1991, pp. 3875-3883.
4. Gu, L., Kelm, M.A., Hamerstone, J.F., Beecher, G., Holden, J., Hautowitz, D., Prior, R.L. Screening of food containing proanthocyanidins and their structural characterization using LC-MS/MS thiolytic degradation. J. Agric. Food Chem., 51, 2003, p. 513.
5. Waterhouse, A.L Determination of total phenolics. Food sci., 2, 2000, p. 567.
6. Schofield P.D., Mbugua, M., Pell, A.N. Analysis of condensed tannins: a review. Anim. Sci. Technol., 91, 2001, pp. 21-40.
7. Miliauskas, G., Venskutonis, P.R., Van Beek, T.A. Screening of radical scavenging activity of some medicinal and aromatic plant extracts. Food Chem, 85, 2004, pp. 231-237.
8. Li, K., Geng, X., Simonsen, J., Karchesy, J. Novel wood adhesives from condensed tannins and polyethylenimine. J. Adhes. Adhes., 24, 2003, pp. 327-333.
9. Zanuttini, R., Cremonini, C. Optimization of the test method for determining the bonding quality of core plywood (blackboard). Mater. Struct., 35, 2002, pp. 126-132.
10. Novarette, P., Pizzi, A., Pasch, H., Rode, K., Delmotte, L. MALDI-TOF and $^{13}$C-NMR characterization of maritime pine industrial tannin extract., Ind. Grops Prod, 32, 2010, p. 106.

# SUSTAINABILITY ASSESSMENT METHODS IN OIL SHALE MINE CLOSURE

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**Abstract.** *The post mining processes impacts on the environment, economy and people, whilst there may be positive contributions to the economy and social progress through mining there may also are negative impacts to the environment. The aim of this study is to elaborate sustainability assessment methodologies suitable for mine closure life cycle stage which allows defining hazardous influences on environment, society and economic dimensions, and helps quickly, conveniently and qualitatively solve, operate, find optimum variants for existing problems. The sustainability assessment methods will provides best decisions on the technological and post technological processes of a mining industry and can be used in the exploration, planning, exploitation and closure stages*

**Keywords:** *sustainable mining, waste management, risk assessment.*

## Introduction

The extraction of oil shale is a temporary land use. Once mining has finished the land can be 'recycled' or reused through restoration. In many cases, restoration involves returning the land to its original use. However, this is not always feasible. Through creative restoration planning, oil shale extraction offers the opportunity to improve the environment in and around mine sites or to create new land uses [1,2,3,4]. Various processes in oil shale mining industry often become dominating in the most dangerous post-technological process, which can pose a hazard to people, cause economic damage and environmental interventions. Providing of favourable conditions for oil shale mine closure in conformity with technological and ecological safety defines the necessity of elaboration the sustainability assessment methods. The reason is related to absence of suitable criteria, skills and methodology of using oil shale resources that is suitable for all parties. The aim of this study is to elaborate sustainability assessment methodologies suitable for mine closure life cycle stage which allows defining hazardous influences on environment, society and economic dimensions, and helps quickly, conveniently and qualitatively solve, operate, find optimum variants for existing problems and optimize usage of mineral resources. Important tasks are analysing a ground surface long-term stability under usage backfill method and determination opportunities to economic of mining waste management.

## Sustainability assessment methods

Sustainability assessment is a comprehensive, integrated and far-sighted approach to decision making. Its basic demand is that all significant undertakings must make a positive contribution to sustainability. The mining industries worldwide are changing their mining practices by developing and implementing a variety of technologies and mining methods are compatible with the principles of sustainable development. Adoption of the principles of sustainable development by the mining industry comes at a cost and requires major changes to current mining practices. Relating the different approaches to sustainability assessment across disciplines and against the background of the conceptual framework allows us to appraise their relative potentials and limitations. The constraints to scientific operationalisation of sustainability and to its translation into policy measures, which are revealed by this reference system, highlight the necessity for continued integrated systems research [1,2,3,4].

Closure planning is an activity that continues throughout the life of a mine, starting with conceptual closure plans prior to production, periodic updates throughout the life of the mine, and a final decommissioning plan. At most mines, progressive reclamation over the life of the mine is used to reduce the reclamation burden at closure.

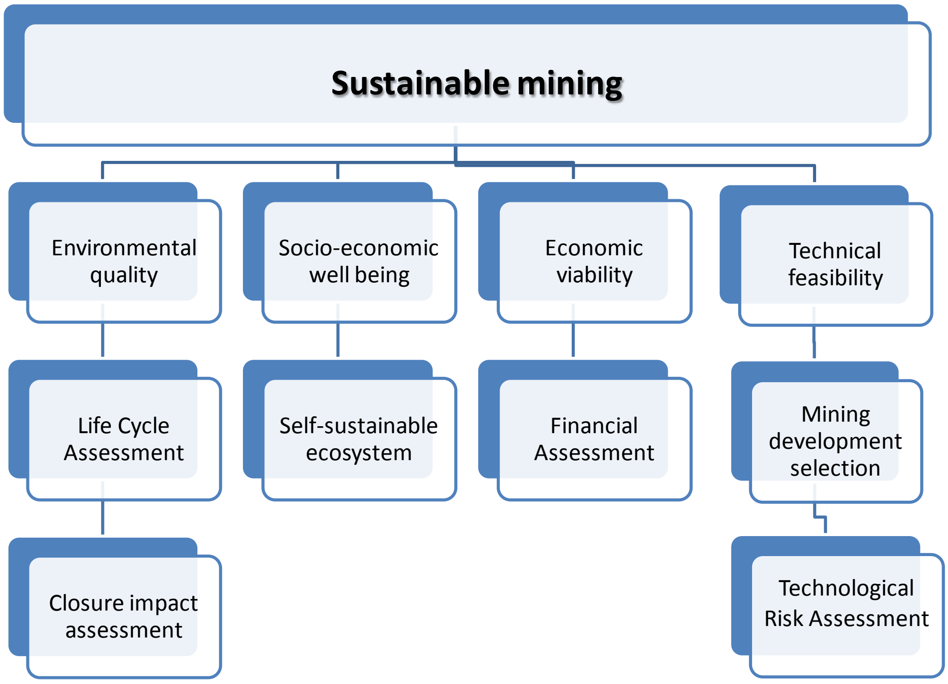


*Fig.1.* **Sustainability assessment methods**

***Environmental Quality***

The environmental impacts associated with oil shale preparation and productions are subsequently variable, as the mining methods used to extract oil shale by open and underground methods result in different environmental impacts [7]. The objective is to include all activities that usually take place around a mining site. In this study, the Life Cycle Assessment (LCA) tool is used to analyze and assess the environmental impact of oil shale mining. The inputs and outputs identified for all the technological chains of underground and open mining methods are under investigation [7,8].

This part contributes in preventing undesired collapses and hazards related to them, emission to atmosphere and aquifer. Conditions for sustainable mining in densely populated regions allows changing large areas of mined areas to suitable farmland or building areas. Mine-water could be used for drinking water after self-cleaning.

***Economical viability***

Economic sustainability is clearly identified information, integration, and participation as key building blocks to help countries achieve development that recognises these interdependent pillars. It emphasises that in sustainable development everyone is a user and provider of information. It stresses the need to change from old sector-centred ways of doing business to new approaches that involve cross-sectored co-ordination and the integration of environmental and social concerns into all development processes. Furthermore, broad public participation in decision making is a fundamental prerequisite for achieving sustainable development [1,4].

***Technical feasibility***

Technical feasibility is one of the important parts of the sustainability assessment methods. Risk assessment techniques defined in its broadest sense, deals with the probability of any adverse event [6]. Various types of risk considered in the mine closure include the engineering risk, human health risk and ecological risk. Risk assessment is the process of deciding whether the existing risks are tolerable and risk control measures are adequate. It incorporates the phases of risk analysis and risk evaluation.

***Socio-economical well-being***

This part provides diminishes the risk of accidents and casualties in mining, low emissions technologies. Socio-efficiency describes the relation between a firm's value added and its social impact. Both eco-efficiency and socio-efficiency are concerned primarily with increasing economic sustainability. The business case alone will not be sufficient to realise sustainable development.

Mine closure is the period of time when the extracting activities of a mine have ceased, and final decommissioning and mine reclamation are being completed. It is generally associated with reduced employment levels, which can have a significant negative impact on local economies. It is also the period when the majority of mine reclamation is completed, making the land safe and useful again [2,3,13].

***The methodology techniques***

- Designing mine closure systems for surface and underground mines
- Determining the elements for mine closure infrastructure
- Integrating life-cycle models of oil shale and energy commodities to describe global geologic occurrences, genetic processes, present and future uses, recycling potential, possible substitutions, disposal strategies, and associated environmental effects. Investigation of bedrock hydrological and mineral-related elements, slope stability, soil formation, and sediment transport and deposition is aid in understanding the structure and function of natural ecosystems
- Assessing geologic and geotechnical risks influencing on subsurface displacement and subsidence
- Defining technogenic deformation processes by geotechnical monitoring
- Identification of the opportunities to economic mining waste management

Predicting the long-term stability behaviour of underground oil shale mines and the attenuation or degradation of rock wastes requires an improved understanding of the rheological processes controlling the changes of physical-mechanical properties. In backfill technologies past fill of underground goaf (using mixture of limestone rock and ash from power plant) are preferred. Effect of backfilling will serve for minimization of surface movement; improvement of safety in mining (high rock pressure, water outflow, etc.; facilitation of mining operations; increase of extraction ratio; binding mobile elements). The methodology helps revealing behaviour of backfill material in-situ conditions and definition physics-mechanical characteristics and rheological properties for various structures of backfill components. Risk estimation will be used for calculation probability of a ground surface subsidence and displacement. Particular attention must go to issues of waste production and storage, old mining waste landfills, waste handling procedures, entrepreneurship development and the legal framework for waste management. Environmental and social assessment tools should be combined to enable a transition to integrated impact assessment. This will be used for future projects consultation with the community to identify local concerns.

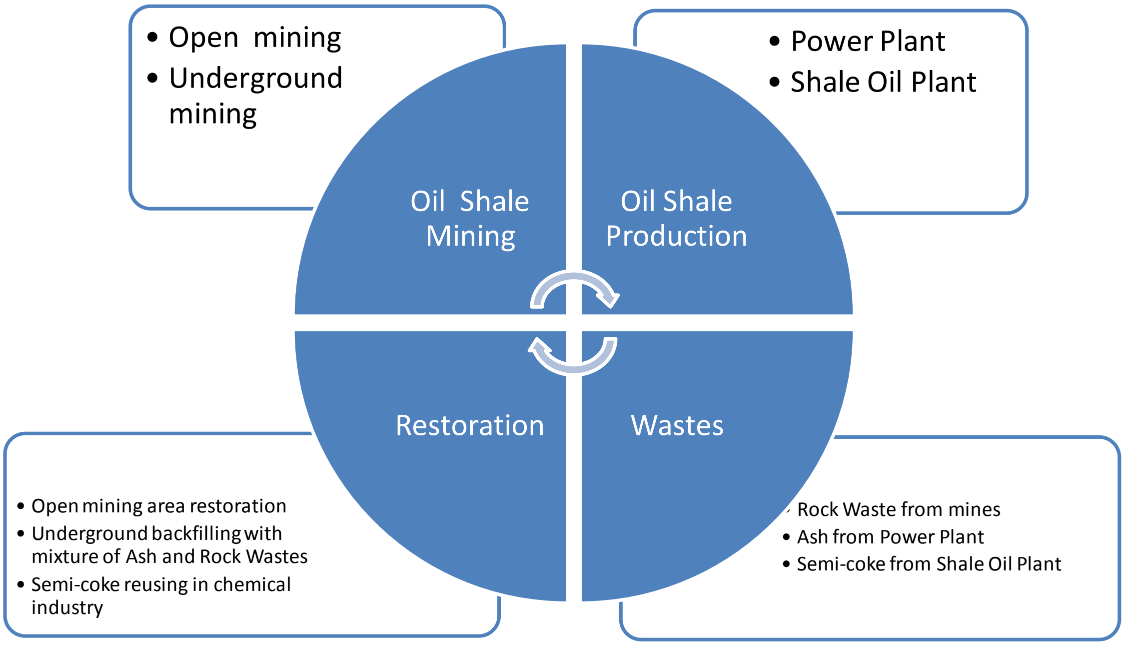


*Fig. 2.* **Shale Life Cycle stages alternatives**

## Conclusions

The sustainability assessment methods can be used for different purposes and at different levels: as a basis for decision-making when selecting among different remedial actions for a mined out area within time and financial restraints; to relate ground surface subsidence risk levels to acceptable risk levels established by the society for other activities, predicting the long-term hydrologic behaviour of aquifers and aquitards and the attenuation or degradation of toxic wastes, methodologies on management of mining wastes. The methods is able to give opportunity to find better way for mine closure planning in according with environmental performances and socio-economical well-being.

## Bibliography


1. Barbara Becker. Sustainability Assessment: A Review of Values, Concepts, and Methodological Approaches. Consultative Group of International Agricultural Research. 1997, Issues in agriculture10.
2. Eijkern, Sander , DiPiazza, S., SAM Corporate Sustainability Assessment. The sustainability year book 2009.
3. Gibson, Robert B. Sustainability-based assessment criteria and associated frameworks for evaluations and decisions: theory, practice and implications for the Mackenzie Gas Project Review, a report commissioned by the Joint Review Panel for the Mackenzie Gas Project, final report 26 January 2006, 67pp.
4. Gibson, Robert B., Sustainability Assessment: criteria and processes, with Selma Hassan, Susan Holtz, James Tansey and Graham Whitelaw (London: Earthscan, 2005), 254pp.
5. Jaber, J.O., Probert, S.D., 1999. Environmental-impact assessment for the proposed oil-shale integrated tri-generation plant. Applied energy 62, pp. 169-209
6. Sabanov, S. (2009). Risk assessment methodology in oil shale mining. The Reading Matrix Inc. Irvine, CA, USA (Toim.). Proceedings of the Eighteenth International Symposium on Mine Planning and Equipment Selection (MPES 2009) and the Eleventh International Symposium on Environmental Issues and Waste Management in Energy and Mineral Production (SWEMP 2009) (711 - 718). Reading Matrix Inc USA
7. Sabanov, Sergei ; Šommet, Julia; Milaševski, Irena; Bashkite, Viktoria; Gulevitš, Julia; Beldjaev, Viktor; Robam, Karin (2010). Sustainability assessment methods for developing advanced mining technologies. In: 9th International Symposium "Topical problems in the field of electrical and power engineering. Doctoral school of energy and geotechnology". II : Pärnu, Estonia, 14.06.-19.06.2010:, 2010, 69 - 74.
8. Sabanov, S.; Milashevski, I.; Beldjaev, V. (2010). Sustainable Mining Under Usage Modern Machines in Estonian Oil Shales Mines. In: Theory and Practice of Geomechanics for Effectiveness. The Mining

Production and the construction: The 4th International Geomechanics Conference, Bulgaria, 3-6 June 2010. , 2010, 551 - 556.

9. Sabanov, S. (2009). Sustainable development of oil shale industry under support of ecological viability of mineral resources. 8th International Symposium, September 19-23, 2009, Tallinn, Estonia. "Resource Reproducing, Low-wasted and Environmentally Protecting Technologies of Development of the Earth Interior" Proceedings of Tallinn: Department of Mining TUT; Russian University of People Friendship
10. Sabanov, S (2009). Sustainability assessment of Estonian oil shale mining using advanced technology. In: 29th Oil Shale Symposium, USA, Colorado, October 19-23, 2009. Colorado School of Mines and Colorado Energy Research Institute:, 2009.
11. Fourie, A., Brent A.C. 2006. A project-based Mine Closure Model (MCM) for sustainable asset Life Cycle Management. Journal of Cleaner Production 14 (2006) 1085e1095
12. FREDERIC CLARIDGE , SOLOMON PHIRI And WES FUNK PLANNING FOR CLOSURE COPPERBELT ENVIRONMENT PROJECT, ZAMBIA.
13. Laurence David. Classification of Risk Factors associated with mine closure. School of Mining Engineering, UNSW.
14. Laurence David. Optimisation of the mine closure process Journal of Cleaner Production Volume 14, Issues 3-4, 2006, Pages 285-298.

# MODIFIED LIGNIN AS AN ENVIRONMENTALLY FRIENDLY SURFACTANT

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**Abstract.** *The effect of softwood sulphate lignin modified by its oxidation in alkaline medium on its behaviour at the air-water and oil-water interface, where rapeseed oil and technical fish fat oil served as the oil phase, was investigated. It has been found that, irrespective of the pH values of the water solution, the ability of the modified lignin to be adsorbed at the interfaces exceeds that of unmodified lignin, which is obviously caused by the pronounced differentiation of the hydrophilic and hydrophobic parts of the molecular structure in the oxidised lignin and the decrease in the content of the high-molecular fraction ($M_w$ > 1000) in it. At low concentrations (≤ 0.01 g/dl), the stabilising action of the modified lignin in the rapeseed oil-water emulsion is the same as that of sodium dodecyl sulphate. The enhanced surface activity of the oxidised sulphate lignin enables it not only to substitute the 30% of the mass of the commercial surfactant in the detergent composition for washing stainless steel plates, used during fish smoking, but also to upgrade its properties.*

**Keywords:** *detergent composition, fish smoking, modified lignin, oil-in-water emulsion, stabiliser, surface tension.*

## Introduction

Due to the increasing requirements to environmental protection, obtaining of "green" surfactants from natural feedstock represents both scientific and practical interest. With this target, it is necessary to use renewable low-cost materials that are available in large quantities and to modify their molecular structures that show improved performance, favourable ecotoxicological properties and reduced environmental impact [1]. The surfactants from by-products of the sugar and oleochemical industries or derived from sea sources are well known [2-3]. Technical lignins, by-products of the industrial wood processing, have found widespread application as an available renewable bioresource for producing different commercially attractive end-products, including dispersants, detergents and surfactants [4]. Lignins, due to the peculiarities of their aromatic structure, can easily adsorb at various interfaces, creating mono- or multi-interface layers, which provide a decrease of interfacial tension. For obtaining "green" surfactants, lignins are chemically modified, using various methods of alkylation, sulphonation, destruction, etc. [5, 6].

In the present study, the effect of the oxidation of technical lignin, a commercial by-product, on its surface active properties at the gas-liquid and liquid-liquid interfaces, as well as its possibility to replace the surface active agent in the commercial detergent composition, which is used for cleaning stainless steel plates in fish smoking, has been investigated. It is known that Latvian fish processing is an export-oriented sector, and one of its export productions is smoked fish.

## Materials and methods

Commercial softwood sulphate lignin (SL) in the form of a high-dispersed brown powder was decontaminated from a strong alkaline solution (pH 13.3) by precipitation with sulphuric acid to pH 2 in accordance with the method [7]. The modification of SL was carried out in alkaline medium at 60°C in the presence of air oxygen under continuous stirring for 1 h. The detailed procedure of its modification with the following drying is described in our previous work [8]. The initial sample and that modified by oxidation, called as SL and SL-1, were subjected to chemical analyses. The elemental and functional analysis of the lignin samples was performed, applying the traditional analytical methods [9], including potentiometric and conductometric titration (InoLab level 3, Germany). The chemical composition of the initial and modified lignin is given in Table 1.

*Table 1.*

**Effect of modification on the elemental and functional composition of SL**

| Lignin | C, % | H, % | O, % | S, % | $OCH_3$, % | CO, % | $OH_{total}$, % | Content of functional groups, meqv/g | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $OH_{ph}$ | COOH |
| SL | 63. 9 | 5. 5 | 27. 9 | 2. 7 | 12. 2 | 3. 5 | 9. 7 | 5.1 | 5.4 |
| SL-1 | 49. 7 | 4. 7 | 43.2 | 2. 4 | 7. 4 | 3. 2 | 7. 3 | 3.5 | 6.7 |

The molecular mass (M) parameters such ($M_z$, $M_w$ and $M_n$) of the lignin samples, represented in Table 2, were determined by the SEC method, using a liquid chromatograph (Gilson, Middleton, U.S.A.). Based on the elemental and functional composition data, the average weight of the phenyl propane unit (PPU) for each sample was calculated.
The found values of molecular masses for SL and SL-1 are given in Table 2. The surface tension ($\sigma$) at the air-water interface was measured by the Wilhelmy method at 25.0 ± 0.1$^{o}$C, using a tensiometer K9 (KRUSS, Germany) and a circular thermostat TC-102 (Brookfield, UK). The values of $\sigma$ were determined for each concentration and pH value of the lignin aqueous solution after 24 h storing at room temperature. The solutions of the lignin samples were obtained by diluting the more concentrated solutions in order to reduce errors in weighing.

*Table 2.*

**SL and SL-1 molecular mass characteristics**

| Lignin | $M_z$ | $M_w$ | $M_n$ | $M_w/M_n$ | Content of high-molecular fraction ($M_w$ > 1000 ), % | PPU |
|---|---|---|---|---|---|---|
| SL | 6 020 | 4 160 | 2 840 | 1.47 | 70. 1 | 178 |
| SL-1 | 8 080 | 5 550 | 3 700 | 1.50 | 62.2 | 225 |

The pH values were regulated by adding 1M HCl and 1M NaOH. The stabilising effect of the lignin samples as well as the detergent composition in terms of the volume (H) and time (t) of water separation was studied in the rapeseed oil-in-water emulsion (40/60, v/v) and the fish fat oil-in-water one (20/80, v/v), prepared with a Disperser T10 (IKA, Germany) ($\gamma$ = 9500 rpm) for 1 min. The fish fat oil represented a by-product of the smoking process at fish working enterprises.
For the study of the ability of the modified lignin to replace the surfactant in the detergent composition, which is commonly used for cleaning stainless steel plates in fish processing, the following commercial detergent composition, containing the surfactant 5%, sodium gluconate 2%, phosphate 1%, NaOH 40% and a distilled water 52%, was used. The detergent composition, in which 30% of the surfactant was replaced by the modified lignin, was prepared for comparing the stabilising action of both surfactants to the oil-in-water emulsions. The time of observation was 2 h. Each experiment was performed at least 3 times, and the results were represented as an arithmetic average.

## Results and discussion

Table 1 shows that, after 1 h of the alkaline modification, the degree of oxidation (O/C) of SL-1 increases twice in comparison with that of the initial lignin. Simultaneously, the content of the methoxyl and phenolic hydroxyl groups decreases by 64% and 33%, respectively, but the content of the carboxylic groups increases by 25%. In spite of the negligible growth of the molecular masses of SL-1 relative to SL (Table 2), the content of the high molecular fraction in the modified lignin decreases. The relatively minor alteration in the average molecular mass parameters against the background of the considerable change in the chemical composition, taking into account the “core-shell” structure of lignin [10], may indicate that, during the oxidation process, the main chemical transformations in the SL macromolecules occur at the “shell” chains level.

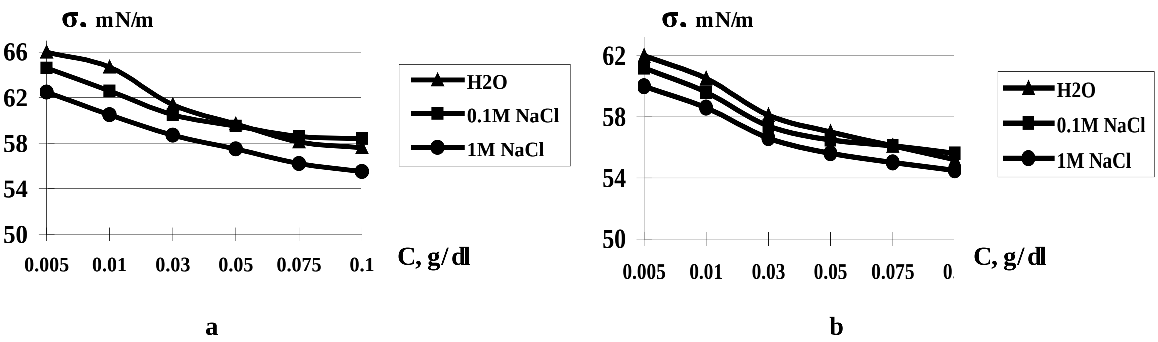



*Fig. 1.* **Surface tension at the air-water interface of SL (a) and SL-1 (b) water solutions with different ionic strength at pH 12.0 *vs.* concentration**

According to Figure 1, the surface tension at the air-water interface of both the initial and modified lignin aqueous solutions decreases with the growth in the concentration of the low-molecular electrolyte in alkaline medium. This indicates the increase in the hydrophobicity of the lignin molecules as a result of the decrease in the Stern potential and the compression in the thickness of the double electric layer around the lignin macromolecules. It can be seen (Fig. 1) that SL-1 is characterised by the lowest values of σ, while the initial lignin has the largest values of the surface tension both in a salt-free medium and in the presence of salts.

The simultaneous presence of the pronounced aromatic hydrophobic fragments and hydrophilic ones, containing the enhanced amount of carboxylic group, in SL-1 at its relatively higher content of the low molecular fractions ($M_w < 1000$) governs the high tendency of the oxidised lignin to self-aggregation and self-organisation at the interface layers, resulting in more dense packing of the lignin macromolecules in them, leading to lowering the surface tension. According to Table 2, the values of the molecular mass parameters for the initial and modified lignin differ negligibly. Hence, the main reason, influencing the favourable joint orientation and re-assembling, as well as the quality of packing at the interface may be the pronounced differentiation of the hydrophilic and hydrophobic fragments in the structure of SL-1.

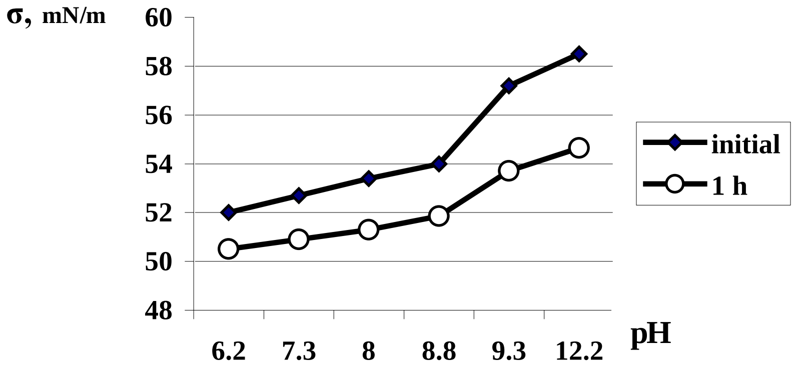
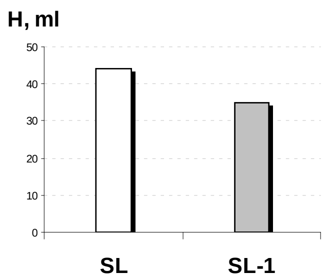



*Fig. 2.* **Surface tension at the air-water interface of SL (a) and SL-1 (b) water solutions *vs.* pH values; concentration – 0.1 g/dl**

The surface tension of both lignin samples decreases with decreasing pH (Fig. 2), which is caused by the hydrophobisation of their structure as a result of the protonisation of the phenolic hydroxyl and carboxyl groups, promoting the association of the lignin macromolecules both in solution and at the interface. At the same time, independently on pH, the oxidised lignin is characterised by lower values of the surface tension at the air-water interface in comparison with the unmodified lignin.



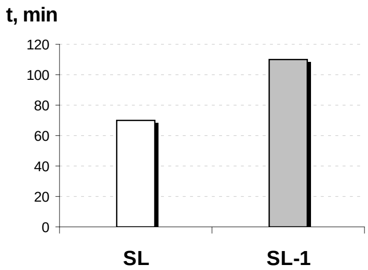




*Fig. 3.* **Final volume of the water and time separation of the rapeseed oil-in-water emulsion, stabilising with initial and modified lignin; pH of water phase 12.0; lignin concentration - 0.1 g/dl**

The comparative stabilising effect of SL and SL-1 in terms of the volume and time of water separation was studied in the rapeseed oil-in-water emulsion. It has been found that, with increasing the pH values of the water phase and growing the concentration of the lignin samples in it, the ability of the lignin samples to be adsorbed at the water-oil interface grows. At the same time, the ability of the SL-1 molecules to stabilise the water-oil emulsion is higher than that of the initial lignin. According to Fig. 3, the time of separation of the emulsion, stabilised by the modified lignin, is higher by 55%, but the volume of separation is less by 20% than those in the case of the emulsion, containing the initial lignin. It is known that the formation of interface layers in such a disperse system obviously occurs as a result of the hydrophobic interaction between the surface groups of the oil drops and the stabiliser molecule.

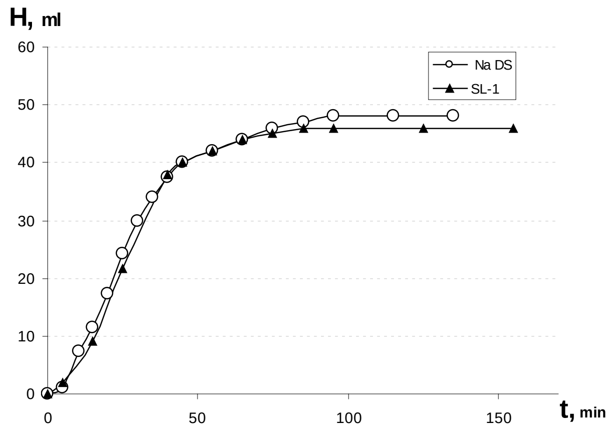



*Fig.4.* **Dependence of the volume of water separation on separation time for the rapeseed oil-in-water emulsion, stabilising with SL-1 and Na-DS sodium dodecyl sulphate; pH 12.0; concentration – 7.5 $\cdot 10^{-3}$ g/dl**

The pronounced differentiation of the hydrophobic and hydrophilic parts in the SL-1 macromolecule, along with its lower content of high molecular fraction, may promote its favourable transfer and fixation at the oil-water interface, similarly to the case of its adsorption at the water-air interface.

*Table 3.*

**Comparison of the stability of the fish fat oil-in-water emulsion, containing the initial detergent composition and the composition with the modified lignin**

| **Composition** | **Final volume of water separation, ml** | **Final time of water separation, min** |
|---|---|---|
| Initial detergent composition | 70 | 60 |
| Composition, in which the surfactant is partially replaced by SL-1 (30% of its content) | 64 | 120 |

It is known that sodium dodecyl sulphate (Na–DS) is a highly effective surfactant, which is used for the removal of oily stains and residues [11]. Fig. 4 demonstrates separation curves of the rapeseed oil-in-water emulsion for Na-DS and ML. The content of the lignin samples in the water phase is less than 0.01g/dl, which is typical for the used working concentrations of the synthetic surfactants. It can be seen that, at the given content in the water phase, the stabilising action of Na-DS and SL-1 is practically the same, which is confirmed by the equal values of the time and volume of separation in the water-in-oil emulsion. It is known that fish smoking releases a fish fat oil, which contaminates the equipment, including the used stainless steel plates. For fish fat oil removal, synthetic surfactants are commonly used, but their impact on the environment does not always comply with the required demands. In addition, with each year, the synthetic surfactant prices increase due to the growth of the oil price in the world.

Taking this into account, an attempt was made to replace a part of the commercial surfactant by the modified lignin in the detergent composition. According to the data listed in Table 3, the partial substitution of the used surfactant with the modified lignin enables not only the equivalent substitution, but also the considerable upgrading of the properties of the commercial detergent composition, which is testified by the two-fold increase in the value of the separation time of the fish fat oil-in-water emulsion, containing the modified lignin.

**Summary**

In the present study, the influence of the softwood sulphate lignin, modified by oxidation in alkaline medium, on its surface active properties at the gas-liquid and liquid-liquid interfaces was investigated. Irrespective of the pH values of the water solution, the ability of the modified lignin to be adsorbed at the interfaces exceeds that of unmodified lignin both in a salt-free water solution and in the presence of sodium chloride. The enhanced surface activity of the modified lignin enables it not only to substitute the 30% of the synthetic surfactant in the detergent composition for washing stainless steel plates, used during fish smoking, but also to upgrade its stabilizing ability.

**Acknowledgement**

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**References**

1. Benvegnu, T., Plusquellec, D., Lemiègre, L. Monomers, polymers and composites from renewable resources. Elsevier, Amsterdam, 2008.
2. Roussel, M., Benvegnu, T., Lognoné, V., Le Deit, H., Soutrel, I., Laurent, I., Plusquellec, D. Synthesis and physico-chemical properties of novel biocompatible alkyl d-mannopyranosiduronate surfactants derived from alginate. Eur. J. Org. Chem., 14, 2005, p. 3085-3094.
3. Goursaud, F., Berchel, M., Guilbot, J., Legros, N., Lemiègre, L., Marcilloux, J., Plusquellec, D., Benvegnu, T. Glycine betaine as a renewable raw material to „greener" new cationic surfactants. Green Chem., 10 (3), 2008, p. 310-320.
4. Sarkanen, K.V., Ludwig, C.H. (Eds.). Lignins: occurrence, formation, structure and reactions. John Wiley & Sons, New York, 1971.
5. Moeller, T., Soldanski, H-D., Kuech, S., Noglich, J. Multiphase cleaning composition containing lignin sulfonate. U.S. Patent 6,288,015, 2001.
6. Yang, D., Qiu, X., Zhou, M., Lou, H. Properties of sodium lignosulfonate as dispersant of coal water slurry. Energy Conversion and Management, 48(9), 2007, p. 2433-2438.
7. Lin, S.Y., Dence, C.W. (Eds.). Methods in lignin chemistry. Springer-Verlag, Berlin-Heidelberg, 1992, p. 568.
8. Shulga, G., Bikova, T., Priede, V., Treimanis, A. Chemical transformations in kraft-lignin matrix during long-term alkali oxidation. Chemical Technology, 1(35), 2005, p. 80-84.
9. Zakis, G.F. Functional analysis of lignins and their derivatives. Tappi Press, Atlanta, 1994.
10. Shulga, G., Priede, V., Shakels, V., Bikova, T., Treimanis, A. Behavior of oxidized kraft lignin as a "core-shell" polymer in aqueous solutions. Abstracts of the 39$^{th}$ IUPAC Congress "Chemistry at the Interfaces" and the 86$^{th}$ Conference of the Canadian Society for Chemistry. Ottawa, Canada, 10-15 August, 2003, p. 271.
11. Sodium lauryl sulfate [retrieved on 14.02.2011], website: http://en.wikipedia.org/wiki/Sodium-lauryl-sulfate.

# PROPERTIES OF ISOLATED LIGNIN FROM MODEL WASTEWATER

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**Abstract.** *Model wastewater, imitating the hydrothermal treatment of birch wood in the basins of veneer production, was obtained under laboratory conditions. Birch lignin (BLIG) was isolated from the model wastewater by precipitation with concentarted sulphuric acid. The increase in reduced viscosity with decreasing concentration of BLIG in the water solutions indicated its polyelectrolyte behaviour. The presence of both ionized functional groups and hydrophobic aromatic fragments in the BLIG molecules favoured its surface active properties. With decreasing pH and increasing concentration, the surface activity of BLIG at the air-water and oil-water interfaces increased, indicating the enhanced hydrophobicity of lignin fragments due to the protonization of its acidic groups. The pronounced surface activity of BLIG was in accordance with the very low value of its critical micelle concentration. The dependence of the emulsion stability on the ionic strength may testify the predominant structural mechanical mechanism of the stabilization of the rapeseed oil-in-water emulsion, containing BLIG as a stabilizer. The revealed surface properties of the isolated lignin allow predicting its application for lowering surface tension in different disperse systems to prevent the coalescence and agglomeration phenomena.*

**Keywords:** *critical micelle concentration, isolated lignin, model wastewater, polyelectrolyte swelling, veneer production.*

## Introduction

Over 50 percent of Latvia is covered by forests and wood represents over 20 percent of Latvia's processing industry. According to forest inventory statistics data, birch is the second largest wood species in Latvia; it contributes to 28.2 percent of total forest area with a total growing stock of 153 million $m^3$. Due to the natural spread of forests to agricultural lands and forest clearings' natural renewing with hardwood species, the proportion of the birch and other hardwood forest stands is increasing. Considering the high proportion of the birch forest stand, its future use is important. One of the most significant birch wood processing ways with a high added value in Latvia is veneer production. Not taking into account the last year's economic situation in the world, the production and demand of veneer is increasing in Latvia and Europe every year [1, 2].

The wood hydrothermal treatment process in veneer production generates a great amount of wastewater, replete with low-molecular lignin fragments, hemicelluloses and extractives. These organic substances are responsible for the high chemical oxygen demand and color of wastewater, obtained during wood hydrothermal treatment that, in its turn, has an adverse effect on the environment. Keeping in mind the zero waste policy for rational use of bioresources and the possible usage of waste wood originated matter in practice [3-5], it is very important to extract quantitatively the biomass components from the basin's wastewater and to characterize the isolated ones.

The aim of this work was to investigate the properties of the lignin isolated from laboratory wood hydrolysate, imitating the wastewater of veneer production, targeting to its practical application.

## Materials and methods

The treatment of birch wood sawdust (cellulose – 40.3%, lignin – 25.2%, extractives – 3.9%) was performed in a water solution with pH 9.0 and the hydromodulus 1/50 (sawdust/water) at the temperature 90ºC for 4 h. The comparison of the elemental and functional compositions of the dry matter derived from the obtained hydrolyzate, imitating the hydrothermal treatment of birch wood in veneer production, and industrial wastewater has shown that their differences in the chemical composition were not significant [6].

Birch lignin (BLIG) was isolated from the obtained wood hydrolysate by using 20% sulphuric acid solution [7]. Elementary analysis of samples was determined using Elementar Analysensysteme Vario MACRO CHNS. Functional analysis was performed by analytical methods according to [7, 8]. FT-IR spectra were recorded on a spectrophotometer Perkin-Elmer Spectra One in a range of 450-4000 $cm^{-1}$, using a KBr tablets, containing finely ground samples. UV spectra were recorded with a Genesys 10UV spectrophotometer in a range of 220-420 nm. The values of the determined extinction coefficient of BLIG varied from 13.5 l $g^{-1}$ $cm^{-1}$ ($\lambda$ = 276 nm) atpH 5.3 to 16.8 l $g^{-1}$ $cm^{-1}$ ($\lambda$ = 280 nm) atpH 12.7. These indices were typical for the lignins of hardwood species [9]. The surface tension at the air-water interface was measured by the Wilhelmy plate method, using the tensiometer KRUSS 9K, after 24 h storage of lignin solutions at room temperature. The viscosity of the diluted solutions was determined in a capillary viscosimeter Schott Ubbelode at a temperature of 25°C. For surface tension and viscosity determination, a BLIG sample was dissolved in 0.1 M NaOH in the concentration range 0.0006-0.10 g/dl. The stabilizing properties of the isolated BLIG were measured by using the emulsion "rapeseed oil-in-water" (40/60, v/v) with a BLIG concentration in the water phase of 0.01-1.0 g/dl. The pH values of the water phase, containing BLIG, were adjusted with 1M NaOH and 1M HCl. The emulsions were prepared with a Disperser T10 (IKA, Germany) ($\gamma$ = 9500 rpm) for 1 min. The aggregative stability of the emulsions was evaluated by the separation volume of water and separation time. The supramolecular structure of the isolated lignin was examined with a scanning electron microscope (Tesla, Czech Republic).

## Results and discussion

To characterize the lignin low molecular fragments, precipitated from the model wastewater, analytical chemical analysis and Fourier spectroscopy were used. In the FT-IR spectra of BLIG (Fig.1), the typical bands, which are common for hardwood lignins, can be seen. The broad band at 3422 $cm^{-1}$ was due to the O-H bond stretching in phenolic and aliphatic structures, and the minor bands at 2928 $cm^{-1}$ and 2855 $cm^{-1}$ were assigned to aliphatic C-H stretching in aromatic methoxyl groups, and in methyl and methylene groups of side chains. A band at 1714 $cm^{-1}$ may be assigned to the presence of unconjugated and conjugated carbonyl and aromatic carboxyl groups in lignin macromolecules. Aromatic skeletal vibrations give three strong peaks at 1606, 1512 and 1419 $cm^{-1}$. A relative higher intensity of the band at 1606 $cm^{-1}$, in comparison with the band at 1512 $cm^{-1}$, may be caused by the presence of a significant amount of syringyl derivatives in the lignin macromolecule and condensed aromatic structures, favouring the increase in the intensity of this absorption band.

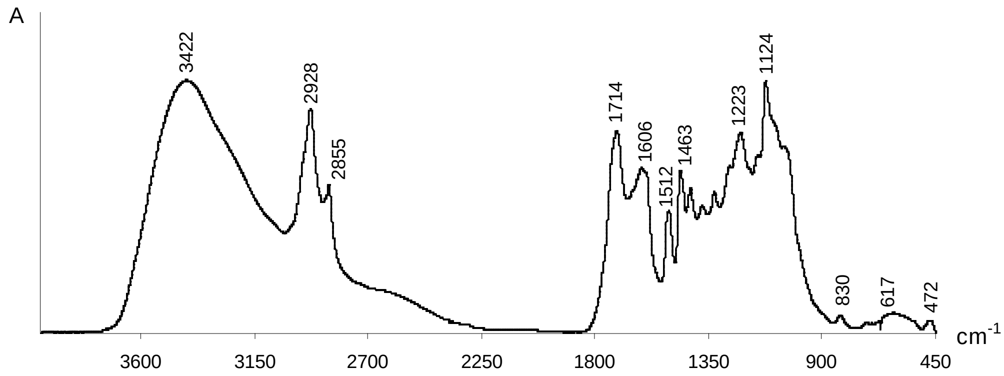


*Fig.1.* **FT-IR spectrum of the isolated birch lignin**

A weak band at 1375 $cm^{-1}$ may be caused by the presence of phenolic OH and aliphatic C-H in methyl groups. The signals at 1327, 1124 and 830 $cm^{-1}$ demonstrate that BLIG contains a certain content of guaiacyl and syringyl units, and the band at 1223 $cm^{-1}$ represent a p-hydroxyphenyl unit [10]. A very strong band at 1124 $cm^{-1}$ may be caused by the C-H deformation in the syringyl units as well as in the secondary alcohols or by C=O stretching vibrations. The band with a maximum at 1051 $cm^{-1}$ is complex and may be governed by both the deformation vibrations of C-H in the aromatic structures with predominating guaiacyl units, and the deformation vibrations of C-O in primary and stretching vibrations of unconjugated C=O groups [11].

*Table 1.*

**Elemental and functional composition**

| Samples | C % | H % | N % | O % | S % | $OCH_3$ % | CO % | OH % |
|---|---|---|---|---|---|---|---|---|
| BLIG | 53.36 | 6.63 | 0.61 | 39.03 | 0.37 | 7.53 | 4.76 | 11.24 |

The content of the main functional groups – methoxyl, carbonyl and hydroxyl groups of BLIG, which were determined by the classical methods of lignin analytical chemistry, is given in Table 1.

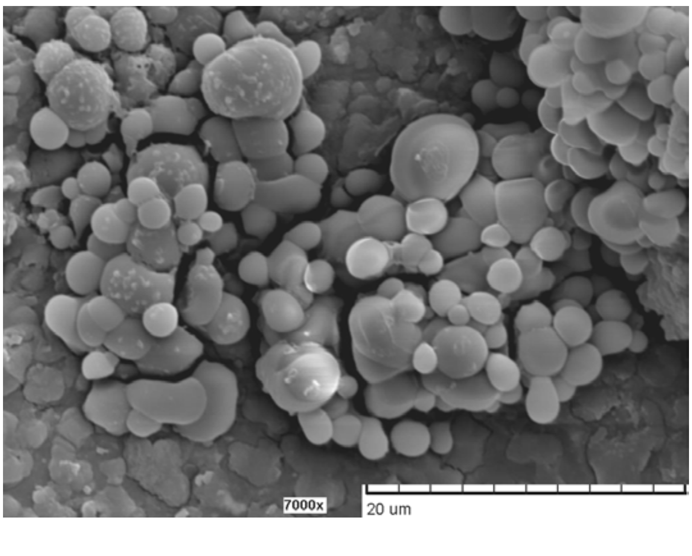


*Fig.2.* **SEM image of the air-dried birch lignin isolated from weak acidic medium**

It has been found [6], that BLIG is rich in a considerable amount of weak phenolic hydroxyl and carboxyl groups, the so-called lignin acidic groups. Their presence is the reason of the polyelectrolyte behaviour of BLIG in aqueous media, which manifests itself in an increase in reduced viscosity with decreasing concentration of lignin in the solution (Fig.3.).

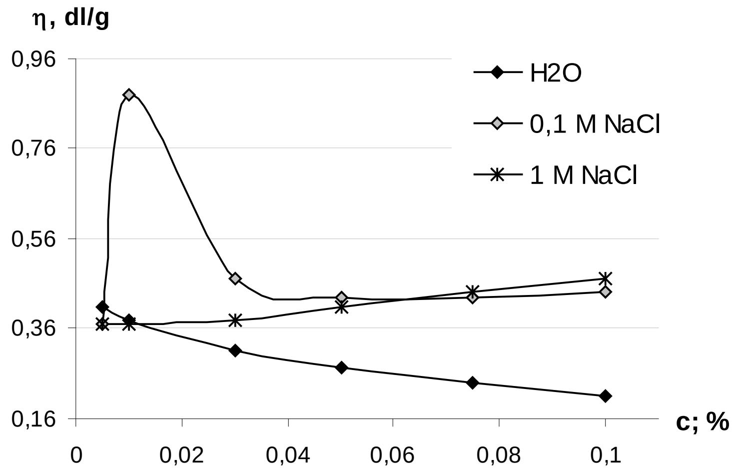


*Fig.3.* **Reduced viscosity of BLIG water solutions vs. their concentration in the presence of NaCl at pH 12.7**

The swelling of lignin macromolecules is expressed, to a greater extent, in strongly alkaline media and in the presence of 0.1 M NaCl. However, the increase in the concentration of NaCl and decreasing pH of the BLIG solution favour the inhibition of swelling. The presence of both the ionized functional groups and hydrophobic aromatic fragments in the molecules of the isolated lignin favours its surface active properties. The latter were studied in BLIG water solutions depending on their pH and concentration values (Fig.4.).

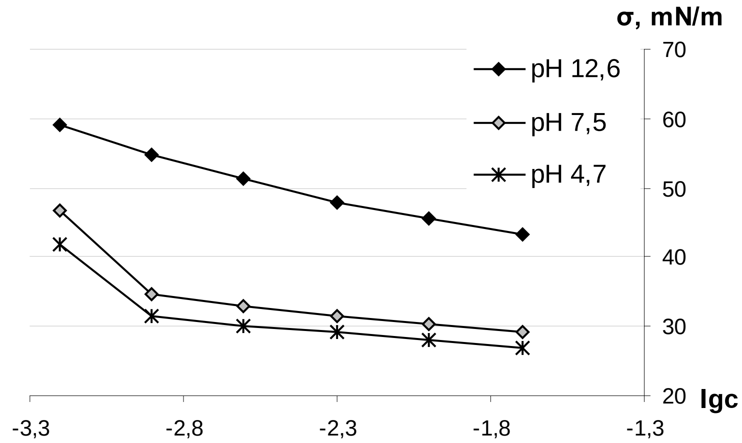


*Fig.4.* **Surface tension at the air-water interface of the BLIG aqueous solutions at different pH vs. logarithm of its concentration**

With decreasing pH and increasing concentration, the surface activity of BLIG at the air-water interface grows, indicating the enhanced hydrophobicity of lignin fragments due to the protonization of phenolic and carboxylic groups**.** In the acid medium, the surface tension of the water solutions at the air-water interface achieves the minimum values, which do not exceed 31.5 $mNm^{-1}$. The pronounced tendency of BLIG molecules to decrease the surface tension at the air-water interface is in accordance with the very low critical micelle

concentration (CMC) values of BLIG molecules in neutral and acid media that are not higher than $1 \cdot 10^{-3}$ g $dl^{-1}$.
Fig.5. shows the values of the volume of water (H) and the time of separation of the rapeseed oil-in-water emulsion (t), in which the isolated lignin as a stabilizer with different concentrations in the water phase with pH 5.5 was used. According to the obtained results, with increasing content of BLIG in the emulsion, the stability of the emulsion increases, which is indicated by the decrease in the separation volume of water and the increase in the separation time. The presence of 0.1 NaCl in the weak acid water phase decreased still to a greater extent the separation volume of the emulsion, with increasing lignin concentration. At the same time, the presence of 1 M NaCl in the water phase dramatically impaired the stabilizing action of BLIG and caused the full separation of the emulsion already within the first 10 min irrespective of the stabilizer concentration.

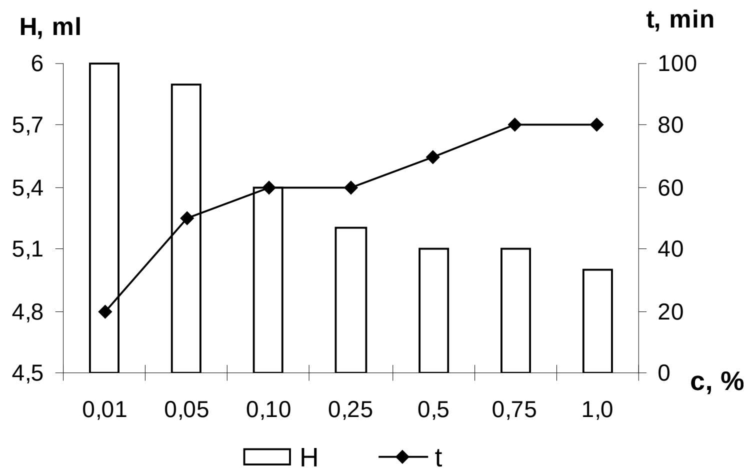


*Fig.5.* **Volumes of water and time of separation of the rapeseed oil-in-water emulsion, containing BLIG of different concentration at pH 5.5**

The dependence of the emulsion stability on the ionic strength may confirm the predominant structural mechanical mechanism of the stabilization of the rapeseed oil-in-water emulsion, containing the isolated birch lignin, in the acidic media. This assumption is also confirmed by decreasing stability of the rapeseed oil-in-water emulsion with increasing pH value of the lignin-containing water phase.

## Summary

In this work, the peculiarities of the chemical composition of birch lignin, isolated from laboratory wood hydrolyzate, imitating the wastewater of veneer production basins, and its surface active properties at air-water and oil-water interfaces depending on the lignin concentration, pH and ionic strength has been studied. The fine surface-active properties of BLIG allow predicting its usage as a surfactant for lowering surface tension at the interfaces in different disperse systems to prevent their coalescence and agglomeration.

## Acknowledgements

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## References


1. Forest industry in Latvia, wood industry [retrieved on 15.12.2010], website: http://www.latforin.info.
2. Andersons, B., Kokorevics, A. Improving Latvia's wood research capabilities. International Inovations, Issue Food, No. 1, 2011, p. 83-85.
3. Shulga, G., Shakels, V., Brovkina, J., Solodovniks, P., Skudra, S. Synthesis and properties of pH-responsible biodegradable lignin-based surfactants. Abstracts of the 7th World Surfactants Congress 'CESIO 2008', Paris, France, June 22-25, 2008, p. 98.
4. Skudra, S., Šakels, V., Neiberte, B., Šuļga, G., Reihmane, S. Physico-chemical characterization of sulphate lignin, obtained from the black liquor of the Kehra Pulp-and-Paper Plant "Horizon" (No Kehras celulozes un papīra rūpnīcas „Horizon" melnā atsārma iegūta sulfātlignīna fizikāli ķīmiskais raksturojums). Proceedings of RTU, Materials Science and Applied Chemistry, Vol. 1, No. 22, 2010, p. 38-43.
5. Šuļga, G., Brovkina, J., Skudra, S., Šakels, V., Aniskeviča, O. New environmentally friendly lignin binder from hardwood waste, its properties and application for obtaining geocomposites (Jauna videi draudzīga lignīna saistviela no lapu koksnes atlikuma, tās īpašības un pielietojums ģeokompozītu ieguvei). State Research Programme No. 1-23/65. Substantiation of Deciduous Tree Growing and Rational Use, Novel Products and Technologies (Lapu koku audzēšanas un racionālas izmantošanas pamatojums, jauni produkti un tehnoloģijas), 2009, p. 150-153.
6. Skudra, S., Shulga, G., Reihmane, S. The study of birch lignin isolated from hydrolyzate imitating wastewater of veneer production. Proceedings of RTU, Material Science and Applied Chemistry, 2011 (submitted for publication).
7. Lin, S.Y., Dence, C. W. (Eds.). Methods in lignin chemistry. Springer-Verlag, Berlin-Heidelberg, 1992, p. 568.
8. Zakis, G.F. Functional analysis of lignins and their derivatives. Tappi Press, Atlanta, 1994.
9. Fengel, D., Wegener, G. Wood - chemistry, ultrastructure, reactions. Walter de Gruyter, Berlin, 1984, p. 613.
10. Sarkanen, K.V., Ludvig, C.H. (Eds.). Lignins: occurrence, formation, structure and reactions. John Wiley & Sons, New York, 1971.
11. Sun, R. C., Tomkinson, J., Ye, J. Physico-chemical and structural characterization of residual lignins isolated with TAED activated peroxide from ultrasound irradiated and alkali pre-treated wheat straw. Polymer Degradation and Stability, No. 79, 2003, p. 241–251.



**Anotācija.** *Laboratorijas apstākļos iegūts modeļšķīdums, kas imitē bērza koksnes apstrādes procesu finiera ražošanas hidrotermiskajos baseinos. No iegūtā modeļšķīduma izdalīts bērza lignīns (BLIG), nogulsnējot ar sērskābi. Samazinoties BLIG koncentrācijai šķīdumā, tā reducētā viskozitāte palielinās, kas liecina par BLIG polielektrolīto dabu. Jonizēto funkcionālo grupu un hidrofobo aromātisko fragmentu klātbūtne BLIG molekulā nosaka tā virsmas aktīvās īpašības. Ar šķīduma pH samazināšanos un koncentrācijas palielināšanos BLIG virsmas aktivitāte gaiss-ūdens un eļļa-ūdens fāzu robežā palielinās, kas norāda uz lignīna fragmentu paaugstināto hidrofobitāti, ko izraisa tā skābo grupu protonēšanās. Izteiktā BLIG virsmas aktivitāte ir saskaņā ar tā zemo micellu veidošanās kritisko koncentrāciju. Emulsiju stabilitātes atkarība no jonu spēka var liecināt, ka rapšu eļļa-ūdens emulsijā, kas kā stabilizatoru satur BLIG, dominē strukturāli mehāniskais stabilizācijas mehānisms. Izdalītā lignīna atklātās virsmas īpašības rada iespēju to pielietot virsmas spraiguma samazināšanai dažādās dispersās sistēmās, aizkavējot to koalescenci un aglomerāciju.*

# COMPACTING MECHANISMS OF COMMON REED PARTICLES

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**Abstract.** *The paper present experimental investigation results of common reeds (Phragmites australis) particle compacting in closed die. Common reeds are important natural biomass resource in Latvia. Compacting of biomass is very complicated process for solid biofuel production and there are many factors influencing to this process. The quality parameters of compacted biomass are described by European countries standards for solid biofuel. Density is the most important quality parameter of biomass compacting. The paper present results of common reeds particles compacting mechanism in closed die. Maximum pressure 212 MPa had been achieved in compacting. For compacting process evaluation has been determined pressing energy and density of briquettes. The minimum of density 0.87 g cm$^{-3}$ have briquettes with particle size 12 – 13 mm, but maximum density 1.03 – 1.04 g cm$^{-3}$ two particle sizes < 0.5 mm and 32 – 33 mm briquettes. Maximum value of energy consumption for compacting (~172 kJ kg$^{-1}$) has been obtained for reed particle size 32 – 33 mm, minimum value (~53 kJ kg$^{-1}$) for particle size less than 0.5 mm.*

**Keywords:** *briquette density, common reeds, compacting.*

## Introduction

European Union energy policy determines the aim to increase using of renewable energy resources providing independence from imported energy and reduction of fossil fuel use. Substitution of fossil feedstock for energy by biomass is important measure also for greenhouse gas (GHG) emission mitigation.

In the rural area of Latvia open water systems (rivers and lakes) and wetlands play an important role. Area of eutrophic lakes has become overgrown by emergent vegetation – mainly common reed. This lake terrestrialization process is natural and so we have another biomass resource – reeds biomass, which can be used like straw material for energy production and also as industrial raw material. Common reeds are important natural biomass resource, because there are more than 2000 lakes with shorelines overgrown by common reeds in Latvia. Naturally reed biomass is material of low bulk density (0.02 – 0.06 g cm$^{-3}$), therefore compacting of biomass is one of the important processes for effective handling, transport and storage of this biomass material for solid biofuel production.

European countries have standards (ŌNORM 7135, SS 18 71 20 and DIN 51731) [1, 2] concerned with wood pellet and briquette properties. Demand of mentioned biofuel density is > 1.0 g cm$^{-3}$ in standards. For compacting process evaluation has been determined pressing energy consumption and density of briquettes. The aim of investigation is to find necessary particle size for compacting common reeds to density > 1.0 g cm$^{-3}$.

## Materials and methods

The main task of this investigation was determination of compacting force – displacement characteristics for compacting of different size reed particles. Reed stalk material biomass with moisture content of 8.7% was chopped to different length and had been used for densification. Recommended moisture content is in the range of 8 – 15% for biomass materials to product high quality briquettes. At this moisture content, the briquettes are strong and free of cracks and the compacting process is preferential [3, 4]. The moisture content was determined using standard ASAE S358.2 DEC93, where oven drying of the samples was carried out at 103 ºC for 24 h [5].

Particle size of chopped common reeds was determinate from sieve analysis: < 0.5; 1 – 2; 3 – 4; 5 – 6; 7 – 8; 12 – 13; 22 – 23; 32 – 33 mm. Fine particles readily absorb moisture then large particles, and therefore, undergo a higher degree of conditioning [3]. An important indicator of particle size is necessary cutting energy. Specific cutting energy per mass unit is growing considerably from 2000 J kg$^{-1}$ to 4000 J kg$^{-1}$ when shredding size is changed from 20 to 10 mm [6]. Biomass compacting represents technology for the conversion of biomass into a solid biofuel in shape of briquettes and pellets. Studying the densification behavior of common reed particles through experiments should help to understand the densification mechanisms that could produce high quality compacted products and to design energy efficient compacting mechanisms.

Compaction experiments had been carried out in closed die with diameter 35 mm by means of hydraulic press equipment (Fig. 1). Maximum pressure 212 MPa had been achieved in compacting. The dosage of 35 grams of chopped common reeds particles was used for every briquette pressing.

*Fig. 1.* **Hydraulic press**

Common reed stalk material ultimate tensile strength is 330 ± 29 N mm$^{-2}$ [6]. As common reeds are the strongest stalk material between other energy crops, they can be used as representative energy crop.

The briquettes with different density had been obtained as result of compacting experiments. For density calculation the weight of briquette was measured on electronic scales Sartorius GM 312 with division 0.01 g and size of briquettes was measured with sliding calipers (division 0.1 mm).

During compacting experiments were recorded pressure and piston displacement values. For force calculation was used equation:

$$F = \frac{p \pi d_1^2}{4}, \quad (1)$$

where $p$ – pressure, Pa;

$d_1$ – hydraulic press piston diameter, m.

Compacting work was obtained from force – displacement curves of graphical integration. Total specific energy (kJ kg$^{-1}$) of common reed compacting is calculated by equation:

$$E = \frac{W}{m}, \quad (2)$$

where $E$ – specific energy of compacting, kJ kg$^{-1}$;

$W$ – work of compacting, kJ;

$m$ – mass of compacted reed, kg.

## Results and discussion

During compacting experiments force – displacement characteristic was determined. The shapes of force – displacement characteristics of compacting of different size reed particles were similar – nonlinear curves with two quasilinear parts are shown in Fig. 2.

The maximum piston displacement required for initial common reed particles compression to 13 MPa. Material final pressing occur with more rapid increase of pressing pressure and at a small piston displacement, about 1 – 2 cm. This force – displacement characteristics are necessary for design of biomass compacting mechanisms. Using different hydraulic circuits can be realized required force – displacement characteristic of compacting. Innovative press mechanism in shape of rhomboid linkage with hydraulic drive (Patent LV 14201) is recommended for briquetting of stalk material biomass.

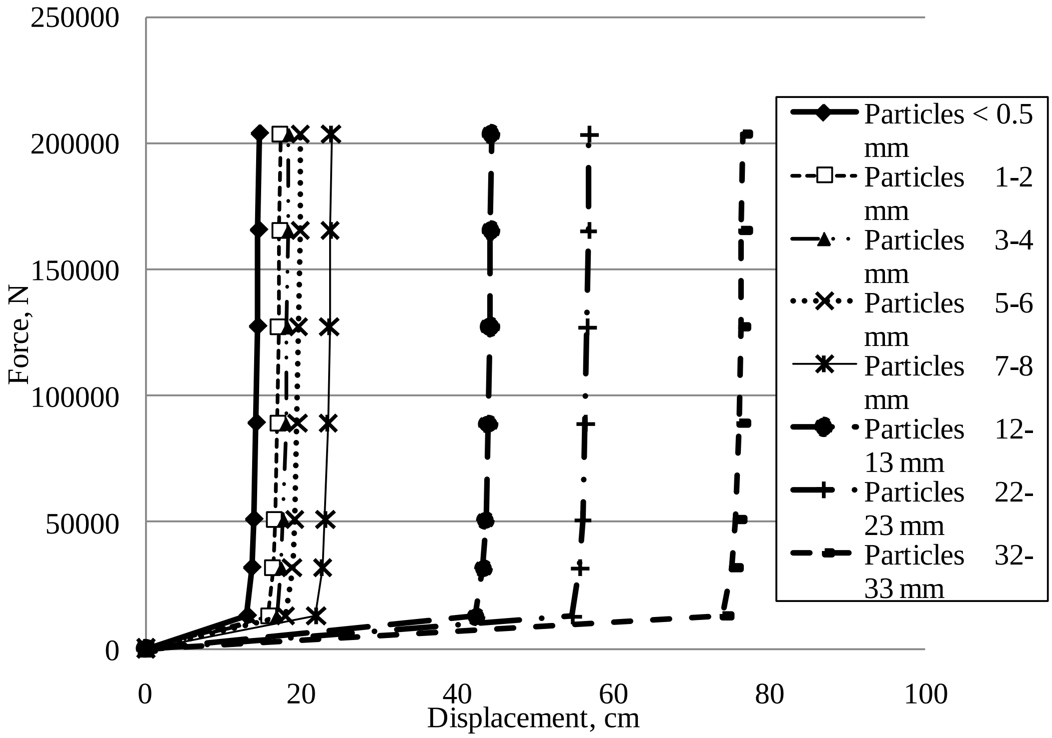


*Fig. 2.* **Force – displacement characteristics of compacting**

Density of reed briquettes obtained during compacting with pressure 212 MPa is shown in Table 1(D1 ÷ D9 – number of briquette). The density of briquettes was determined 0.87 – 1.04 g $cm^{-3}$ with uncertainty ± 0.01 g $cm^{-3}$.

*Table 1.*

**Common reed briquettes density**

| Particle size, mm | D1, g $cm^{-3}$ | D2, g $cm^{-3}$ | D3, g $cm^{-3}$ | D4 g $cm^{-3}$ | D5, g $cm^{-3}$ | D6, g $cm^{-3}$ | D7, g $cm^{-3}$ | D8, g $cm^{-3}$ | D9, g $cm^{-3}$ | Average density, g $cm^{-3}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| < 0.5 | 1.014 | 1.025 | 1.026 | 1.034 | 1.046 | 1.052 | 1.058 | 1.022 | 1.032 | 1.034 ± 0.012 |
| 1 - 2 | 1.005 | 0.999 | 1.000 | 1.010 | 1.002 | 1.003 | 1.011 | 1.004 | 0.998 | 1.004 ± 0.011 |
| 3 - 4 | 0.964 | 0.960 | 0.985 | 0.982 | 0.974 | 0.982 | 0.990 | 0.985 | 0.994 | 0.980 ± 0.012 |
| 5 - 6 | 0.922 | 0.959 | 0.961 | 0.953 | 0.946 | 0.942 | 0.947 | 0.949 | 0.969 | 0.950 ± 0.009 |
| 7 - 8 | 0.894 | 0.879 | 0.886 | 0.921 | 0.893 | 0.903 | 0.920 | 0.923 | 0.933 | 0.906 ± 0.014 |
| 12 - 13 | 0.879 | 0.879 | 0.888 | 0.891 | 0.883 | 0.893 | 0.887 | 0.902 | 0.889 | 0.888 ± 0.008 |
| 22 - 23 | 1.013 | 0.980 | 0.970 | 0.954 | 0.957 | 0.958 | 0.977 | 0.971 | 0.964 | 0.972 ± 0.014 |
| 32 - 33 | 1.026 | 1.019 | 1.000 | 1.045 | 1.004 | 1.038 | 1.029 | 1.047 | 1.028 | 1.026 ± 0.016 |

The minimum of density 0.87 g $cm^{-3}$ have briquettes with particle size 12 – 13 mm (Fig. 3), but maximum density 1.03 – 1.04 g $cm^{-3}$ two particle sizes < 0.5 mm and 32 – 33 mm briquettes. Maximum density 1.026 g $cm^{-3}$ of common reeds particle size 32 – 33 mm can be explained by particle orientation. This material size is nearly equal to die diameter and during filling particles start orientation for denser die filling.

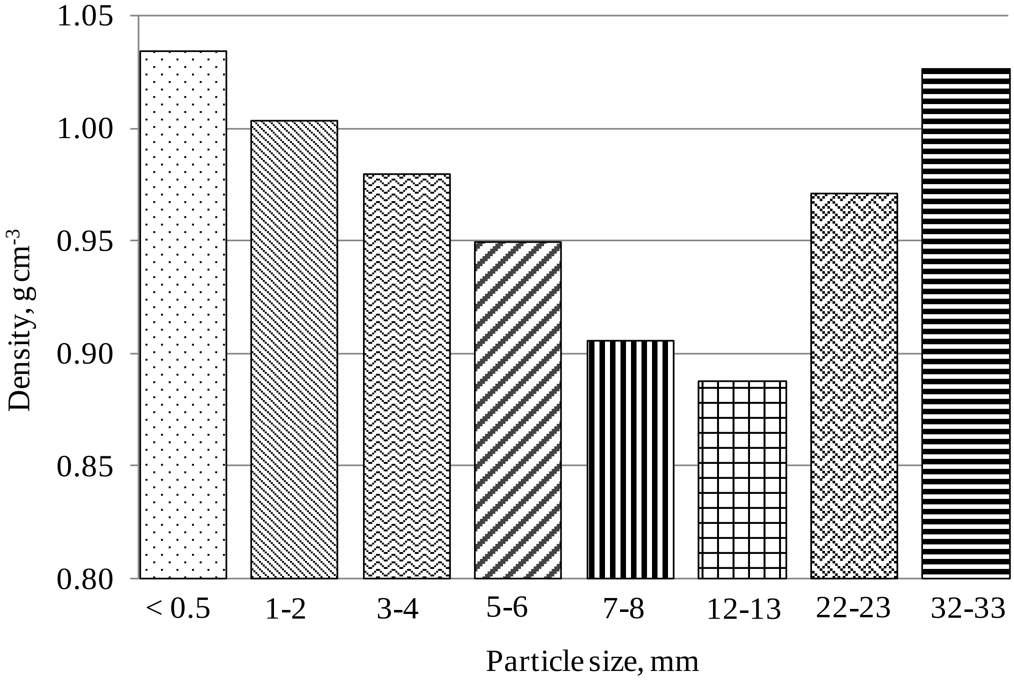


*Fig. 3.* **Common reed briquettes density**

Fig. 4 shows the pressing energy consumption for briquetting of chopped common reeds. Maximum value (~172 kJ kg$^{-1}$) has been obtained for reed particle size 32 – 33 mm, minimum value (~53 kJ kg$^{-1}$) for particle size less than 0.5 mm. For energy evaluation necessary compare pressing energy and cutting energy.

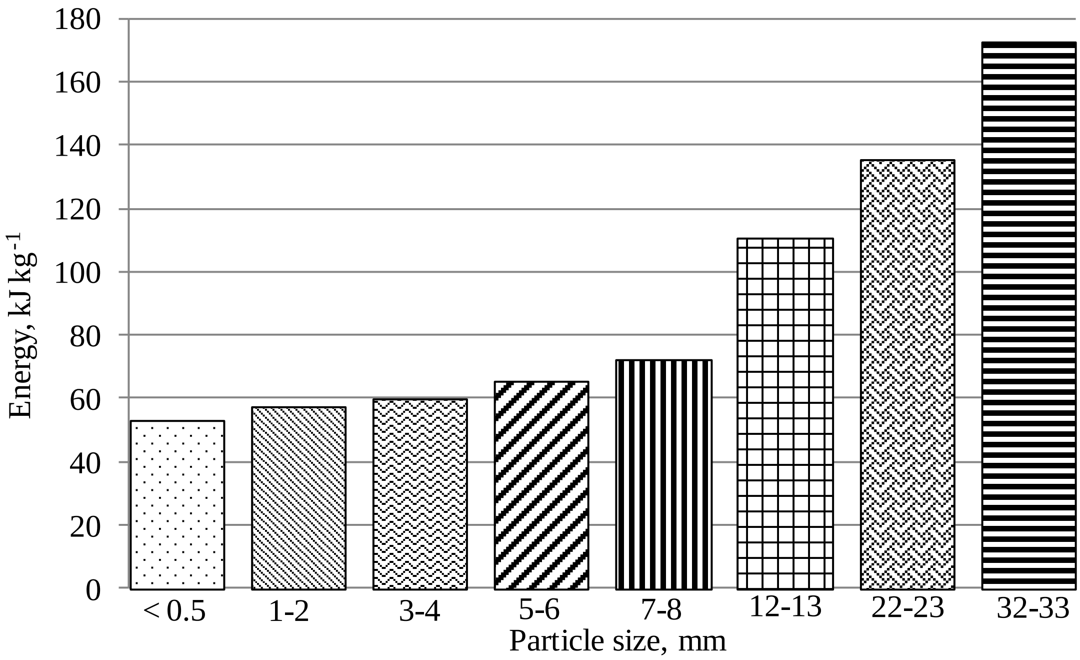


*Fig. 4.* **Compaction energy**

Specific cutting energy has been calculated for different particle of common reeds with density 615 kg m$^{-3}$ and average specific cutting energy – 20 J m$^{-2}$ by formula [6]:

$$E_c = \frac{E_{sc}}{l\rho}, \tag{3}$$

where $E_c$ – specific energy of cutting, kJ kg$^{-1}$;
$E_{sc}$ – average specific cutting energy for square unit, kJ m$^{-2}$;
$l$ – particle size, m;
$\rho$ – density, kg m$^{-3}$.

Maximum value (~62 kJ kg$^{-1}$) has been calculated for reed particle size less than 0.5 mm and minimum value (~1 kJ kg$^{-1}$) for particle size 32 – 33 mm. Energy economy we has 58 kJ kg$^{-1}$ for pressing particles size less than 0.5 mm comparing with pressing reed particle size 32 – 33 mm then cutting energy is taken into account.

## Conclusions

1. The minimum of density 0.87 g cm$^{-3}$ have briquettes with particle size 12 – 13 mm, but maximum density 1.03 – 1.04 g cm$^{-3}$ two particle sizes < 0.5 mm and 32 – 33 mm briquettes compacted with pressure 212 MPa in closed die.
2. The shape of force – displacement characteristics of compacting of different size reed particles were similar – nonlinear curves with two quasilinear parts.
3. Innovative press mechanism in shape of rhomboid linkage with hydraulic drive (Patent LV 14201) is recommended for briquetting of stalk material biomass.
4. Pressing energy consumption maximum value (~172 kJ kg$^{-1}$) has been stated for reed particle size 32 – 33 mm, but minimum value (~53 kJ kg$^{-1}$) for particle size less than 0.5 mm. The energy consumption difference is 119 kJ kg$^{-1}$.
5. Specific cutting energy maximum value (~62 kJ kg$^{-1}$) has been calculated for reed particle size less than 0.5 mm but minimum value (~1 kJ kg$^{-1}$) for particle size 32 - 33 mm. Energy economy we has 58 kJ kg$^{-1}$ for pressing particles size less than 0.5 mm comparing with pressing reed particle size 32 – 33 mm then cutting energy is taken into account.


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### References


1. Hahn B. Existing Guidelines and Quality Assurance for Fuel Pellets. PELLETS FOR EUROPE. Available at: http://www.pelletcentre.info/resources/1020.pdf, 10.01.2011.
2. Matúš M., Križan P. Influence of structural parameters in compacting process on quality of biomass pressings. Journal of applied mathematics. Volume 3, Number 3, 2010, p. 87 – 96.
3. Adapa, P., Tabil L and Schoenau G. Compaction characteristics of barley, canola, oat and wheat straw. BIOSYSTEMS ENGINEERING, Volume 104, Issue 3, 2009, p. 335-344.
4. Grover P., Mishra K. BIOMASS BRIQUETTING: TECHNOLOGY AND PRACTICES. Available at: http://www.fao.org/docrep/006/AD579E/ad579e00.pdf, 20.01.2011.
5. Moisture Measurement-Forages. Available at: http://m.doa.go.th/aeri/files/pht2008/lecture%20slides/mr%20viboon/grain%20drying/aeae- 1998/pdfs/section5/513.pdf, 15.12.2010.
6. Smits M., Kronbergs A., Kronbergs E. Herbaceous energy crop shredding size determination. In Proc. of 9th International Scientific Conference „ENGINEERING FOR RURAL DEVELOPMENT", Jelgava, Latvia, 2010, pp. 275 – 279.



**Anotācija.** *Eiropas Savienības direktīva (2009/28/EK) nosaka, ka Latvijai līdz 2020. gadam no visiem izmantotajiem energoresursiem 40% jābūt atjaunojamajai enerģijai. Atjaunojamo energoresursu izmantošanas uzdevums ir ne tikai palielināt Latvijas enerģētikas pašnodrošinājumu un līdz ar to palielināt neatkarību no importētiem energoresursiem, bet arī dot ievērojamu ieguldījumu siltumnīcefekta gāzu emisiju samazināšanā.*

*Biomasa ir būtisks atjaunojamo enerģijas avotu resurss, tāpēc nepieciešami pētījumi par biomasas cietā kurināmā ražošanas procesu.*
*Kompaktējot dažādu frakciju niedres (< 0.5; 1 – 2; 3 – 4; 5 – 6; 7 – 8; 12 – 13; 22 – 23; 32 – 33 mm), noskaidrots brikešu blīvums, presēšanas specifiskā enerģija un spēka – pārvietojuma līkņu raksturs. Eiropas Savienības valstu standarti nosaka to, ka brikešu, kas tiek izmantotas kā cietais kurināmais, nepieciešamais blīvums ir ~1 g cm$^{-3}$. Eksperimentāli noteiktā brikešu blīvuma mazākā vērtība (0.87 g cm$^{-3}$) ir briketēm ar frakciju lielumu 12 – 13 mm, bet lielākās brikešu blīvuma vērtības (1.03 – 1.04 g cm$^{-3}$) ir briketēm ar frakciju lielumiem < 0.5 un 32 – 33 mm. Aprēķinot specifisko kompaktēšanas enerģiju, maksimālā vērtība ir ~172 kJ kg$^{-1}$, bet minimālā – 53 kJ kg$^{-1}$. Kompaktēšanas eksperimenti veikti slēgtā matricā, kuras diametrs ir 35 mm, līdz 212 MPa spiedienam. Spēka – pārvietojuma līknes nepieciešamas kompaktēšanas mehānismu projektēšanai.*

# OPTIMIZATION OF KERATINASE PRODUCTION BY ACTINOMYCES FRADIAE 119 AND ITS APPLICATION IN DEGRADATION OF KERATIN CONTAINING WASTES

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**Abstract.** *The aim of this study was to identify and optimize significant technological parameters influencing keratinolytic enzyme production by A. fradiae 119 and to study its ability to degrade keratin. In the present work chicken feathers meal (CFM) was found to be an excellent substrate for keratinase induction by A. fradiae 119. The strain produced 164 KU/mL keratinolytic activity in basal medium containing 7.5 g/L CFM as the sole source of carbon and nitrogen. Increased keratinolytic activity was achieved in media with ammonium sulfate as nitrogen source, the application of additional nitrogen sources to media containing CFM slightly decreased keratinase synthesis. Optimal parameters of the cultivation process were determined: pH of cultivation medium – 7.2, temperature – 34 ºC and inoculum's size – 8 %, using the response surface methodology. The yield of keratinase activity was increased by 46 % (267 KU/mL) after optimization of the cultivation process. The good ability of cultural liquid to degrade feathers and wool was detected.*

**Keywords:** *Actinomyces fradiae, keratin degradation, keratinase, optimization, response surface methodology.*

## Introduction

Keratin is a fibrous and insoluble structural protein extensively cross-linked with disulphide, hydrogen and hydrophobic bonds, resulting in mechanical stability and resistance to common proteolytic enzyme such as pepsin, trypsin and papain [1]. Keratins represent the major constituents of skin and its appendages such as nails, hair, feathers, and wool.

The leather and fur plants throw away considerable amounts of materials containing keratin. Until recent years, these materials along with other animal wastes were treated at high temperatures and milled in order to produce the so called „animal flour" and used as „protein supplement" into the feed mixtures of domestic animals. However, it was established that this flour is the carrier of the enigmatic cause of some related diseases, for example mad cow, swine fever and etc. Utilizing poultry feathers as a fermentation substrate in conjunction with keratin-degrading microorganisms or enzymatic biodegradation may a better alternative to reduce environmental waste [2].

A group of proteolytic enzymes which are able to hydrolyze insoluble keratins more efficiently than other proteases are called keratinases, produced by some microorganisms [3].

The growth and enzyme production by microorganisms are strongly influenced by medium composition, thus optimization of media components and cultural parameters is the primary task in biological process [4].

The aim of this study was to identify and optimize significant technological parameters influencing keratinolytic enzyme production by *A. fradiae* 119 and to study its ability to degrade keratin.

## Materials and methods

*Actinomys fradiae* 119 strain, obtained from JSC „Biocentras" microorganism culture collection, was used for the investigations. Keratinase production was investigated in basal medium composed of (g/L): carbon source – 7.5 g/L, nitrogen source ($NH_4Cl$) – 1 g/L,

$KH_2PO_4$ – 0.45, $MgSO_4 \cdot 7H_2O$ – 0.90, $ZnSO_4 \cdot 7H_2O$ – 0.20, $FeSO_4$ – 0.01, $MnSO_4 \cdot 5H_2O$ – 0.01, $CaCO_3$ – 4.0, pH 7.4. The medium was autoclaved at 121 ºC for 30 min.

To optimize the composition of the medium, various carbon sources (including chicken feathers, chicken feathers meal, wool, casein, glucose, starch); as well as organic (yeast extract and gelatine) and inorganic ($NH_4Cl$; $(NH_4)_2SO_4$) nitrogen sources were individually evaluated for their performance in keratinolytic enzyme production.

The keratinolytic enzyme was produced in a 500 mL Erlenmeyer flask containing 100 mL culture medium maintained for 24 h at 30 ºC and 200 rev/min. The medium was inoculated with 5 % of 20 h preculture suspension.

Keratinolytic activity was detected using azokeratin as substrate. Azokeratin was prepared by reacting ball-milled feathers with sulfanilic acid and $NaNO_2$ by use of a method described by Shih and Williams [5]. For a standard assay, 9.6 mg of azokeratin was added to a centrifuge tube along with 1.92 mL of 50 mM Tris-HCl buffer (pH 7.5). This mixture was agitated until azokeratin was completely suspended. 0.48 mL aliquot enzyme solution was mixed with azokeratin, and then was incubated for 1 h in a 45 °C thermoshaker. The reaction was terminated by the addition of 1.6 mL of 25 % trichloroacetic acid, and the mixture was filtered. $A_{450}$ of the filtrate was measured with a UV–1601 spectrophotometer. Control was prepared by adding tricholacetic acid to reaction mixture before adding the enzyme solution. One unit (U) of keratinase activity, under the given conditions, was defined as the amount of enzyme causing 0.01 increases in absorbance between sample and control at 450 nm after 1 h. The result was taken as an average of three replicates.

Caseinolytic activity was determined by modified Anson method [6]. Tirosine was used as a standard.

Optimal parameters of cultivation process, namely pH, temperature and inoculum's size, were studied by response surface methodology (RSM). The experimental optimization procedure consisted of four steps:

1. Selection of preliminary values of cultivation process parameters using a *priori* knowledge about the culture under optimization.
2. Design and realization of statistical experiment in the selected area of technological parameters values variations around the predetermined point.
3. Identification of statistical model for the response surface estimation. A second order polynomal, which includes all interaction terms, is used to calculate the predicted response:

$$Y = a_0 + \sum_{i=1}^{n} a_i x_i + \sum_{i=1}^{n} a_{ii} x_i^2 + \sum_{i=1}^{n} \sum_{j=i+1}^{n} a_{ij} x_i x_j \;, \qquad (1)$$

   where $Y$ – predicted response (maximal ceratinolytic activity); $x_i$ – independent variables (parameters of cultivation process); n – number of independent variables. Parameters of the polynomal model (1) are identified using the least-squares method.
4. Model-based prediction of cultivation process point parameters, at which the maximum keratinolytic activity is obtained, and investigation of the calculated point location. If the point is on the boundary of experimental design area, a normalized gradient vector at this point is calculated:

$$grad_n Y(\mathbf{x}) = \frac{\nabla Y(\mathbf{x})}{\left\| \nabla Y(\mathbf{x}) \right\|}\bigg|_{\mathbf{x}=\mathbf{x}_{\mathbf{max}}} \qquad (2)$$

The gradient vector (2) determines the search direction of the optimum parameters of cultivation process point outside the experimental design area. Along the calculated direction the expected optimum point is chosen and procedure returns to the step 2. If the point is inside the experimental design area, the point is assumed to be an optimum and the test experiment is carried out at that point [7].

Disintegration of whole chicken feathers was estimated by incubation with the cultural liquid for 24 h in 100 mL Tris-HCl, pH 7.5 buffer at 45 ºC. Degradation of wool keratin was observed for 9 days under the same conditions.

## Results and discussion

Each microorganism has its own special conditions for the maximum enzyme production. Keratinase production was first tested in medium containing different carbon sources (5 g/L). The obtained results are presented in Table 1. The *A. fradiae* 119 exhibited highest productivity of keratinase in the culture media that contained chicken feathers meal (CFM) as the carbon source (167.0 KU/mL), followed by chicken feathers (158.5 KU/mL), casein (128.5 KU/mL) and wool (128.0 KU/mL). Glucose and starch carbon sources resulted in a weak enzyme production level, but did not repress the synthesis of keratinase production. This is in contrary to the most of the reports on keratinase and protease production where starch and glucose inhibited enzyme production [3, 8]. The highest caseinolytic activity levels were obtained with CFM (0.60 CU/mL) followed by raw chicken feathers (0.47 CU/mL). Caseinase production by *A. fradiae* 119 was repressed when the strain was grown in the presence of wool, casein, glucose, or starch as carbon sources. Chicken feathers meal was selected as the best carbon source for keratinase and caseinase production by *A. fradiae* 119.

*Table 1.*

**Effect of different carbon sources on keratinase and caseinase production by *A. fradiae* 119**

| Carbon source | Keratinolytic activity, KU/mL | Caseinolytic activity, CU/mL |
|---|---|---|
| Chicken feathers meal | 167.0 | 0.60 |
| Chicken feathers | 158.5 | 0.47 |
| Wool | 128.0 | 0.04 |
| Casein | 128.5 | 0.07 |
| Glucose | 78.0 | 0.04 |
| Starch | 95.0 | 0.05 |

The effect of CFM concentration on keratinase production was investigated. As shown in *Fig. 1.*, keratinase activity reached a maximum value (163.8 KU/mL) at concentration of 7.0 g/L. Further addition of CFM decreased the level of enzyme.

The effect of various additional nitrogen sources on keratinase and caseinase production, in media containing 7.0 g/L of chicken feathers meal as a carbon source, was also carried out. The obtained results are presented in Table 2. Keratinase and caseinase production was improved by adding $(NH_4)_2SO_4$ to the medium containing CFM (control). The other nitrogen sources (yeast extract, gelatin, peptone, $NH_4Cl$) did not enhance keratinases and caseinases production and supported similar or lower levels compared to the medium containing only CFM as a carbon and nitrogen source. Fakhfakh-Zouari et al. (2010) estimated, that the addition of ammonium chloride and ammonium sulfate to media containing chicken feathers meal as a carbon source slightly decreased protease synthesis [4].

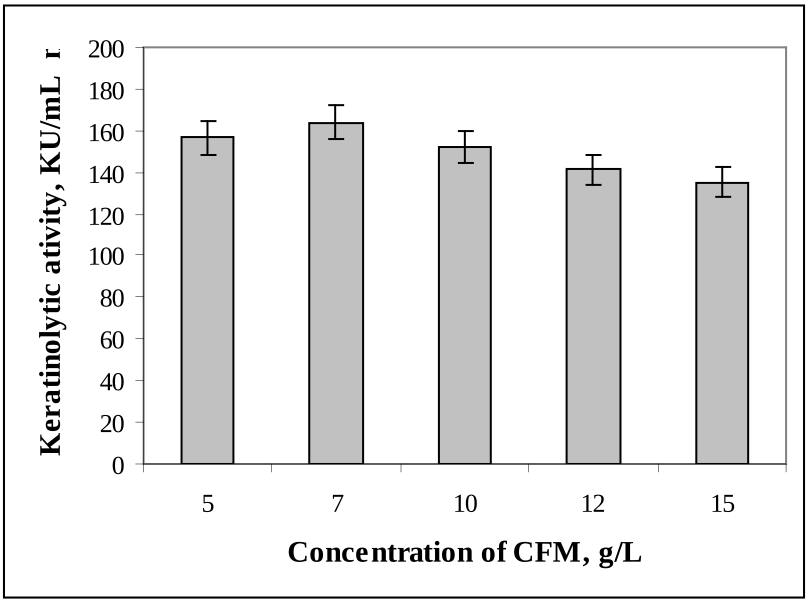



*Fig. 1* **Effect of chicken feathers meal concentration on keratinase production by *A. fradiae* 119**

Whereas, the ability of the strain to grow in media containing chicken feathers meal as organic substrate indicated that it can obtain its carbon and nitrogen directly from this substrate. This is in line with previous scientific findings [3, 4, 8].

*Table 2.*

**Effect of different additional nitrogen sources on keratinase and caseinase production by *A. fradiae* 119**

| Nitrogen source | Keratinolytic activity, KU/mL | Caseinolytic activity, CU/mL |
|---|---|---|
| Control | 162.0 | 0.47 |
| Yeast extract | 136.5 | 0.24 |
| Gelatin | 132.0 | 0.43 |
| $NH_4Cl$ | 151.0 | 0.22 |
| $(NH_4)_2SO_4$ | 169.8 | 0.51 |
| Peptone | 124.5 | 0.43 |

Keratinase secretion by microorganisms is substantially influenced not only by carbon and nitrogen sources, but also by main technological parameters of cultivation process. Optimization of cultivation process parameters is the primary task in biological process. The goal of optimization procedure was to evaluate optimal technological parameters of cultivation process in order to maximize the yield of keratinolytic enzyme at the end of bath cultivation processes. The parallel experiments were realized using the $B_3$ experimental plan, which contains 15 experimental points. Experiments were repeated two times to evaluate the reproducibility of experimental results. The main factors that were considered to influence the cultivation process efficiency are: cultivation temperature, initial medium pH and inoculum‘s size. Two series of factorial experiments were performed. In the first experiment,

technological parameters were changed within the range: temperature ($x_1$) – $25 \div 40$ $^0$C; pH ($x_2$) – $6.5 \div 8.5$; inoculum's size ($x_3$) – $2 \div 10$ %.
Analysis of obtained results demonstrated that the point, at which maximum keratinolytic activity is predicted, lies on boundary of experimental design area. At this point the gradient vector was calculated and expected direction of optimal point was determined (data not shown). Experimental design of matrices together with experimental results of 2nd experiment is presented in Table 3.

*Table 3.*

**Experimental design matrices with code ($x_i$) and real ($X_i$) variables for *Actinomyces fradiae* 119 cultivation process and the keratinolytic activity ($Y_{exp}$) as dependent variable**

| Nr. | Code values | | | Real values | | | $Y_{exp}$, KU/mL | |
|---|---|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $X_1$ | $X_2$ | $X_3$ | 1 | 2 |
| 1 | +1 | +1 | +1 | 38 | 7,5 | 8 | 159.3 | 144.0 |
| 2 | -1 | +1 | +1 | 30 | 7.5 | 8 | 173.3 | 173.3 |
| 3 | +1 | -1 | +1 | 38 | 6.5 | 8 | 120.0 | 118.7 |
| 4 | -1 | -1 | +1 | 30 | 6.5 | 8 | 128.0 | 129.3 |
| 5 | +1 | +1 | -1 | 38 | 7.5 | 4 | 125.3 | 121.3 |
| 6 | -1 | +1 | -1 | 30 | 7.5 | 4 | 144.0 | 140.7 |
| 7 | +1 | -1 | -1 | 38 | 6.5 | 4 | 130.7 | 126.0 |
| 8 | -1 | -1 | -1 | 30 | 6.5 | 4 | 95.3 | 96.7 |
| 9 | +1 | 0 | 0 | 38 | 7.0 | 6 | 133.3 | 138.0 |
| 10 | -1 | 0 | 0 | 30 | 7.0 | 6 | 141.3 | 149.0 |
| 11 | 0 | +1 | 0 | 34 | 7.5 | 6 | 131.3 | 134.0 |
| 12 | 0 | -1 | 0 | 34 | 6.5 | 6 | 98.0 | 101.3 |
| 13 | 0 | 0 | +1 | 34 | 7.0 | 8 | 156.0 | 158.3 |
| 14 | 0 | 0 | -1 | 34 | 7.0 | 4 | 174.7 | 182.7 |
| 15 | 0 | 0 | 0 | 34 | 7.0 | 6 | 182.7 | 188.0 |

Experimental data were used to identify parameter values of statistical model (1), which was used to calculate the predicted responses corresponding to results of the experiment. The response surfaces are illustrated by the isoresponse contour plots (Figure 2).

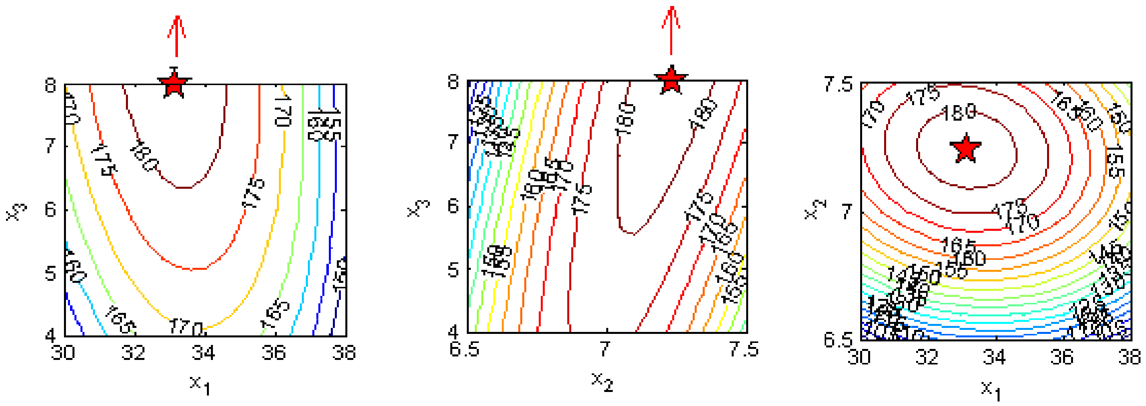



*Fig.2* **Isoresponse contour plots of *Actinomyces fradiae* 119 keratinolytic activity**

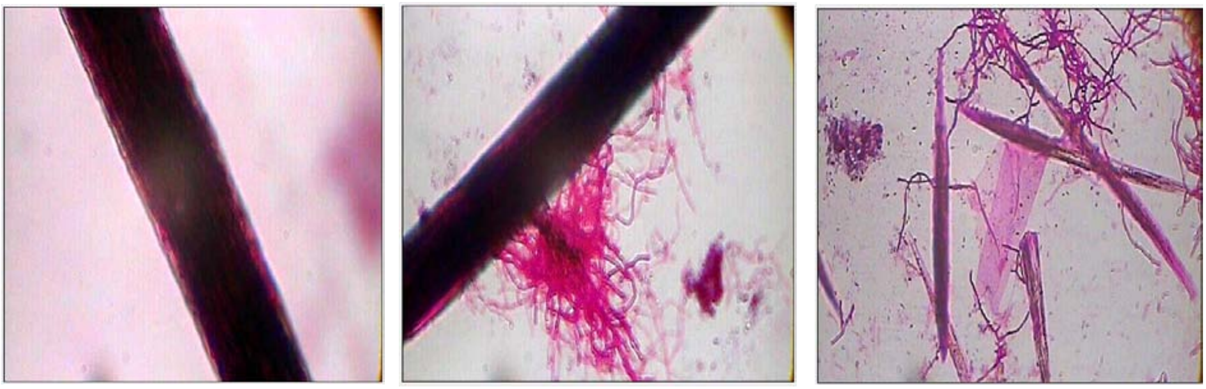
On regression analysis of experimental data, following equation was obtained for keratinase production:

$$Y = 179.54 - 2.807x_1 + 13.28x_2 - 1.395x_3 - 21.70x_1^2 - 32.18x_2^2 - \\ - 2.895x_3^2 - 6.141x_1x_2 - 3.704x_1x_3 + 16.14x_2x_3$$

Optimal parameters of the cultivation process of *A. fradiae* 119 predicted by statistical model were determined: initial pH of cultivation medium – 7.2, temperature – 34 ºC and inoculum's size – 8 %. The bacterium produced 183 KU/mL keratinase in 24 h. The test experiment was carried out at that optimum point and keratinase production increased by 46 % (267 KU/mL) after optimization of the cultivation process.

Cultural liquid, grown under optimal conditions, was used to evaluate its ability to degrade native chicken feathers and wool. The degradation of feathers started at 4 h and the degradation of barbules was observed. Full disintegration of feather barbules and rachis was detected after 24 h of the treatment. However, earlier studies have reported longer incubation periods of 48 h to 28 days [9, 10].

Degradation of wool was assessed using electron microscopy (*Fig.3*). *Actinomyces fradiae* 119 formed the branched networks of hyphae on the wool fiber surface after one day of treatment. After 9 days of incubation, the great majority of wool fibres showed complete disintegration and appeared as separate, irregular fragments. This indicates that wool fibre structure had been altered by the activities of *A. fradiae* 119.



a) b) c)

*Fig. 3* **Hydrolization of wool fibers by A. fradiae 119**:
a) unhydrolized wool fiber; b) after 1 day treatment; c) after 9 days treatment

Solubilization of native feathers and wool fibers by the cultural liquid showed the biotechnological potential involving keratin hydrolysis in the processing of keratin containing wastes.

## Conclusions

Chicken feathers meal was found to be an excellent substrate for keratinase production by *A. fradiae* 119. The strain produced 164 KU/mL keratinolytic activity in basal medium containing 7.5 g/L CFM as a sole source of carbon and nitrogen.

Organic nitrogen sources were used efficiently for keratinase production. Increased keratinolytic activity was achieved in media with ammonium sulfate as additional nitrogen source, whereas the addition of other nitrogen sources to media containing chicken feathers meal slightly decreased keratinase synthesis.

Optimal parameters of the cultivation process were determined: initial pH of cultivation medium – 7.2, temperature – 34 ºC and inoculum's size – 8 %, using the response surface methodology. The bacterium produced 183 KU/mL keratinase in 24 h which was increased by 46 % (267 KU/mL) after optimization of the cultivation process.

The good ability of cultural liquid to degrade feathers and wool was detected.

**References**


1. Radha, S., Gunasekaran, P. Cloning and expression of keratinase gene in *Bacillus megaterium* and optimization of fermentation conditions for the production of keratinase by recombinant strain. Journal of Applied Microbiology, 103. 2007, p. 1301-1310.
2. Matikevičienė, V., Masiliūnienė, D., Grigiškis, S. Degradation of keratin containing wastes by bacteria with keratinolytic activity. Proceedings of the 7th international scientific and practical conference “Environment. Technology. Resources”, June 25-27, 2009. Rezekne. 2009, p. 284-289.[1] Shih, J. C. H.; Williams, C. M. 1992. Purified *Bacillus licheniformis* PWD–1 keratinase. United States Patent. Nr. 5171682. 14 p.
3. Hossain, M.S., Azad, A.K., Abu Sayem, S.M., Mostafa, G., Hoq, M.M. Production and partial characterization of feather-degrading keratinolytic serine protease from *Bacillus licheniformis* MZK-3. Journal of Biological Sciences, 7-4. 2007, p. 599-606.
4. Fakhfakh-Zouari, N., Haddar, A., Hmidet, N., Frikha, F., Nasri, M. Application of statistical experimental design for optimization of keratinases production by *Bacillus pumilus* A1 grown on chicken feather and some biochemical properties. Process Biochemistry, 45. 2010, p. 617-626.
5. Shih, J. C. H.; Williams, C. M. Purified *Bacillus licheniformis* PWD–1 keratinase. United States Patent. Nr. 5171682. 1992, p. 14.
6. Lanoë, J.; Dunnigan, J. Improvements of the Anson assay for measuring proteolytic activities in acidic pH range, Analytical Biochemistry, 89-2. 2004, p. 461-471.
7. Levišauskas, D., Tekorius, T., Čipinytė, V., Grigiškis, S. Experimental optimization of nutrient media for cultivation of *Arthrobacter* bacteria. Latvijas Kīmijas Žurnāls, 1. 2004, p. 75-80.
8. Fakhfakh, N., Kanoun, S., Manni, L., Nasri,M. Production and biochemical and molecular characterization of a keratinolytic serine protease from chicken feather-degrading *Bacillus lichiniformis* RPk. Canadian Journal of Microbiology, 55. 2009, p. 427-436.
9. Ignatova, Z., Gousterova, A., Spassov, G., and Nedkov, P. Isolation and partial characterization of extracellular keratinase from a wool degrading thermophilic actinomycete strain *Thermoactinomyces candidus*. Canadian Journal of Microbiology, 45. 1999, p. 217–222.
10. Nam, G.W., Lee, D.W., Lee, H.S., Lee, N.J., Kim, B.C., Choe, E.A., Hwang, J.K., Suhartono, M.T., and Pyun, Y.R. Native feather degradation by *Fervidobacterium islandicum* AW-1, a newly isolated keratinase producing thermophilic anaerobe. Archives of Microbiology, 178. 2002, p. 538–547.

# ENVIRONMENTAL POLLUTION WITH OIL PRODUCTS AND REVIEW OF POSSIBILITIES FOR COLLECTION THEREOF

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**Abstract.** *The largest global pollution nowadays gives oil and oil products. This contamination poses a danger to the environment and aquatic eco-systems. Not only seas but also small water bodies and watercourses, as well as coastal areas, soil and groundwater are contaminated with oil products. Contamination results in destruction of some plants or animals, but in events of high oil contamination also of the entire ecosystem. Latvia has inherited the oil pollution from both the Soviet Union large-scale industry and its military facilities, as well as at present the oil products are getting into environment from petrol stations, accidents, and from the cross-border pollution. In many cases of oil spills, people are trying to collect them in order to have no impact on the environment, but unfortunately very often, even in most cases this does not occur. Financial resources, as well as the lack of appropriate technologies or restricted possibilities for their application are the limiting factors. The article deals with the traditional methods of oil collection in water and also describes options for decontamination of polluted soil from the oil products. A brief insight is provided into application of ferromagnetic sorbents, which is a new method for collection of oil and oil products.*

**Keywords:** *ferromagnetism, oil spills, pollution*

## Introduction

The biggest cause of environmental pollution today is just the oil and oil products. Most oil pollution in the World Ocean originates from the tank-ship accidents, for example, from the tank ship Erika (1999) [1], from oil pumping in ports or from the oil production platforms, as well as from accidents associated with the oil production platforms themselves. This results in a tremendous amount of oil and oil products getting into the water. It is estimated that this level amounts to 25-30 million tons of petroleum products. This group of pollution is mainly associated with the accidents, which are not always predictable and the amounts of pollution can not always be identified. Ship ballast waters are other very important polluters of the water environment. These are deliberately discharged into the seas and oceans when contaminated with petroleum products, as well as other highly hazardous substances and compounds. In any case, aquatic ecosystems are suffering, which results in perishing birds, fish, mammals and other representatives of marine flora and fauna. [2] In addition, a large proportion of all the perished organisms are concentrated exactly in the coastal area, where oil products are washed ashore, which interferes with access to oxygen in water.
Oil pollution can be reduced through additional safety measures in course of the extraction from entrails of the Earth, by using other resources, which would be less harmful and prevent leakage of industrial raw materials and products into the waters, by collecting and purification of rainwater runoff from roads and grounds. Although the human race is striving to limit oil spills, these still happen and then fast and efficient oil collecting techniques should be used, as well as new ones should be developed.

Purification of the contaminated areas from oil can be divided in three types:
1) water purification from oil products;
2) purification of coastal areas from oil products;
3) purification of contaminated ground from oil products.

Practically in all the producing enterprises their process of operations results in formation of the waste containing oil products. Substantial risk of pollution is present in comparatively small facilities, such as petrol stations, car washes, which represent a potential small-scale pollution, and in large facilities, which create or have potential to create very large amounts of oil-containing waste, such as oil handling terminals.

The main facilities creating pollution with oil products in Latvia are:
1. Former Soviet military bases,
2. Former industrial sites, where groundwater pollution has been developed from the oil products,
3. Consequences of accidents resulted in contaminated soil,
4. Petrol stations and car services,
5. Enterprises engaged in oil production, processing, handling or using oil products (lubricants, fuel, oil) in their operations,
6. Polluted soil and water bodies of the areas adjacent to railway and motor roads.

One petrol station produces from 0.5 to 2.5 $m^3$ as the total annual amount of pollution by oil products getting into the environment. Taking into account a sufficiently large number of petrol stations across the territory of Latvia, the annual pollution volume amounts to approximately 500 $m^3$. There is a reason to believe that the majority of pollution created by petrol stations is not accurately accounted for, collected and processed properly. [3] Also in the Latvian inland waters (rivers, lakes) oil product (mostly diesel or petrol) spills are pretty often taking place, but as a rule they are minor ones and being operatively eliminated. At the service of State Fire and Rescue Service are booms of the delimiting type (in rivers), and absorbent booms (in lakes), as well as airtight containers (for collection of contaminated soil), which can be duly delivered to any place in Latvia, for the purpose of delimiting further pollution of waters as soon as possible, and to eliminate the existing pollution with oil products. However, the oil products from motor roads and grounds are getting into the water, which is also a global problem currently being difficult to tackle.

One of the most threatening situations in Latvia during the recent years was when in the spring of 2007 unknown quantity of diesel fuel has made stream into Latvia along the flow of the Daugava River from Belarus, which threatened to develop into an ecological disaster. The diesel pollution flown into the Daugava has proved to be a number of times greater than Belarus has previously brought to notice of Latvia, which was the greatest cause for concern.

The Baltic Sea is shallow, but its bed is very uneven, with sharp rises and falls, large depths and shallow places. Pollution has a strong negative impact exactly on shallow water bodies, because there are specific ecosystems that are rapidly affected by changing external factors and, in particular, such as pollution with oil products.

Technologies for treatment of the contaminated soil and associated groundwater in Latvia, taking into account the Latvian possibilities, are divided into two main groups:
1. Soil purification on the spot (*in situ*) in the contamination area (in fully or in partially localized area),
2. Soil purification in facilities, which can be located as a temporary purification plants in sites of the contaminated areas or located outside the said (*ex situ*), which require excavation of the contaminated soil.

This article analyzes the current methods and technical solutions to eliminate pollution with oil products applied on the global scale, evaluates efficiency of these methods.

**Elimination of consequences of the oil product spills in the water**

Mechanical collection of oil products, first by localising them is preferred in the elimination of consequences of the oil spills. The most common manner for localization of the spilled oil is containment for holding the movement of contamination with the booms (see Figure 1) and then by its collection with mechanical devices. At present application of booms is the most commonly used oil collecting method in the world, which has both its advantages and its disadvantages.

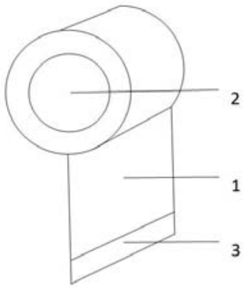


*Fig. 1.* **Cross-section of a boom**

1 - plastic material performing the oil retention function; 2 - floating material, which is capable for holding of the boom at surface; 3 - sinking material performing the plastic material (1) tension function, does not allow it to spin

**Fence-type booms** (see Figure 2.) is the most common variety, widely used in rivers to keep the oil products from spreading further downstream, by collecting it from running water to one place, in order to further collect the contamination by use of other technologies. They are relatively inexpensive and easy to install.

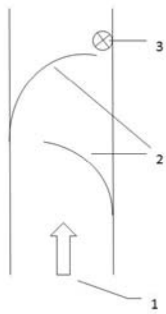


*Fig. 2.* **Fundamental scheme of operation of the fence-type booms**

1 - river stream flow direction; 2 - fence-type booms; 3 - mechanical oil collecting equipment

***Spring-loaded type booms*** has the same function as fence-type booms, but they are easier to install, because as can be inferred from the title, their construction contains springs adjusting to the desired width of the delimitation. Springs are embedded in a buoyant material. Feature of the ***coastal booms*** is that this kind of booms is strengthened on the bank with anchors and is intended for continued operation.

***Booms for detention of burning oil and chemical products*** are different from other types of booms in their incombustible and chemicals-resistant material used in the construction of booms.

***Adsorbent booms*** differ from other types of booms in that the booms are filled with adsorptive material that adsorbs oil products and after multiple usage of these booms there is no need to collect it mechanically. Adsorbent booms are mounted one behind the other in running water, and each row of booms absorbs the oil products until the water runs clear.

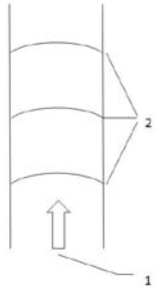


*Fig. 3.* **Principal scheme for operation of the adsorbent booms**
1 - river stream flow direction; 2 - adsorbent booms

Mutual comparison between the types of booms (see Table 1.) presents evident that each of them has both their positive and negative features. For example, the booms containing oil products only ensures their moving to a certain place where the collecting of contamination is going to take place. Consequently, efficiency of the boom performance is highly dependent on the water level undulation, wind strength and direction, the river width and other factors.

*Table 1.*

**Comparison of booms according to type of their use and characteristics**

| ***Type of booms*** | ***Positive characteristics of the booms*** | ***Negative characteristics of the booms*** | ***Application of booms*** |
|---|---|---|---|
| Fence-type booms | Of simple structure, the least expensive from all the types of booms | Do not perform any additional functions | The most widely used type of booms for localization of the oil products |
| Spring-type booms | Quickly installable, quickly removable, occupies small space in a „rest state” | Do not perform any additional functions | Used for the purpose to localize spills as fast as possible, rare type of booms |
| Coastal booms | May be left for longer time due to the coast anchors | Do not perform any additional functions | Used in places where the pollution will arrive after undetermined time |
| Booms for containment of burning oil and chemical products | Incombustible material contains burning oil helping to extinguish the same | No | Are used in the oil extraction sites, most often after accidents, when burning oil is extinguished |
| Adsorbent booms | After multiple rows of adsorbent booms, mechanical collecting of pollution is not required | No | Used in rivers with small stream flow, used in multiple rows |

In Latvia collecting and delimitation of pollution with oil products in the water bodies is carried out by the Latvian Naval Forces having several types of booms at their disposal. They have several types of containment booms at their disposal, which are characterized by their length, depth of the draught, the principle of installation and speed. For example, the marine boom RO-BOOM 1500 is 600 m long, boom draught 700 cm, these booms are spooled, pull-driven with mechanical gear. Coil weight together with booms constitutes 4000 kg. These booms are intended for use in elimination of accidents on sea, the Ventspils naval forces are equipped with them. In Latvia light, fast-installable booms HV-2040 SC are also used, intended for inland waters with the wave height of less than 30 cm, booms are spooled. Coil weight together with booms is 880 kg, length - 220 m. The Latvian Naval Forces are equipped also with the adsorbent booms. Like the containment booms they vary in length, but this type of booms are mounted one after the other, therefore, to use adsorptive surface of the booms more effectively, the boom length can be varied, by constructing the required length from the package rolls and the remaining rolls to be used for re-adsorption. The length of adsorbent boom ranges from 200 to 3000 m.

One of the latest methods for collecting of oil products is the use of ***ferromagnetic sorbents***. In order to combat pollution with oil products, physical properties of the spilled oil film have to be changed, to invest it with magnetic properties. To achieve this water is supplied with a specially designed ferromagnetic adsorbent based on an iron powder produced by processing of the metal industry waste. [4, 5] Experimental method tested in laboratory conditions enables modification of physical properties of the surface oil film by adding ferromagnetic sorbent. Powder "Fe-S1" is sprayed on the oil spot (see Figure 4) by using spray devices, and after 5-10 min. ferromagnetic powder absorbs them, forming the surface with a powerful magnetism.

*Fig. 4.* **Water surface after reaction with the ferromagnetic adsorbent**

Due to magnetic interaction the suspension turns into balls, vacating large water area (80%) from oil. The resulting suspension can be effectively collected using a specially developed magnetic catcher. [6]

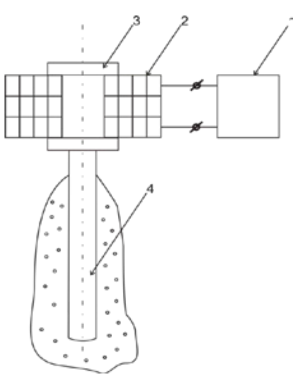


*Fig. 5.* **Apparatus for collecting spilled oil products**
1 - power source; 2 - electromagnetic coil; 3 - core; 4 – catcher

Principal scheme of apparatus for collection of the spilled oil products is provided in Figure 5. At development of this sorption method to a commercially viable one, additional research must be conducted, as well as possible combinations have to be created with other sorbents, to increase buoyancy and efficiency of the sorbent. The method has the advantage that by the same it is possible to assemble also the sunken waste of oil products that previously has reacted with the adsorbent.

## Purification of contaminated ground

Pollution with oil products or their components should be considered as one of the most significant forms of soil and groundwater contamination. Currently, such pollution is found in virtually all the major enterprises for transport, handling and storage of oil products. Due to several reasons, mainly historically and for Latvia as a transit country, large amount of this hazardous waste has developed, which poses a serious threat to the development of a number of Latvian territories because of contamination, including by creation of groundwater pollution risks as well as by overall negative impact on the environment.

Under influence of this contamination, adverse environmental impact on adjacent areas is taking place, mainly in the groundwater flow direction. To improve the situation in the urban industrial zone, the environmental restoration activities are enforced mainly aimed at gradual elimination of the soil and groundwater contamination and of the causes for its formation. Ground contamination may be result of failures in diesel, heavy fuel oil and thermoils' pipelines in the event of oil spill without ignition. In event of such an accident, depending on its degree (from small leakages to complete pipe failure) and type of the spilled oil product, also the extent of soil pollution is evaluated, which can take up even very large areas. Removal of pollution of the contaminated soil is carried out using physical or chemical means.

***Sieve or physical separation***. The separation process uses sieves and screens of different sizes for effective concentration of oil and oil products in smaller quantities. Physical separation is based on the fact that organic and inorganic matters combine with each other both chemically and physically, especially becoming apparent in clay and mud. Clay and mud particles are physically attached to the coarse sand or soil, perfectly concentrating the oil products in a small unit volume, so it is easier to handle. Physical separation is usually carried out prior to chemical treatment, provided that the majority of oil products remain with large-scale soil particles. The major advantage of physical separation is that high level of purification can be achieved with a relatively small amount of devices. However, there are many factors that can limit effectiveness and usability of both these processes. One of such is the high content of clay and moisture in the soil, which increases purification costs.

Removal of oil products with the help of ***gravitational force***. The process is based on a difference of densities between the solution phases. Equipment size and removal efficiency with the gravitational force is dependent on the size of particles of oil or its products, density difference, viscosity and concentration of particles. Separation by gravitation is used also to remove unmixable oil layers, and to classify the particles with different sizes. Usually it is preceded by coagulation and flotation to increase the size of particles, which facilitates the separation process.

***Biodegradation***. This technology can be used in large quantities. Soil is mixed with soil improvers and subjected to further treatment. For example to soil ventilation. It is used to reduce concentration of oil products in the soil resulting from biological decomposition. Humidity, high temperature, nutrients, oxygen and pH are the main parameters of biological decomposition, which, of course, micro-organisms. The soil is placed in a limited field where soil piles are formed. Most often the soil piles (maximum 2 - 3 m high) are covered by a film to maintain moisture and heat under the film. Biodegradation is aimed at modification or destruction of oil and stimulation of micro-organisms in order for the latter consume the oil as a source of nutrients and energy. Certain groups of oil products do not decompose completely, but their degradation products become even more toxic, and they have other by-products, decomposition of which is difficult (such as vinyl chloride). Biodegradation is a relatively short-term technology, although the process can last for weeks and even months. The biggest advantage is low cost. However, disadvantages include relatively high costs associated with excavation and transportation of contaminated land.

***Soil rinsing.*** Oil products are sorbed on the ground particles. During the ground rinsing process (see Fig. 6) water is saturated with leaching agents, surface active substances, pH regulating substances or coagulants that help to separate the organic matter. In the soil leaching process oil products are separated in two ways:

1. by releasing or creating other substances,
2. by exercising concentration of oil products.

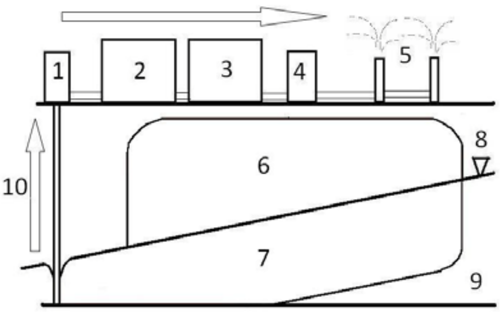


*Fig. 6.* **Rinsing of soil contaminated with oil products**
1 – pump; 2 – groundwater treatment; 3 – rinsing additives; 4 – pump; 5 – spraying equipment; 6 – contaminated area; 7 – contamination diffusion with groundwaters; 8 – groundwater level; 9 – unpolluted ground; 10 – water circulation direction

Concept of purification of the contaminated soil by reducing the particles is based on the fact that oil and oil products tend to be connected physically or chemically with the clay, mud or organic soil particles. While the clay and mud is attached to the sand by physical methods, such as compaction and adhesion. During the washing process not only clay and sand is separated from the ground, but the oil particles in ground are also reduced in order to make work with them easier. Also for this method there are a number of factors that may limit the effectiveness and usability of the process. Washing the ground, which is contaminated by oil products can result in emergence of many and various unnecessary solutions (e.g., organic matters, heavy metals) requiring additional treatment thus increasing the costs and complicating the purification process. High content of humus in the soil can lead to high costs, because in clayey soils separation of the humus substances is difficult.

***Hot gas dezactivation***. During the heating process, the material or the substance is heated to temperatures where gaseous oil compounds are emitted, which are burnt in special incinerator. The disadvantage is that eventual explosivity and ignition speed of the substance should be foreseen, as well as the costs of this method are much higher than for incineration on the open flame.

***Incineration***. Mobile equipment is used for evaporization, and incineration of oil and oil products at a temperature of 870-1200 ºC. Fuel is often used to assist in starting and ensuring of complete incineration. The method is used in particularly heavily polluted grounds (above 5000 mg/kg) for utilization in the areas due to long distances of geographical location not allowing for cost effective transportation of the contaminated ground to stationary treatment plants. The method is one of the most efficient when compared to others in cases where the volumes of polluted ground are not too large (up to 100 tons), it is situated locally, area is placed at a long distance, and the ground can not be utilized via other processing technologies. Incineration achieves 99.99% efficiency. According to qualitative criteria the method is one of the cleanest and the fastest, but at the same time the most expensive of methods for utilization of the ground polluted with oil products. Rotary kilns are widespread installations of this method.

***Pyrolysis*** converts oil pollution to gaseous components, liquid and coke. In course of pyrolysis the oil products emit hot gases, including carbon monoxide, hydrogen and methane, as well as other compounds. Pyrolysis takes place at low pressure and temperatures above 430 $^{0}$C. Gases emitted during pyrolysis are requiring further processing. This is done in the second chamber, where gases can be burned to allow them to ignite and to be recycled. Disadvantage of the technology is that it requires soil drying in order to achieve low soil moisture (<1%), which also increases the total cost of treatment.

***Stabilization***. This method is used to stabilize the oil and its compounds, and they do not spread further into environment. In cementing and stabilization technologies, processes are directed towards the sealing or stabilization of oil products, as well as including treatment of excess or contaminated ground. There are 4 groups, which may be involved in the cementing process of oil and its products:

1. bitumenization,
2. asphalt emulsion,
3. modified cement sulfur,
4. glass vitrification.

Under the bitumenization process the contaminated area is placed in liquid asphalt and it is hardened. The process combines heated asphalt and concentrated unnecessary material in a form of sludge. From the mixture water evaporates to about 5% level. The final product constitutes homogenized mixture of oil products and asphalt.

Asphalt emulsion is made of small asphalt droplets placed in the water, and being stabilized by chemical emulsion agents. There are cationic and anionic emulsions. Asphalt emulsion process is taking place in hydrophilic solvents where asphalt emulsion is mixed with oil products. After mixing the excess water is drained and the asphalt emulsion membrane covers remains of the oil products. Additional neutralizing agents, such as gypsum or lime are sometimes required. After hardening even the water can not access the oil mass incorporated in the hard mass.

The modified cement sulfur commercially is one of the most available thermoplastic materials. It is easy to melt, then mixed with oil products to form a homogeneous liquid solution, which is placed in special containers for freezing or chilling, and for subsequent use.

Vitrification or glass casting - solidification methods, which is heated up to 1.200 EC, to melt and to transform unnecessary materials in glass or other vitreous products. The high temperature destroys any organic elements with a few by-products. Materials such as heavy metals and petroleum products turns resistant to rinsing by incorporation into a glass structure that is rigid and durable material. To solid material also liquids, dry or wet waste, as well as combustible materials can be added. Borosilicate and soda lime are the main constituting elements of the vitrification matrix. However, in relation to oil and its products, the stabilization process has one major disadvantage - all organic materials, including, of course, oil and oil products are difficult to stabilize, and this stabilization can not be enduring.

***Integrated pumping out of pollutants and water***. Unlike pumping out the emulsion of oil products and water, in this case boring holes are created below the groundwater level. The method is used both in event of diffuse and local groundwater pollution. Within the pollution area boring holes are created and pumping out of the borehole water is ensured. Similar to the previous method, development of a cone of depression is achieved, where pollutants and contaminated groundwater is moving. Further through pumps the pollution and water emulsion is collected in tanks and transported to the stationary treatment plants.

***Pumping out of emulsion of oil products and water*** is done by means of making boring holes within the pollution area above the groundwater layer and by pumping out developing a cone of depression. As a result, pollution of the floating layer of groundwater is pumped out and removed. Further the oil and water mixtures collected in reservoirs should be transported to the stationary treatment plants.

## Conclusions

In elimination of consequences from the oil spills, priority is given to mechanical collecting of the oil products, first by localizing them with booms. The most widespread types of booms are containment booms and adsorbent booms. Adsorbent booms have the advantage that after their use the collecting of oil products with mechanical devices is not required, but as the negative feature of these booms may be pointed out that in the adsorbent booms adsorption material has to be replaced and the booms can be used only once.

Currently the purification of ground contaminated with oil products is based on methods such as soil rinsing, thermal treatment, biodegradation and so on. Methods are widely applied, but are expensive. Consequently, for the time being in Latvia there are lots of sites contaminated with oil products, where their owners can not afford to clean up the polluted ground.

Use of ferromagnetic adsorbents is a new method for collecting of oil products, which has not yet been explored to the commercial product. Research studies are ongoing, but the results are evident that this could be one of the ways to clean up the surface from the oil pollution without degrading the environment.

## Acknowledgements

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### Bibliography

1. Ernst, S.R., Morvan, J., Geslin, E., Le Bihan, A., Jorissen, F.J., 2006. Benthic foraminiferal response to experimentally induced Erika oil pollution. Marine Micropaleontology 61, 76–93.
2. Camphuysen, C.J., Heubeck, M., 2001. Marine oil pollution and beached bird surveys: the development of a sensitive monitoring instrument. Environmental Pollution 112, 443-461.
3. Blumberga, A., Blumberga, D., Kļaviņš, M., Rošā, M., Valtere, S., 2010. Vides tehnoloģijas. Rīga: LU, 212 lpp.
4. „Processing of Powder Materials by Pulse Electromagnetic Field”, Viktors Mironovs, 2010.
5. LV Patent 13927B Sorbent for collection of oil products, Mironovs, V., Lapkovskis, V., Zemčenkovs, V.
6. LV patent 13911B 2009/08/20, Int. Cl E02B15/04. V. Mironovs, V. Belova, V. Zemčenkovs. Apparatus for collection of spilled oil products. LR patents, RTU.

# SPECIFIC OF HEMP FIBER'S PLASTIC COMPOSITE PROJECTION

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**Abstract.** *In the report there are reflected research results of new board type biocomposites creation for furniture and equipment manufacturing for public segment, replacing traditional petroleum-based components with fully or partly renewable, biodegradable raw materials as one of the major global environmental problems today is non-renewable resource depletion and waste of petroleum-based plastic products. Performed research of biopolymer composites development shows that they are cheaper, environmentally friendlier, lighter, more easily to recycle and to dispose at the end of the product life cycle.*
*For biopolymer's reinforcement industrial flax and hemp fibers in terms of mechanical qualities are competitive with the glass fiber, they are strong enough in many applications, $CO_2$ neutral, have a relatively low cost, low production energy requirements. By creating new biocomposites it is taken into account that the designed material mechanical properties are mainly dependent on the fiber mass in the matrix, orientation and adhesion to the matrix material. The maximum theoretical amount of fiber weight in composite can reach 91%, specific weight of the fiber component used in practice is usually between 45-65%, but can reach also 70%. For improvement of the adhesion the chemical treatment and drying of the fibers need to be done, also adjuvants that promote development of the hydroxyl group links should be incorporated in the matrix.*

**Keywords:** *biodegradable composite, mechanical properties, natural fiber, polypropylene processing , renewable resources.*

## Introduction

One of the most actual environmental issues today is plastic waste. The large amount of plastics manufacturing and product use in every day life creates vast amount of plastic waste. In year 2008 in the world there were about 245 million tons of plastic used that in relation to the year 1950 when 1.5 million tons were used is a huge amount. The increase is much higher than consumption of other materials such as steel or paper [1] that creates comparable fast-growing volumes of waste.

Evaluation of waste is strictly regulated in the European regulations and criterions about cleaner and safer environment, as well scientific research about ecological materials and ecocomposites development are promoted. This trend is particularly topical in the last decade, when more and more attention from both academic and industrial environment is focused on solutions of the problems that are associated with development of renewable, biodegradable components and to pack up into stable composite structures.

So that materials could be classified as biodegradable, they must meet specific criteria set by the European standard EN 13432 [2] and define biodegradable plastics as ones which are experiencing major changes in the chemical structure under specific environmental conditions. Biodegradable plastics submit degradation as a result of influence of the natural micro organisms - bacteria and fungi. In most of the international standards it is required that at least 60% of corrosive product need to be corrosed in 180 days. Plastics can be created as photo corrosive, corrosive as the result of oxidation, hydrophytes - corrosive, or one who may be decomposed [3].

## Materials and methods

### *Filling of the composite materials*

Plastic composites that are strengthened with natural fibers are demanded raw materials in many economical sectors including vehicle industry, building and furniture manufacturing. In the former practice while making the plastic composites, the reinforcements from wood or

textile fibers (predominantly synthetic) are implemented in the plastic matrixes. Natural fibers are environmentally friendly, completely recyclable, widely available, and regularly renewable, comparatively cheep, with sufficiently good physical and mechanical qualities, with low density as plant fibers are lighter than traditional for technical uses glass, carbon or aramid fibers (Table 1). If the natural ability of decomposition solves ecological problems, then low costs and good qualities makes economical interest. Natural fibers recycling at the end of the life cycle by burning or in the waste polygon, exempted volume of $CO_2$ balances the volume that is received during the growth. Abrasive qualities of natural fibers are much lower which ensures benefits in the treatment of composite material. Natural fiber composites are completely recyclable at the end of their lifetime which makes them nature friendly materials. These are also renewable resources contrary coal, oil or natural gas. In the composite materials which are made by using unmodified plant fibers required mechanical qualities are not reached very often. To avoid it before the making the composite in many cases additional treatment of the surface or usage of reagents is necessary.
The natural fibers that are more investigated lately are hemp fibers. Although hemp usage in natural fiber composites is relatively new market it has proved itself already in a good way. Hemp composites work well in different ways – if water absorption and exuding is necessary, thermal and acoustic isolation, firmness and hardness. Since hemp and other natural fibers usually are used in the polypropylene matrix (or with other polymers), the saving of manufacturing energy results in the glass fiber replacement and bigger proportion of natural fiber in the matrix. Consumption of energy for manufacturing glass fibers is five times bigger than needed for hemp fiber refinement, for manufacturing epoxy resin it is 10-20 times bigger.[4]

*Table 1.*

**The comparison of physical properties of natural and glass fibre**

| | Fibre | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | E-glass | flax | hemp | jute | ramie | coir | sisal | cotton |
| Density ($g.cm^3$) | 2,55 | 1,4 | 1,48 | 1,46 | 1,5 | 1,25 | 1,33 | 1,51 |
| Tensile strength (MPa) | 2400 | 800-1500 | 550- 900 | 400- 800 | 500 | 220 | 600- 700 | 400 |
| Elongation (%) | 3 | 1,2- 1,6 | 1,6 | 1,8 | 2 | 15-25 | 2- 3 | 3- 10 |
| Young's Modulus (Gpa) | 73 | 60-80 | 70 | 10- 30 | 44 | 6 | 38 | 12 |
| Moisture absorption (%) | - | 7 | 8 | 12 | 12- 17 | 10 | 11 | 8- 25 |

***Composite matrixes***

Traditional composite materials are stable against biological degradability (are not biodegradable). Micro – organisms that are in the soil can not take down part of the plastic in order to create collapse in the matrix system. In this group of materials there are composites with oil base matrix that is strengthened with carbon or glass fiber. Such materials are recycled and used again.
Research in the field of biodegradable composites is now focusing on two out of three polymer composite material classes: 1) partly biodegradable; 2) completely biodegradable composites.
Partly biodegradable composite materials are created so that they would divide faster than most of the composites from the synthetic materials. In the manufacturing these types of materials, usually natural fibers are used, a polymer from the oil products works as a binder. At the end of the lifetime composite structure gradually decline while micro – organisms recycle natural fiber macro molecules that is the plastic matrix armature. As a result micro – organisms penetrate inside the composite and stimulate degrability of the material.

In the class of completely biodegradable polymer materials there are polymer materials that take down in a biological way. It is a new field and at the moment has big attention from researchers and manufacturers. Matrix polymers are attempted to be created from natural raw materials (starch or microbiologically planted polymers), but armature fibers are created from the renewable resources (flax, hemp, other cellulose based fiber plants). As a result micro – organisms can completely recycle these composite materials in biological processes in two stages. Fiber plants are made from twisted macromolecules' chains that are split in smaller fragments as a result of action of enzymes. In the influence of oxygen and as a result of enzyme action the divided macromolecules take part in the next metabolism processes, as a result of degrability processes they divide in $CO_2$ and $H_2O$, that are environmentally friendly side products. [5]

In many usages in a shape of matrix fiber, granule or polythene **PP** (Polypropylene) is used, which is thermoplastic, colorless (white) polymer with high melting temperature (158-170C$^o$) and high tension durability. It is widely used in engineering industry, textile industry, building, furniture manufacturing and in other industries. PP is resistant against different organic liquids, alkali, acids, poorly absorbs water. Polymer submits well to the recycling and in the composites with natural fibers it is partly biodegradable. PP is the most widely used thermoplastic material in the industry of natural fiber composites because of its low density, excellent processing, good mechanical qualities, high temperature resistance, good shape stability and resistance of the influencing strength. Increase of the PP usage describes also wide research and publications that are dedicated to the research of this material. Advantages and disadvantages of the polypropylene matrix are visible in the table 2 [6].

*Table 2.*

**Advantages and disadvantages of polypropylene matrix [6]**

| | |
|---|---|
| Low specific gravity (density)<br>Excellent chemical resistance<br>High melting point (relative to volume plastic)<br>Good stiffness/ toughness balance<br>Adaptability to many converting methods<br>Great range of special- purpose grades<br>Excellent dielectric properties<br>Low cost (especially, per unit volume) | Flammability<br>Low- temperature brittleness<br>Moderate stiffness<br>Difficult printing, painting ang gluing<br>Low UV resistance<br>Haziness<br>Low melt strength |
| PP advantages | PP disadvantages |

*Table 3.*

**Mechanical properties of polymers that are used a s matrixes in fibre composites [7]**

| Matrix | Density (g/cm$^3$) | Melt Temp ($^o$C) | Tensile Strength (Mpa) | Young Mod. (GPa) | Elong. To Break (%) |
|---|---|---|---|---|---|
| High density Polyethylene (HDPE) | 0,94- 0,96 | 120- 130 | 32 | 1,1 | 150 |
| Low density Polyethylene (HDPE) | 0,91- 0,93 | 105- 115 | 20 | 0,2- 0,3 | 300- 600 |
| Polypropylene (PP) | 0,9 | 176 | 35 | 1,1- 1,6 | 150 |
| Poly (lactic acid) (PLA) | 1,25 | 140- 152 | 48 | 3,8 | 2,5 |
| Poly (hydroxybutyrate) (PHB) | 1,25 | 175 | 40 | 3,5 | 6 |
| Polybutyleneadipate/ terephthalate (PBAT) | 1,25- 1,27 | 110- 120 | 35 | <0,2 | 560- 700 |

***Production of composite materials***

Fibers in the composite material work as intensifier while the pressure is directed from the matrix to the fibers as a result of interaction. Geometrical factors that separate different fiber composites are:

1) Fiber amount; 2) Fiber length; 3) Fiber allocation; 4) Fiber orientation.

Such layers can consist not only from the adjusted fibers but also from the differently oriented fibers. They can be located differently, for example, in the composite order or in the right angle one against another.

Theoretically the maximum amount in the composite can reach 91% which can be created if fibers are placed in the twisted shape. Fiber amount in the location prevalently reaches 45 - 65%, but it is possible to reach also 70%.

Composite can have various fibers' structure as it is shown in Fig.1.

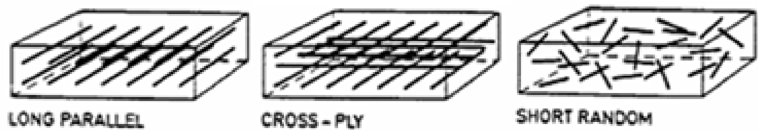
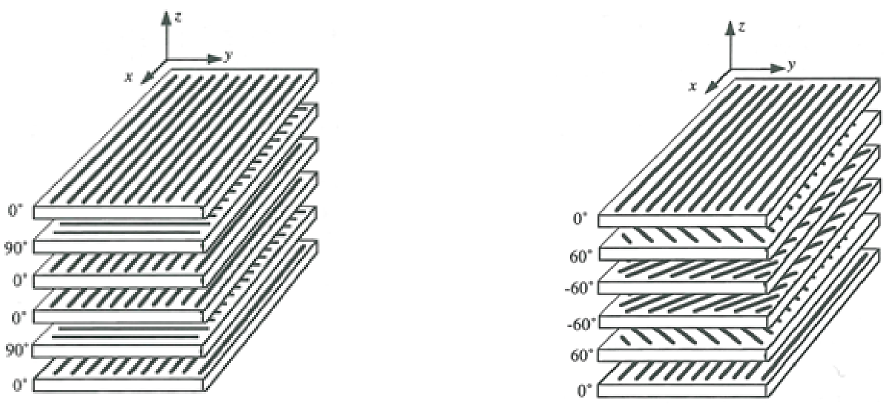



*Fig.1.* **Fiber structure in composite**

High performance polymer components usually consist of layers or in layers which are arranged in particular order. In order to anticipate total material flexibility, each layer is considered as homogeneous in a way that fiber planking and layout is equal in all the material. Fibers can be short or long, laid out in one or several layers in one or various directions. If the fibers are laid in one layer it is called *ply* but if it is laid in several layers it is called a *laminate*. Flat laminate is made from one direction laid fiber layers that are arranged in the angle of $90^o$ one above another. This is a typical construction that is used in the aircrafts because of its strength.

Simple condition is used to describe the layer sequences. It is described with simple layers. As you can see in the Fig.2a layers are formed in $0^o$/ $90^o$/ $0^o$/ $0^o$/ $90^o$/ $0^o$, which can be simplified to [0/ 90/ 02/ 90/ 0], where digit 2 means that there are two layers with $0^o$ orientation. As in this case claddings are in the symmetric relation to the middle layer, then it is possible to simplify the designation [0/ 90/ 0], which means that layers repeat symmetrically. Similar is also the situation that is shown in the Fig.2b where [0/ +60/ -60/ +60/ 0] is shortened to [0/ +60/ -60] or [0/ +-60]. [8]




(a) (b)

*Fig.2.* **Arrangement of plies in (a) a crossply laminate and (b) an angle-ply laminate sandwiched between $0^o$ plies [8]**

Composites reinforced with natural plant fibers have also negative aspects like unconformity between hydrophile natural fibers and hydrophobe thermoplastic and termoset matrix, wherewith it is necessary to use appropriate physical and chemical processing methods to improve adhesion between fiber and matrix.

**Experiment**

***The Composite Materials***

For a composite material hemp variety "Bialobrzeskie" was used cultivated in the Latvia's Kraslava district at year 2009 (Fig. 3). As L. Freivalde's research shows [9], this type is very suitable for composite materials and weather conditions in Latvia are also appropriate for its' growth.

As composite matrix material polypropylene fibers „FiberMesh 300" imported from England were used (Fig.4). These fibers are already lengthened by 12 mm. In order to make the more even planking, lengthened fibers were rarefied to make the mono fiber planking out of fiber entirety.

*Fig.3.* **Hemp fibres**

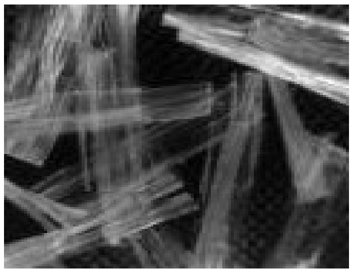


*Fig.4.* **Fibers of polypropylene "FiberMesh 300"**

Hemp fibers were scutched to clear out shives, separate long fibers from the short ones and get regular fiber planking. For the first samples of the experiment (parallel fiber orientation) long fiber complexes with the length 260mm were used measured by die size. For samples 50% and 70% fiber share from the total sample weight was used. Before samples preparation fibers were dried in the drying cupboard (CHBC-45.4.54) at the temperature of $60^oC$ with the exposure time of 4 hours.

Since the process is happening in the fever heat and the polymer is melting, aluminium foil plates in size of 265 x 265mm is used that ensure homogeneous pressed composite surface and possibility to take out ready made composite from the termopress device more easily. Aluminium foil, polypropylene fibers and hemp fibers were put in layers, making the composition of laminate type. (Fig. 5.)

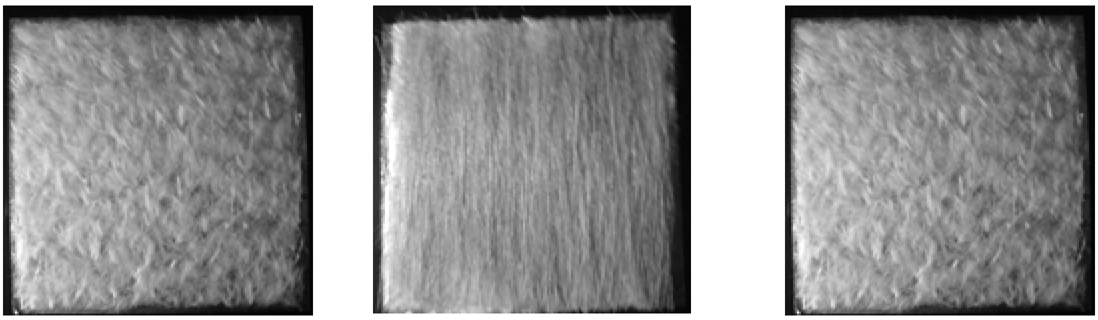


*Fig.5.* **Sample preparation stages**

Samples were prepared taking into account the experiment plan. Fixed factors were weight - 14g, pressure – 7,66kg/cm$^2$, time - 20 min. As the independent variables were chosen proportion of hemp in the sample ($x_1$) and temperature ($x_2$) - 170oC or 190oC. Sample size 260 x 260 x 0,65 mm.

***Tensile Testing***

Tension tests of the composite samples from the parallel long hemp fibers and polypropylene matrix were executed on universal testing device ZWICK Z100 (maximum strength 100 KN) using Tension 100kN.ZPV testing method. Tests were carried out with the clamp speed 10 mm/min and clamping distance 90mm at room temperature 22+/-2C$^o$. Total number of tested samples 16, including 4 samples for each processed set. Obtained test results are shown in graphs of Fig. 6 and 7.

## Results and discussion

***Tensile Properties***

The degree of effectiveness of reinforcement can be characterized by the Young's modulus of the composites (Fig. 6) and tensile strength and elongation (Fig. 7).

As seen from graph of Fig. 7 tensile strength parallel to the fibers direction tended to increase with the increasing hemp fibers share in composite and temperature decrease, with the following tensile elongation increase. Tensile strength lower values for 70% reinforcement and processing temperature 190 $^0$C witness that such processing temperature is too high for hemp fibres as structure of these fibres are stable till 170 $^0$C and after this level is exceeded some destruction of fibers could start.

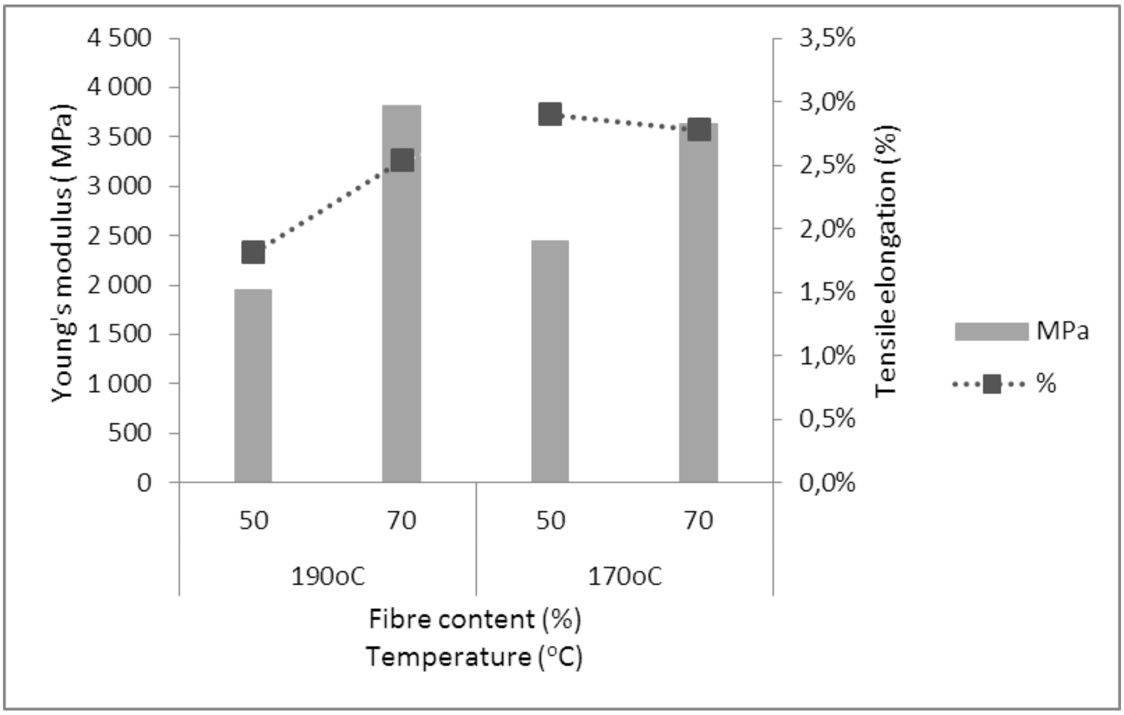



*Fig.6.* **Young's modulus as function of fiber content, temperature and tensile elongation**

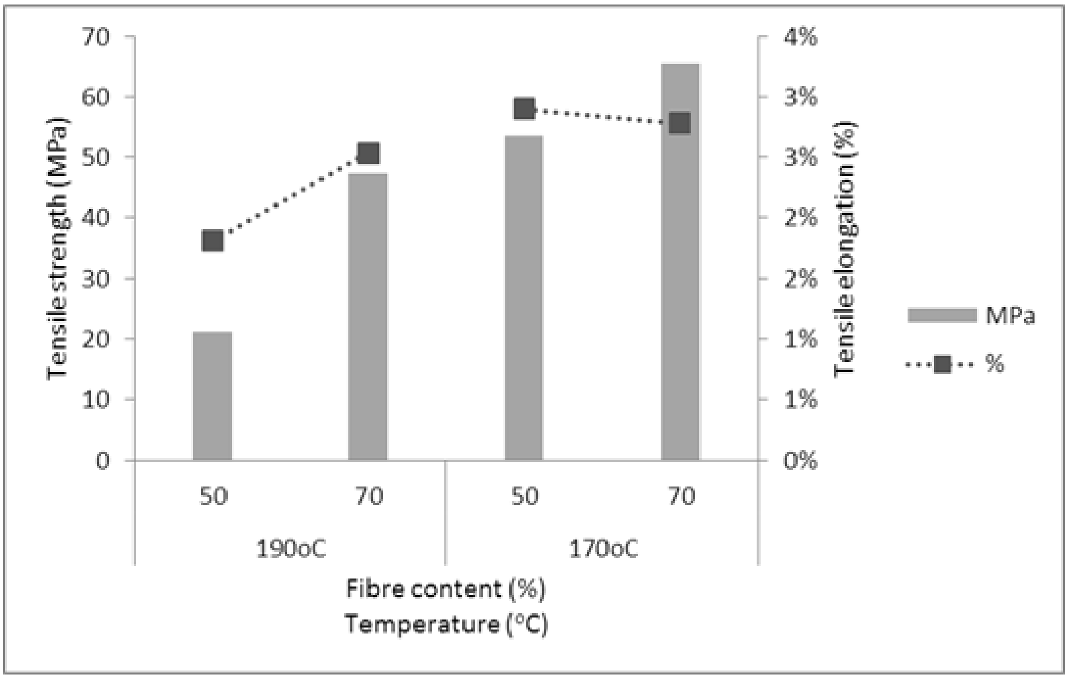



*Fig.7.* ***Tensile strength as function of fiber content, temperature and tensile elongation***

Comparison of Young's modulus for variants shows that module is a little higher for sample with 70% hemp fibers and processing temperature 190 $^0$C compared to 70% hemp fibres sample in 170 $^0$C, but difference does not exceed 5%. For samples with 50 % hemp reinforcement Young's modulus are strong lower 2000 (190$^0$C) and 2500 (170$^0$C) respectively.

## Summary

Long hemp fibers as a reinforcement of fiber plastic composites could be used to ensure Young's modulus values in range 1954- 3816 MPa and tensile strength in range 21,16- 65,47 MPa. Higher values of hemp fiber PP composite tensile strength could be provided by long fiber content 70% and processing temperature 170 $^0$C. Young's module 3816 processing temperatures higher than 170 $^0$C are not recommended. Hemp fibers reinforcement of PP base composite provides biodegradability of final product at the end of its usage in natural environment.

Further experiments to improve mechanical properties of hemp fiber-PP composites and development of hemp fiber-natural matrixes composites are needed.


## Acknowledgements

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## References


1. Sustainability of Fiber-Reinforced Plastic- An Assessment Based on Selected Examples of Application,Frankfurt, 2010, http://www.eucia.org/publications/documents, p.23.
2. http://www.european-bioplastics.org, Standard EN 13432
3. E.Kirilovs, S.Kukle, Biopolimers and their development and use, Scientific journal of Riga Technical university, Material science, 9.serie, RTU, volume 5, p.77.
4. S.Smith- Heisters, Illegally Green: Environmental Costs of Hemp Prohibition, Reason Foundation, Los Angeles, 2008, p.20- 23.

5. G.Bogoeva-Gaceva, M.Avella, M.Malinconico, A.Buzarovska, A.Grozdanov, G.Gentile, M.E.Errico, “Natural Fiber Eco-Composites”,Polymer Composites,Macedonia vs Italy, Society of Plastics Engineers, 2007, p.98- 101.
6. I.I. Rubin , Handbook of plastic materials and technology, Wiley-Interscience, New York, 1990, p.446- 447.
7. S.Thomas, L.Pothan, Natural Fiber Reinforced Polymer Composites: From Macro to Nanoscale, Old City Publishing, 2009, p.115.
8. D.Hull, T.W.Clyne , An Introduction to Composite Materials, Cambrige University Press, 1996, p. 43- 46.
9. V.Stramkele, L.Freivalde, S.Kukle, Analysis of the renewable fiber properties and uses in scale of Latvia In: 41st International Symposium on Novelties in Textiles, Ljubljana, Slovenia, 2010, p.300- 325.

***Anotācija.*** *Šajā publikācijā ir atspoguļoti pētījumu rezultāti jauna plātņu tipa biopolimēra kompozītu izveidei mēbeļu un iekārtu ražošanai sabiedriskajam segmentam, aizstājot tradicionālās naftas bāzes komponentus ar pilnībā vai daļēji atjaunojamām, bioloģiski noārdāmām izejvielām, jo viena no lielākajām pasaules mēroga vides problēmām mūsdienās ir neatjaunojamo dabas resursu sarukšana un atkritumu apjoms no naftas bāzes plastmasas izstrādājumiem. Veiktie pētījumi biopolimēra kompozītu attīstībā rāda, ka tie ir lētāki, videi draudzīgāki, vieglāki, vieglāk pārstrādājami produkta dzīves cikla beigās.*
*Rūpnieciskās linšķiedras un kaņepju šķiedras kā biopolimēra pastiprinātāji mehānisko īpašību ziņā ir konkurētspējīgas ar stikla šķiedru. Tās ir pietiekami konkurētspējīgas daudzos aspektos- $CO_2$ neitrālas, ar salīdzinoši zemām izmaksām, zemām ražošanas enerģijas prasībām. Radot jaunus biokompozītus, jāņem vērā, ka izveidotā materiala mehāniskās īpašības galvenokārt ir atkarīgas no šķiedru daudzuma matricā, šķiedru novietojuma un adhēzijas ar matricas materiālu. Maksimāli teorētiskais šķiedru masas daudzums kompozītā var sasniegt 91%, ko iespējams izveidot, ja šķiedras iestrādātas savītā veidā. Praksē lietojamais šķiedru komponentes īpatsvars parasti ir robežās 45-65%, bet iespējams sasniegt arī 70%. Adhēzijas uzlabošanai jāveic ķīmiska šķiedru apstrāde un žāvēšana. Arī matricā nepieciešams iestrādāt papildvielas, kas veicina hidroksilgrupas saišu veidošanos.*

# THIXOTROPIC PROPERTIES OF LATVIAN CLAYS

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**Abstract.** *This research studies Latvia originated Devon (Tūja, Skaņkalne), quaternary (Ceplīši), Jurassic, (Strēļi) and Triassic (Vadakste) deposit clays as well as Lithuania originated Triassic (Akmene) deposit clays. Thixotropic properties of clay were researched by measuring relative viscosity of clay in water suspensions.*

*Relative viscosity is measured with a hopper method. It was detected that, when concentration of suspension is increased, clay suspension's viscosity also increases. It happens until it reaches a certain boarder point when viscosity increases significantly – a dramatic rise is shown on the curve. It means that clay particles make a lace-like, easily broken structure. Impact of chemical reagents on clay suspensions' thixotropic properties is researched. Experimental results obtained on the new materials with thixotropic properties will allow precise definition of production technologies and usage of a new approach in development of motivation products. Likewise, the results will make an important investment in establishing a thixotropic material description methodology.*

**Keywords:** *clays, concentration, suspension, thixotropy, viscosity.*

## Introduction

In the meantime, clay minerals are widely used in various fields of manufacturing and agriculture. In manufacturing, they are used as adsorbents for cleaning and clarifying wines, various juices, as well as waste waters. Also they are used in building as bonding and forming materials. In agriculture, clay suspensions are used as fortifiers of sand zones and for improvement of hydrophilie and adsorption properties of soil dispersions. Another interesting property of clay, thixotropy, is far less known [1].

The word thixotropy, which was first introduced by Freundlich, is put together by the two Greek words "thixis" (stirring, shaking) and "trepo" (turning, changing) [2].

Thixotropy is an ability of the "clay – water" system to restore its structure after some time, when it was influenced mechanically. This is a reverse isothermal transition sol↔gel and it is characteristic to the clays of smectyte type. Thixotropic properties are more characteristic to the clay suspensions of expansive type. These clays can be used for preparation of boring solutions, in cosmetology, medicine, etc.

In the latest years, with the field of clay usage expanding, a necessity of broadening clays' variety, assign them certain properties like high viscosity, thixotropic properties as well as substituting currently used imported materials by locally originated ones.

In water suspensions, clays exist in form of plates. In water solution, clay surfaces have a negative charge, but their edges carry positive charges. If concentration of suspension is high enough, then spaces between the plates grow smaller, making the plates collide so that weakly positive plate edges are drawn to the negatively charged clay plate surfaces. A lace-like three dimensional structure, called "House of cards", is formed. Thanks to such structure, expansive type clays have high thixotropic properties.

## Materials and methods

Objects of this research are Latvia originated Devon (Tūja, Skaņkalne), quaternary (Ceplīši), Jurassic, (Strēļi) and Triassic (Vadakste) deposit clays as well as Lithuania originated Triassic (Akmene) deposit clays. Clay fraction of Latvian and Lithuanian Triassic sediment contains the following clay minerals: smectyte (67-80%), illyte (6-25%), chlorite (0-25%) and kaolinite (2-5%) [3].

Description of the researched clay samples is given in Table 1. From the studied clays, two series of clay suspensions are prepared: suspensions of the first series are prepared from clay samples which are visually cleared from additions, crashed in a mortar, dispersed and swollen in a distilled $H_2O$ for 1 month. Swollen clays in suspension form are sieved and dried in 100°C temperature, by that obtaining a fine clay fraction with particle size < 63 μm and a 50% clay suspension in distilled $H_2O$.

Suspensions of the second series are prepared from clay samples which are visually cleared from additions, crashed in a mortar and, as concentrated suspensions, mechanically activated in a planetary ball mill for 20 min, in a 250 rpm speed. Obtained concentrated suspension is diluted with distilled water up to 50% clay suspension.

*Table 1.*

**Characteristics of clay samples**

| Name of clay deposit | Period | Layer thickness of taken samples (m) | Humidity ( %) |
|---|---|---|---|
| Strēļi | Jurassic | 2,5 – 3,5 | 30 |
| Tūja | Devon | 0,1 – 0,2 | 20 |
| Skaņkalne | Devon | 2,0 – 3,0 | 19 |
| Ceplīši | Quaternary | 2,2 – 3,0 | 24 |
| Vadakste | Triassic | - | - |
| Akmens | Triassic | 4,8 – 7,7 | - |

It is known that viscosity, thixotropic properties and stability of clay suspensions often depends on the solid phase and mineral contents. Since the mentioned properties are coherently changing due to the solid phase contents of clay suspensions, by using the dilution method, from 50% suspensions there were 15, 20, 30 and 40% suspensions prepared and kept in a quiescence state for 24 hours in order to achieve an equilibrium condition. On the next day the system was stirred again and the conditional viscosity was defined by the conic funnel method. For this, 300 ml of the mixture was put in a funnel and the outflow time of 200 ml of suspension in a 20 $^0$C temperature was detected. Based on the obtained data, variation of relative viscosity was calculated, depending on the solid phase concentration, using the following formula (1):

$$\eta_{relative} = \frac{t_1}{t} \qquad (1)$$

where $t_1$- outflow time of the clay solutions, sec.

t- outflow time of 200 ml of distilled water ( 10 sec.)

pH of the clay suspensions is measured using a “HANNA HI 8424 pH meter”.

## Results and discussion

Studying suspensions of the first series, it was found that, with a suspension concentration increasing, a clay suspension’s relative viscosity also increases. It happens until the moment when the viscosity increases significantly, a dramatic rise is shown on the curve. It proves that the clay particles form a lace-like, easily breakable structure and demonstrate thixotropic properties. Concentration of clays from the Strēļi and Akmene deposits lies within the suspension boundaries of 33 % - 39%, but clays from the Skaņkalne, Ceplīši and Tūja - from 39% up to 45%.(see figure 1.)

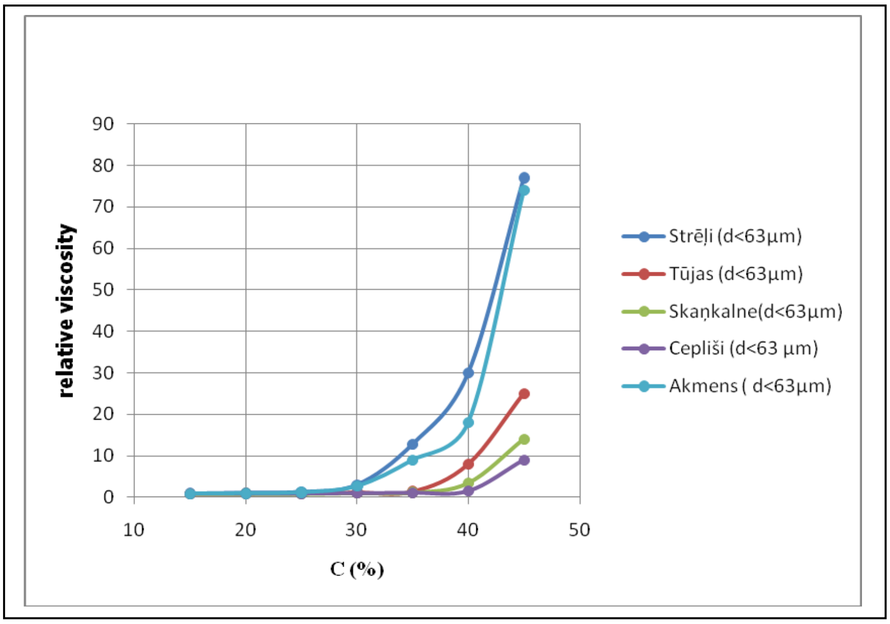


*Fig.1*. **Dependence of relative viscosity of the natural clay samples from the clay concentration in suspensions**

Fig.2 shows dependence of relative viscosity of the mechanically activated clay samples from the clay concentration in suspensions. Obtained results testify that while solid phase concentration of mechanically activated clays increases viscosity of the clay sample suspensions dramatically increases starting from 35% concentration.

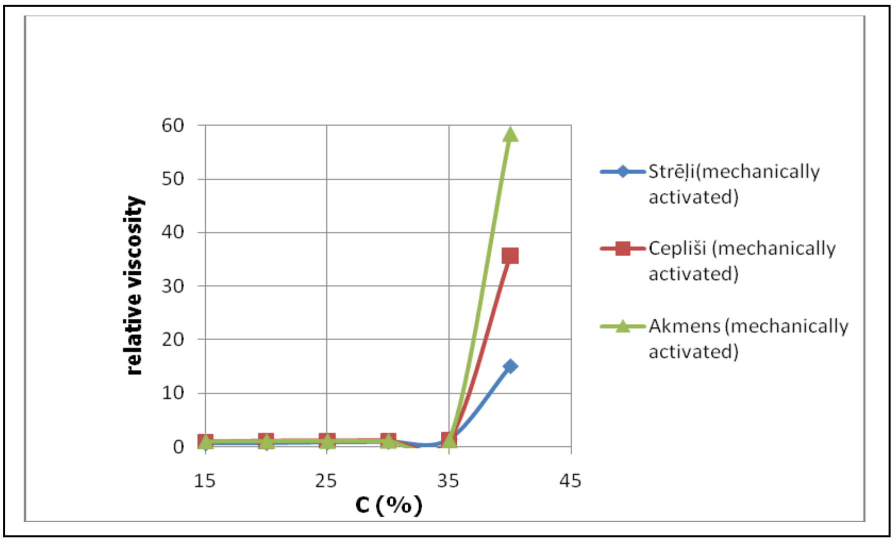


*Fig.2*. **Dependence of relative viscosity of the mechanically activated clay samples from the clay concentration in suspensions**

This is because not only clay sample dispersity increases as a result of mechanical activation, but also its reactivity. Dispersity of clay minerals is the most important criteria that determine its main physical chemical properties: thixotropic structurization, adsorption ability, coagulation, ion exchange, etc.

Thixotropic properties of clay suspensions are amended, modifying the samples with sodium carbonate ($Na_2CO_3$) and methylcellulose. It is defined that modification of clay suspensions with methylcellulose (0,1%) increases concentration of structurization. However, modification of clay suspensions with sodium carbonate (0,1%) lowers concentration of structurization (Fig.3) [4].

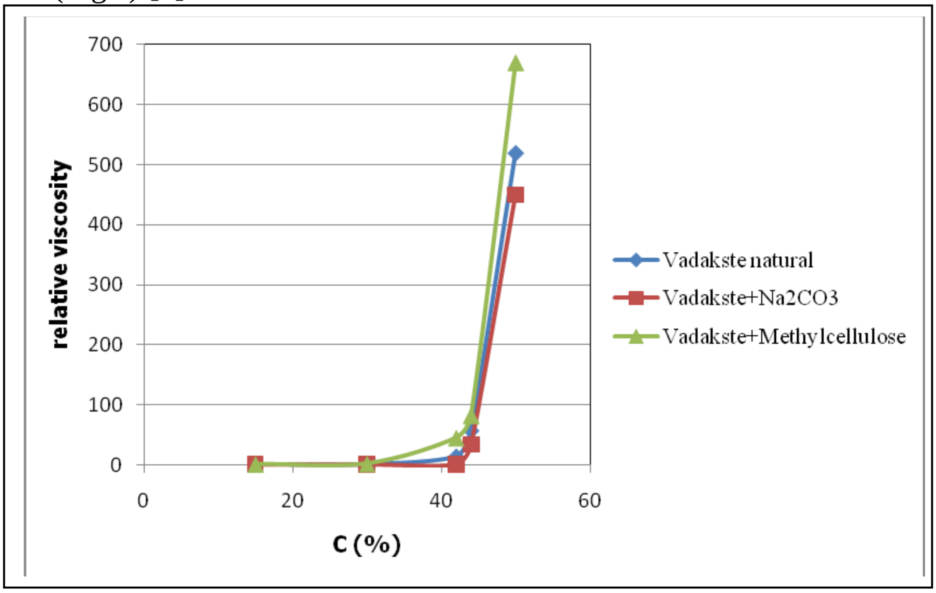


*Fig.3*. **Dependence of relative viscosity of Vadakste deposit clay samples from the modifier**

While mixing sodium carbonate with a clay sample, there is almost no exchange of $Ca^{2+}$ onto $Na^{+}$. Their interaction occurs only after putting clay powder in the water, but mechanically adsorbed salts weakly interacts with clay particles. Methylcellulose is a highly molecular organic soluble material. It gives a serious impact on the contents of water. Breaking the contents of clear water by its hydrophilic fragment and structuring it with hydrophobic groups, it structurizes the water around itself in a specific way by forming thixotropic systems [5].

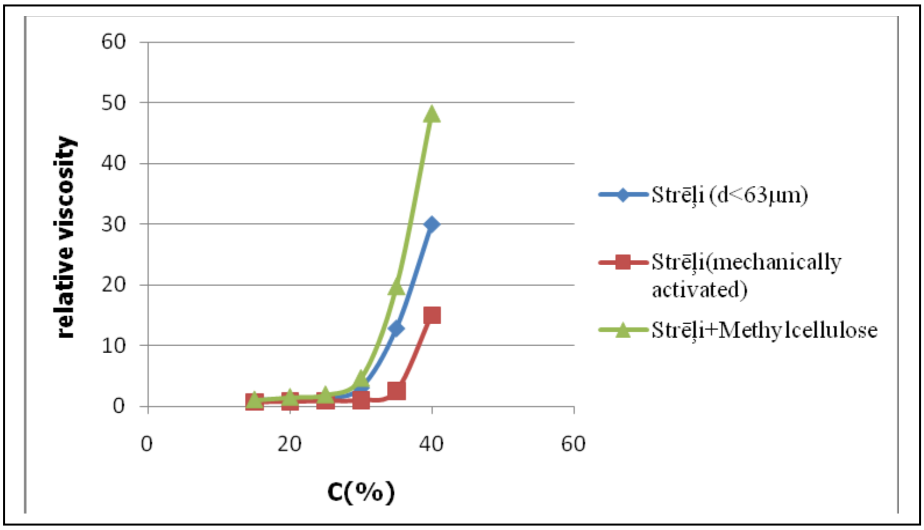


*Fig.4*. **Dependence of relative viscosity of Strēļi deposit clay samples from the modifier**

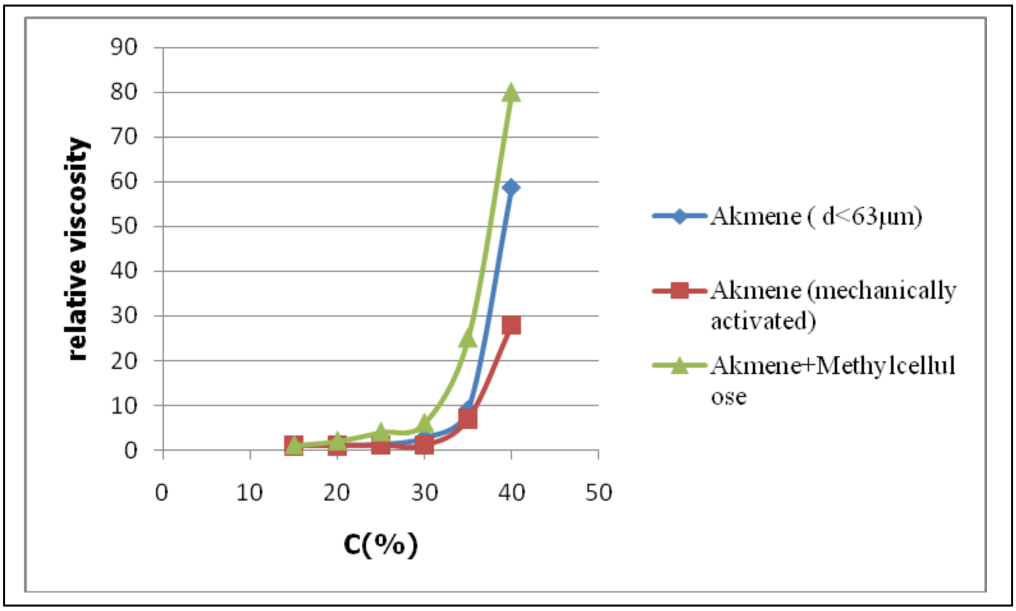


*Fig.5*. **Dependence of relative viscosity of Akmene deposit clay samples from the modifier**

The largest conditional viscosity is found at the clay samples modified by 0,1 % metilcellulose (Fig.4). Similar regularity is detected at the clays of Akmene deposit. (Fig.5)

## Conclusions

1. It is found that Latvian originated clays have thixotropic properties.
2. It was found that modifying clay suspensions with methylcellulose (0,1%) increases the structurization concentration. In the same time, modifying clay suspensions with sodium carbonate (0,1%) lowers the structurization concentration.

## References

1. Lakevičs V., Bērziņa - Cimdiņa L., Ruplis A., Pelšs J. Sorption properties of Latvian clays and environmental protection survey, VII Starptautiskās zinātniski praktiskās konferences materiāli,1.sējums, Rēzeknes augstskola, 2009, 222.-227. p.
2. Chi H. Lee, Venkat Moturi, Yugyung Lee Thixotropic property in pharmaceutical formulations, Journal of Controlled Release 136 (2009) 88–98.
3. Sanita Reide-Zēģele, Ģirts Stinkulis Triassic deposits of Latvia and Lithuania: Composition and origin. Material science and applied chemistry, 2009-7353.
4. Lakevičs V. , Stepanova V., Ruplis A. Pētījumi par Latvijas mālu tiksotropām īpašībām, LU 69. Zinātniskās konferences tēzes, LU, 2011.
5. Шарафутдинов З.З., Шарафутдинова Р.З. Буровые растворы на водной основе и управление их реологическими параметрами. Нефтегазовое дело, 2004, 1-24 с.

# POSSIBLE USE OF HEMP AND WOOD IN PRODUCTION OF THE HEAT INSULATION MATERIALS

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**Abstract.** *Obtaining of a new ecological heat insulation material from always renewable raw material in nature, wood and hemp, derived from wood and hemp fibre remains left from the production process. The study was carried out to find hemp wood parts (shives), fiber, and material first possible compositions together with wood fibres, to produce heat insulation materials. The use of the heat insulation material would be meant for dwelling and recreation houses. In the present research the main characteristics of these materials are determined: moisture content, density, water absorption, as well as the coefficient of heat transmission.*

**Keywords:** *hemp, hemp heat insulation, wood-fibre heat insulation.*

## Introduction

Already from the ancient times the world has known natural materials such as wood, hemp, clay, stone and other materials that easily return to natural circulation after their usage and require the least energy in manufacture and processing.

One of the fundamental principles of the economical, social and environmental policy of the Republic of Latvia is the maximal usage of the advantages of geographical location by promoting the development of industries with access to the local raw materials. The forest sector and agriculture is one of the few sectors in which it is possible to achieve economical mobility and increase production on the basis of the renewable raw materials, ensuring economical stability of the environment in the country.

Though the forest and agricultural areas can not be measured solely in monetary terms; they perform essential environmental, ecological and social functions at both national and international level [1]. Due to the development of agriculture in Latvia and the interest about the acquisition of new market niches there were experimentally planted hemp plantations in Kraslava.

Initial aim of the production was to produce fibres, but due to the fact that it is possible to obtain from the hemp 23-27% fibres, but more than 65% - shafts, there occurred a problem with the large amount of shive.

Since in the wood-working process there are many different wood wastes, it led to a conclusion to carry out a study about the possibility of joining both wastes as well as the possibility of the heat insulating material production, in which the first heat insulation composite material samples would be obtained.

In the world there are only few researches available about the joining of hemp and wood, resulting in heat insulation materials. The obtained results are often very controversial and ambiguous.

Due to the development of human thinking about a healthy environment, there is a need for new environmentally friendly materials. Hemp, hemp and wood materials for heat insulation in the world are still new products, being only in stage of development. That is why it is necessary to carry out researches about the creation of new materials and improvement of the existing ones, besides they should meet all the necessary standards and construction norms of Latvia and European Union (EU). This is the first study of this kind in Latvia.

## Materials and methods

The aim of the study is to create an insulation material from Latvian-grown hemp fibres and hemp wooden parts, as well as from wood fibres and pulp and to test the physical properties of the insulation materials. At the beginning stage of the research I select the necessary relation of binders and various fibres.

Physical properties which I am going to study will be: density, water absorption capacity temporarily standing in water, moisture content, and heat conductivity.

The first material, which was made of hemp fibre, is hemp-fibre insulation material (soft plate). Hemp fibre wood parts (shive) were obtained from the company "ZALERS" in Kraslava district, but the wood fibres - from the company "Yelt Wen" in Aizkraukle district. The process proceeded as follows.

Hemp is harvested from the field, ground in hammermill and the wooden part is separated from the fibre parts in the drum separator. Then to separate the fibres from the impurities (sand, small stones) they must be blown with an air flow. In the shive fraction there still remains an average of 4-12% fibres, so it requires another technological operation with the help of a sieve, where with the flow of air fibres are separated from the shives.

In the study I used two binders, NaSl Sodium silicate solution (water glass), as well as potato starch, since these materials are known with their moisture-repellent function and are created from natural ingredients. During the course of the process, soda as an agent against burning was added to the composition.

Binder was applied on both sides with a spray method. At first one side was covered with a binder, and then it was repeated on the other side. After that comes the cutting of insulation according to how long this soft insulation board will be. All samples including the insulation materials presented in the table were produced with an area of 300 mm * 300 mm, but with different thicknesses depending on the necessity for each study.

The next operation is smoothing of the fibre by the rollers. This technological operation is required to smooth the fibres and to make equally thick technological isolation work pieces. Then these work pieces are formed according to how thick the insulating plate is foreseen. After that the finished plate is pressed and dried in oven at $150^0$ C, and by the end of the operation – 120°C, as the fibre was already heated through previously.

In conclusion, plates are kept 24 hours in a room with constant air and temperature values to stabilize the moisture content.

Then the insulation material is kept in a conditioning chamber at 23 ± 2 ° C with a relative humidity of WR 50 ± 5%. In the study, due to the fact that in order to check the coefficient of heat transmission $\lambda$ W/(m*K), the maximum sample thickness that can be inserted into the test facility, is 25mm. 10 samples of each type were produced.

The next samples were made by mixing wood fibres in different proportions with hemp - shive parts mixed in different proportions, according to the principle of board production technology, by the dry method.

After the production of the samples, 4 types of samples were selected and further in text they will be marked as A1, B1, C1, D1, whose compositions can be seen in Table 1.

Product samples were examined visually and by the mechanical strength by breaking them with the hands, as a part of the samples after pressing did not have sufficient stiffness. The material, for that potato starch was used as a binder, had the greatest mechanical strength.

The study was carried out in accordance with the Latvian National Standards: Thermal insulating materials for the usage. Determination of the apparent density LVS EN 1602:1996 + AC: 1997. [2].

Thermal insulation products for building. Water absorption determination temporarily and partly standing in water. BS EN 1609:1996 + AC: 1997. [3]. Thermal insulation. Thermal

resistance and determination of the related properties in steady condition. Enclosed hot plate device, LVS ISO 8302:1991 [4].
For the determination of the thermal conductivity Laboratory for Mathematical Modelling of Environmental and Technological processes was used. The data were processed with program Isis v.1.0.1.

## Results and Discussion

Experimental data confirm that it is possible to get insulating composite materials from wood and hemp production processing remains, which are seen in Fig 1 to 4.

*Fig.1.* **A1 Hemp fiber composite material**

*Fig.2.* **B1 Hemp shive and wood fiber composite material**

*Fig.3.* **C1 Hemp shive and cellulose composite material**

*Fig.4.* **D1 Hemp shive and wood fiber composite material**

Interrelation proportions of the produced insulation board ingredient research samples are seen in Table 1.
Viewing the obtained results about the insulating composite materials, it can be concluded, that it is possible to produce heat insulation materials of a high quality from the existing raw materials. It is possible to use in their composition only ecological binders and raw materials, and make the production process maximally simple. The obtained results are viewed in pictures 5 to 8 below.

*Table 1.*

**Interrelation between the Insulation Board Ingredients**

| No. | Wood Fiber Content,% | Hemp Fiber Linters, % | Hemp Wood (Shive) %, | Cellulose (newspapers) % | Used Binder, % | Used Agent against Burning, % | Samples Used in the Further Research |
|---|---|---|---|---|---|---|---|
| 1. | | 92-94 | - | - | Na silicate solution,5 | Soda, 2-3 | **A1** |
| 2. | 30-33 | - | 50-56 | - | Na silicate solution,8 | Soda, 2-3 | **B1** |
| 3. | - | - | 50-56 | 40-43 | 4 Na silicate solution | Soda, 2-3 | **C1** |
| 4. | 30-33 | - | 50-56 | - | Starch,8 | Soda, 2-3 | **D1** |

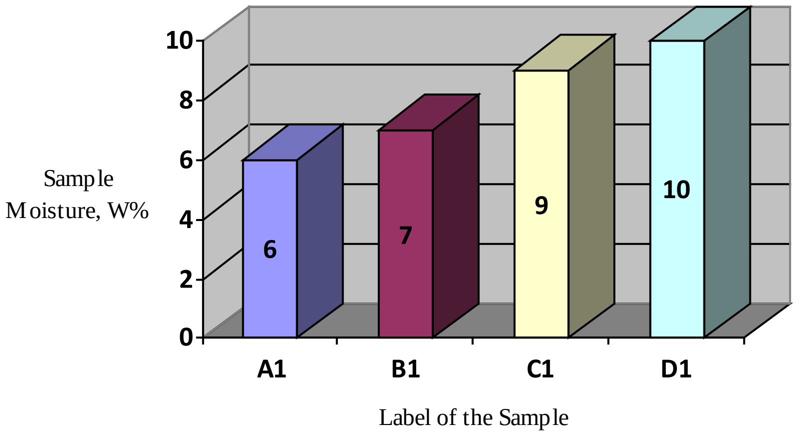


*Fig.5.* **Average moisture of the produced samples after the drying, W%**

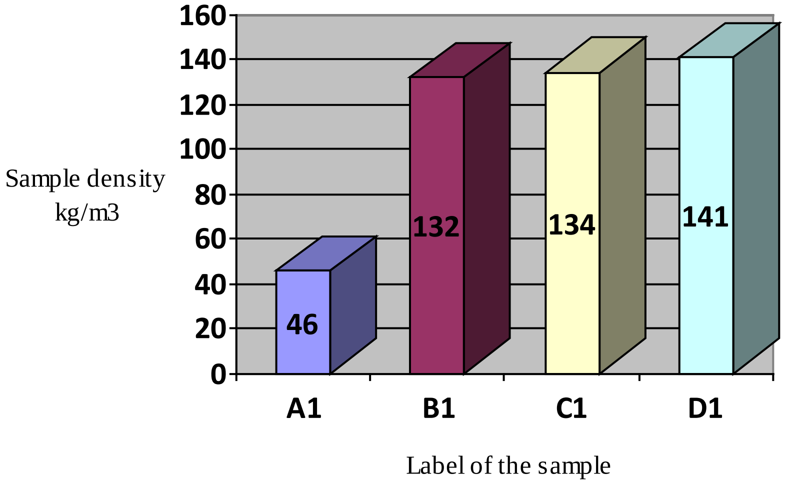


*Fig.6.* **Average density of the tested samples kg/m$^3$**

Hemp, hemp and wood thermal insulation materials in the world are still new products that are in the developing phase, so it is necessary to study the creation of new materials and improvement of the existing ones. All the necessary Latvian and European Union (EU) standards and building codes should be taken into consideration as well.

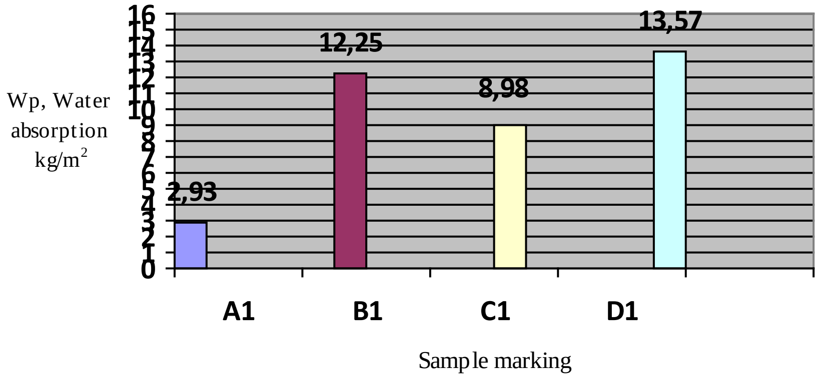


*Fig.8.* **Water absorption capacity of the material samples**

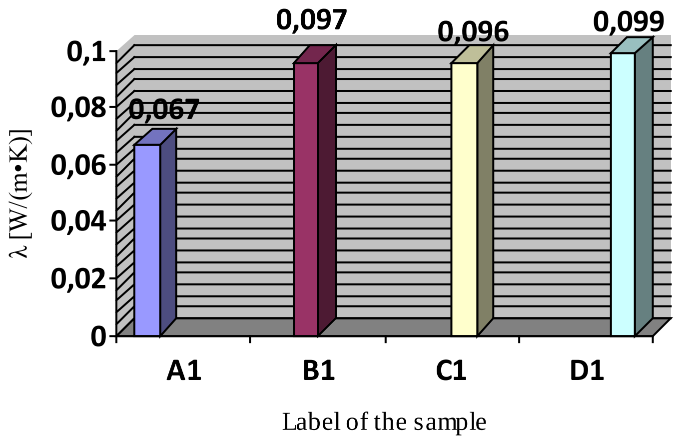


*Fig.9.* **Thermal conductivity of the heat insulation materials**

## Conclusions

1. In the laboratory were carried out first studies and produced 80 samples. The results confirm that it is possible to produce the insulation plates from the production remains
2. During the testing of properties, the following results were obtained:
   - 2.1. water content [W%]: A1- 2.8-8.1%, average 6%; B1- 9.4-11.6%, average 7%; C1 2.0-10.8%, average 9%; D1- 6.7-11.4%, average 10%.
   - 2.2. density, [kg/m$^3$]: A1- 46 kg/m$^3$; B1-132 kg/m$^3$; C1- 134 kg/m$^3$;D1- 141 kg/m$^3$.
   - 2.3. determination of the water absorption temporarily or partially keeping in water: A1- 2.93 kg/m$^2$; B1- 12.25 [kg/m$^2$]; C1- 8.98 kg/m$^2$; D1- 13.57 kg/m$^2$.

2.4. determination of the thermal conductivity coefficient λ [W/(m•K)]: A1- 0.067; B1- 0.097; C1- 0.096; D1- 0.099.

Results are in line with EU requirements and construction standards.

3. Hemp and wood blend is a new insulation material, for which it is advisable in the future:
   3.1. to determine properties of the optimal compositions,
   3.2. to solve technological issues.

## Discussion

For the analogue A1, produced worldwide, the thermal conductivity coefficient is λ= 0.045 W/ (m•K), but the data obtained in this research show that λ= 0.067 W/(m•K). That could be explained by the specificity of the used method. For the soft insulation plates the hot box method has to be used, instead of the hot plate method that was used in this research. As a result, the material was squeezed and lost its heat insulating capacity, thus increasing thermal conductivity coefficient λ.

### Reference


1. Enerģētisko augu audzēšana izmantošana, Valsts SIA „Vides produkti", 2007
2. LVS EN 1602:1996+AC:1997. Siltumizolācijas materiāli lietošanai. Šķietamā blīvuma noteikšana, 2002. Page 9
3. LVS EN 1609:1996+AC:1997, Siltumizolācijas materiāli lietošanai būvniecībā. Ūdens absorbcijas noteikšana īslaicīgi un daļēji izturot ūdenī, 2002. Page 10
4. LVS ISO 8302:1991, Siltuma izolācija. Siltuma pretestība un ar to saistīto īpašību noteikšana stacionārā režīmā. Norobežotās karstās plāksnes ierīce, 2001. Page 48

# DETERMINATION AND SEPARATION OF DIARYLHEPTANOIDS FROM ALDER GROWING IN LATVIA

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**Abstract.** *The composition of diarylhepatnoids fraction isolated from bark of two alder species (grey alder and black alder) was studied. The efficiency of three extraction methods used for isolation of diarylhepatnoids from alder bark was compared. Two diarylhepatnoids: 1,7-bis-(3,4-dihydroxyphenyl)-heptan-3-one-5-O-β-D-xylopyronoside (oregonin) and 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside were isolated from the bark of grey alder. The phenolic components of the extracts were analyzed by high-performance liquid chromatography (HPLC). Quantitative determination of oregonin was performed using an internal standard method. The results obtained show that alder barks are rich source of diarylhepatnoids.*

**Keywords:** *alnus species, bark extracts, diarylheptanoids, oregonin, 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside.*

## Introduction

Large amounts of waste and byproducts are formed during wood mechanical and chemical processing. One of these wastes is bark usually used for energy production. However, bark of many tree species contains bioactive chemicals that can give added value to this resource [1].
The genus *Alnus* (*Betulaceae*) consists of about 35 species of deciduous trees and shrubs. At present, two alder species, grey alder (*Alnus incana*) and black alder (*Alnus glutinosa*) are of the great interest in for industrial application in Latvia [2].
Extractive compounds isolated from bark of *Alnus spp.* plants include numerous diarylhepatnoids along with triterpenoids. Diarylheptanoids belong to a class of natural products based on 1,7-diphenylheptane frame and appear in both linear and cyclic forms. It has been reported that diarylheptanoids reveal a strong antioxidant activity not only in food compositions but also in human/animal organisms providing high level of their protection [3-4]. One of the most known diarylheptanoids is 1,7-bis-(3,4-dihydroxyphenyl)-heptan-3-one-5-O-β-D-xylopyronoside or oregonin, which displayed anti-inflammatory and antioxidant activities [5-6].
Traditionally, classical Soxhlet extraction is used for isolation of extractives from plant materials. New extraction methods have been introduced for reducing the amount of solvents, operation time and the cost of the procedure. Accelerated solvent extraction (ASE) and fluidized bed extraction (FBE) are among these new extraction techniques [7]. In the present study, a series of extracts were obtained from grey and black alder barks by three different extraction methods (Soxhlet, FBE and ASE) using organic solvents of different polarity (hexane, ethyl acetate and ethanol).

## Materials and methods

The species examined in this work were grey alder (*A.incana)* and black alder (*A.glutinosa).*
The barks were collected in Ogre, Latvia in July 2010. Bark was ground before extraction using a Wiley mill to pass a 420 μm sieve.
*Extraction and isolation*
Barks (5.00 g) were extracted using three extraction methods:

- Soxhlet extraction. Barks were sequentially extracted with 200 ml of hexane, ethyl acetate and ethanol for 8 hours.

- FBE procedure was performed sequentially with 50 ml of hexane, ethyl acetate and ethanol using IKA Solid-liquid extractor.
- In the ASE procedure the lipophilic extractives were first extracted with hexane (solvent temperature 90°C, three 5-min static cycles), then more hydrophilic extractives were extracted with ethyl acetate in the same conditions and finally the hydrophilic extractives were isolated with ethanol (solvent temperature 100°C, three 5-min static cycles).

Diarylheptanoids were isolated from ethyl acetate extracts and purified by SP1™ Purification System using Biotage column KP-C18-HS (12 x 150 mm, 35-70 µm) with solvent systems: solvent A = ethanol/ water/ acetic acid (200: 790: 10, v/v) and solvent B = ethanol. The gradient was from 0 to 25% solvent B; injection volume 1ml.

*HPLC analysis of diarylheptanoids*

HPLC analysis was performed with an HPLC Agilent Technologies 1100 Series coupled with a UV diode-array detector. The separation of the analytes was done with a column Zorbax Eclipse XDB - C18, 4,6 x 150 mm. Elution was carried out with a flow rate of 1ml/min using the following solvent systems: solvent A = water/methanol/acetic acid (890:100:10v/v) and solvent B = methanol. The elution conditions were: 0 – 20 min 25% B; 20 – 25 min from 25% B to 100% B; 25-28 min 100% B; 28 - 30 min from 100% B to 25% B. The operating conditions were: column temperature 30°C; injection volume 20µl. The oregonin calibration curve was made by diluting oregonin solutions with methanol to give concentration of the standard in the range 10-100 mg/l. The curves were plotted from chromatograms as a peak area *vs*. concentration of the standard.

*The reduction of ethyl acetate extracts by sodium tetrahydridoborate*

One gram of *A.incana* ethyl acetate extract was dissolved in 20 ml of methanol, and then 0.5g of $NaBH_4$ was added and the mixture was stirred for 1 hour at room temperature. The reaction solution was poured into 50 ml of distilled water and diluted to 200 ml. Then the reaction solution was passed through a C18 column, washed with water and eluted with EtOH. The ethanol eluate was freeze-dried and analyzed with HPLC/MS using a reversed phase column and 25% MeOH as solvent. The methanol eluate was purified by SP1™ Purification System using Biotage column KP-C18-HS (12 x 150 mm, 35-70 µm) with solvent systems: solvent A = ethanol/ water/ acetic acid (200: 790: 10, v/v) and solvent B = ethanol. The gradient was from 0 to 15% solvent B, injection volume 1ml.

## Results and discussion

The gravimetric amount of the extractives was determined for all alder bark extracts (Table 1). It is difficult to compare these results with earlier published data, since over the years a number of different solvents, including dichloromethane, chloroform, diethyl ether and acetone have been used. Each solvent dissolves slightly different amounts of material, and also different compounds, from the bark.

*Comparison of efficiency of the extraction methods used*

As shown in the Table 1, Soxhlet extraction, FBE and ASE have similar extraction efficiency for isolation of lipophilic extractives. It was found that the highest efficiency of diarylheptanoids extraction was obtained by Soxhlet procedure. At the same time, for such components of the ethanol extract as tannins or polyglycosides, ASE was more effective than other two extraction methods. These results are in good agreement with the data reported in the literature about extraction efficiency of different methods for analysis of terpenoids and sterols in tobacco [7].

*Table 1.*

**Amounts of extractives isolated from A.incana and A. glutinosa barks, in w% on o.d. bark**

| Extraction method | Hexane extract | | Ethyl acetate extract | | Ethanol extract | |
|---|---|---|---|---|---|---|
| | *A.incana* | *A.glutinosa* | *A.incana* | *A.glutinosa* | *A.incana* | *A.glutinosa* |
| Soxhlet | 4.5 | 2.5 | 18.1 | 13.9 | 11.9 | 11.8 |
| FBE | 4.3 | 2.4 | 14.8 | 12.8 | 12.8 | 12.0 |
| ASE | 4.4 | 2.4 | 15.8 | 12.3 | 14.7 | 15.0 |

*Identification and quantification of diarylheptanoids*

Compounds **1-2** were isolated from the ethyl acetate extracts. It was found using HPLC-UV/MS analysis that the grey alder bark ethyl acetate extract contained a dominant compound with a molecular mass of 478 Da. This compound was isolated from grey alder bark ethyl acetate extract using Biotage SP1™ Purification System and identified from UV, FTIR, mass spectra and $^{1}H$,$^{13}C$-NMR as 1,7-bis-(3,4-dihydroxyphenyl)-heptane-3-on-5-O-β-D-xylopyranoside or oregonin (**1**). The identification was based upon comparison of the results obtained with published data [8].

Reduction of oregonin with sodium tetrahydridoborate gave a mixture of 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside (**2**) epimer alcohols.

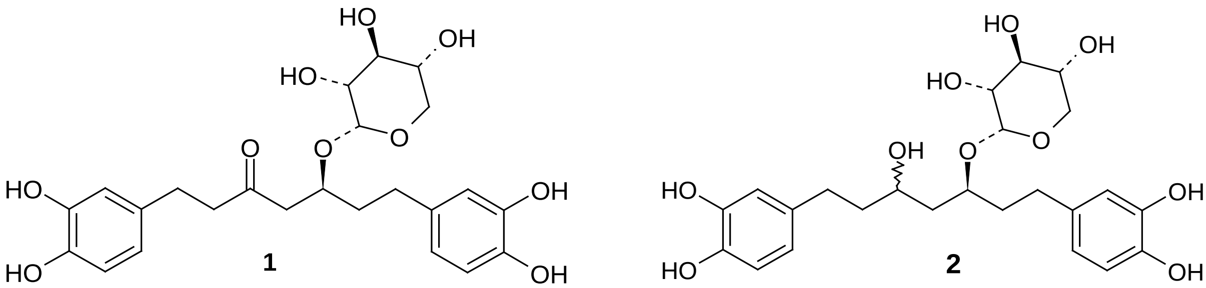


*Fig.1.* **Chemical structure of oregonin (1) and 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside (2)**

The content of oregonin in the ethyl acetate extract was determined from the calibration curve using the oregonin sample separated by Biotage SP1™ Purification System as a standard. The content of oregonin in ethyl acetate extract of grey alder bark was 80% or 20% on dry bark. The isolated oregonin could be utilized for example as antioxidant for health care.

Comparing the chromatogram retention times, UV, FTIR spectra, and molecular weight of reduced oregonin and an unknown compound isolated also from the ethyl acetate extract it was found that the grey alder bark contained small amounts of 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside. Figure 2 showed (+)-ESI-MS spectrum and fragmentation of 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside.

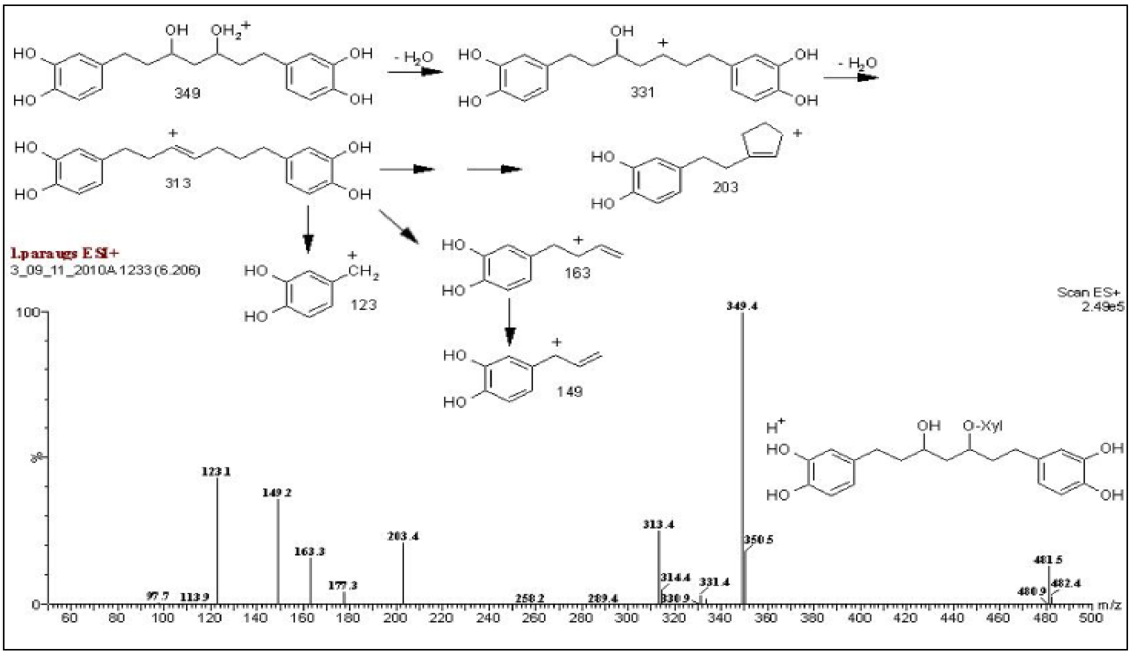


*Fig.2.* **(+)ESI/MS mass spectrum and fragmentation of 1,7-bis-(3,4-dihydroxyphenyl)-3-hydroxyheptane-5-O-β-D-xylopyranoside isolated from grey alder bark**

## Conclusions

The comparison of extraction results indicates that for components with high molecular mass ASE is more effective than other two extraction methods used, whereas the highest efficiency of diarylhepatnoids extraction was achieved Soxhlet extraction. Oregonin was isolated from grey alder ethyl acetate bark extract with 80% yield. It means that oregonin content in grey alder bark is of 20%. The received results show that the grey alder bark is a prospective resource for production of valued diarylheptanoid - oregonin.


## Acknowledgement

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### References


1. Pietarinen S., Willför S., Ahotupa M., Hemming J. and Holmbom B. Knotwood and bark extracts: strong antioxidants from waste materials. J. Wood Sci., 52, 2006, pp. 436-444.
2. Pavlovics G., Antons A., Alksne A., Lavnikovica I., Cirule D., Dolacis J., Daugavietis M., Daugaviete M.Comparison of the anatomical structure elements and physical properties of the wood of different alder species growing in Latvia. Annals of Warsaw University of Life Sciences - SGGW, Forestry and Wood Technology, 69, 2009, pp. 173-177.
3. Kuroyanagi M., Shimomae M., Nagashima Y., Muto N., Okuda T. New diarylhepatnoids from Alnus japonica nad Their Antioxidative Activity. Chem. Pharm. Bull. 53, 2005, pp. 1519-1523.
4. Kim H.J., Kim K.H., Yeom S.H., Kim M.K., Shim J.G., Lim H. W., Lee M.W. New diarylheptanoid from the barks of Alnus japonica Steudel. Chin. Chem. Lett., 16, 2005, pp. 1337-1340.
5. Guz N.R., Lorenz P. and Métraux J.-P. Oregonin from the bark of European Alnus species. Biochem. Syst. Ecol. 30, 2002, pp. 471–474.
6. Kuo C.H., Lee C.W., Lai Y.C. and Lee S.S. Determination of oregonin in Alnus plants and biological samples by capillary electrophoresis. J. Pharm. Biomed. Anal. 47, 2008, pp. 195-200.
7. Shen J., Shao X. A comparison of accelerated solvent extraction, Soxhlet extraction, and ultrasonic-assisted extraction for analysis of terpenoids and sterols in tobacco. Anal Bioanal Chem, 383, 2005, pp. 1003–1008.
8. Suga T., Ohta S.,Hirata T., Aoki T. The absolute confuguration of diarylheptanoid xyloside, oregonin, isolated from the female flowers of Alnus serrulatoides. Chem. Lett., 1982, pp. 895-898.

# EUROPE 2020 – THE NEW STRATEGY FOR SMART, SUSINABLE AND INCLUSIVE GROWTH AND BULGARIAN INDUSTRIAL COMPETITIVENESS

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**Abstract.** *This paper present one decision on innovation European industry contributes to output, jobs, innovation and exports and is interrelated with service industries. Indeed, many service industries such as transport, health and Information and Communication Technologies (ICT) depend on competitive industry to produce the equipment and hardware which they use [1, 2].*

**Key words:** *Europe, innovation, policy.*

## Introduction

The performance of European industry in terms of exports is largely due to its competitiveness, which is influenced by the business environment, which is in turn created by the regulatory framework both at national and European level:

- the creation of a single market
- a very effective competition policy
- an industrial policy which enables industry to undergo the necessary adjustment processes.

Providing new solutions to customers and remaining at the leading edge of innovation require the protection of related intellectual property, which serves as an incentive to invest in product and process innovation.

EU industry has been seriously affected by the recent economic crisis, revealing a number of structural weaknesses. Industries, together with public authorities, have to undertake the necessary structural adjustments in a politically and socially acceptable way.

Some other longer-term challenges are kept on the policy agenda [1]:

- globalization
- demographic change
- climate and energy.

Policy highlights overview: Europe 2020; European standards; Industrial competitiveness; Innovation; International affairs; Raw materials; Satellite navigation; Security research and development; Single market for goods; Single market for services; Small and medium-sized enterprises (SMEs); Space; Sustainable and responsible business.

## Exhibition

### *Europe 2020 – the new strategy for smart, sustainable and inclusive growth*

At the European Council meeting on 26 March 2010, European Union leaders set out their plan for "Europe 2020", a strategy to enhance the competitiveness of the EU and to create more growth and jobs.

The strategy is implemented in close partnership between the Commission and the Member States. Regional, local and non-governmental actors are encouraged to contribute. Member States set out their reform agendas in their National Reform Programmes and report on progress annually. The Commission develops supplementary actions at EU level and maintains a dialogue with the Member States.

DG Enterprise and Industry contributes to the implementation of the Europe 2020 strategy in particular via the flagship actions on An Industrial Policy for the Globalisation Era, and An Innovation Union, but also contributes to the other flagship actions where relevant. DG Enterprise and Industry monitors and assesses competitiveness policies in the Member States, including areas such as industrial policy, business environment, innovation policy, SME and entrepreneurship policy, better regulation and the internal market for goods. A report on Member States' competitiveness policies and performance will be published annually starting in autumn 2010. More information about the Europe 2020 strategy can be found on the European Commission's central Europe 2020 website.

***Europe 2020 flagship: An Industrial Policy for the Globalization Era***

Industry must be placed centre stage if Europe is to remain a global economic leader. This is the core message of the Communication on "An integrated industrial policy for the globalization era" adopted by the European Commission on the 28th of October 2010 on the initiative of Vice-President Antonio Tajani. The Communication, a flagship initiative of the Europe 2020 strategy, sets out a strategy that aims to boost growth and jobs by maintaining and supporting a strong, diversified and competitive industrial base in Europe offering well-paid jobs while becoming less carbon intensive. It is accompanied by a report on the competiveness performance of individual Member States and the annual European Competitiveness Report.

European Commission Vice-President Antonio Tajani, responsible for industry and entrepreneurship said: "Industry is at the heart of Europe and indispensable for finding solutions to the challenges of our society, today and in the future. Europe needs industry and industry needs Europe. We must tap into the full potential of the Single Market, its 500 million consumers and its 20 million entrepreneurs."

In this era of intensifying globalization, the concept of national sectors and industries is obsolete. Coordinated European policy responses are needed. Europe also needs an approach that looks at the whole value chain, from infrastructure and raw materials to after-sales service. Promoting the creation and growth of small and medium-sized enterprises has to be at the core of EU industrial policy. Moreover, the transition to a sustainable economy has to be seized as an opportunity to strengthen competitiveness. Only a European Industrial Policy targeting competitiveness and sustainability can muster the critical mass of change and coordination needed for success. Antonio Tajani added: "There will be no sustainability without competitiveness, and there will be no long-lasting competitiveness without sustainability. And there will be none of them without a quantum leap in innovation!"

**Ten key actions for European industrial competitiveness [2]:**

- An explicit and thorough **"competitiveness proofing" of new legislation** will be undertaken. The impact on competitiveness of all policy proposals will be properly analyzed and taken into account.
- **"Fitness checks" of existing legislation** will identify the potential for reducing the cumulative effects of legislation so as to cut the costs for businesses in Europe.
- The **creation and growth of SMEs** will be supported by making it easier for them to access credit and help their internationalization.
- A strategy to **strengthen European standardization** will be presented to meet the needs of industry.

- European **transport, energy and communication infrastructure and services** will be upgraded to serve industry more efficiently, taking better into account today's changing competitive environment.
- A **new strategy on raw materials** will be presented to create the right framework conditions for sustainable supply and management of domestic primary raw materials.
- Sector-specific **innovation performance** will be addressed through actions in sectors such as advanced manufacturing technologies, construction, bio-fuels and road and rail transport, particularly in view of improving resource efficiency.
- The challenges of **energy-intensive industries** will be addressed through actions to improve framework conditions and support innovation.
- A **space policy** will be pursued, developed in collaboration with the European Space Agency and Member States. The Commission will develop a space industrial policy to create a solid industrial base covering the whole supply chain.
- The Commission will **report on Europe's and Member State's competitiveness**, industrial policies and performances on an annual basis .

Living up to the ambitions of a strong, diversified and competitive industrial base in Europe requires mutually reinforcing policies. This concerns notably the various flagship initiatives developed under the Europe 2020 strategy and strategies such as the one on the EU' s Single Market, adopted on 27 October [3].

**1. Competition policy**

Antitrust rules prohibiting agreements that restrict competition and abuses of dominant positions as well as merger rules are at the heart of EU Competition policy. Control of state aids to enterprises constitutes the third pillar of this policy which is very specific for the EU. Competition policy is crucial for the achievement of the objectives of the Lisbon strategy for growth and jobs, because it creates the conditions for an efficient internal market and is necessary to stimulate knowledge and innovation. The enforcement of EU competition policy is the responsibility of DG Competition. DG Enterprise and Industry is closely associated to such enforcement and it also ensures coherence between the objective to strengthen the competitiveness of EU industry and the competition policy objectives. In addition DG Enterprise and Industry contributes to draft legislative proposals related to antitrust, mergers and State aids and moreover to individual cases with its knowledge of the regulatory and competitiveness situation of specific sectors of industry.

**2. Competitiveness analysis**

The Lisbon Strategy for Growth and Jobs focuses the efforts of the EU on effective response to challenges of demographic change and globalization. Raising the long-term economic potential by increasing productivity growth is one of its fundamental objectives. With the relaunched Lisbon Strategy, the annual Competitiveness Report is designed to contribute to the analytical underpinning of its microeconomic pillar. It presents recent developments of overall competitiveness performance and focuses on issues of economic reform bearing on various drivers of productivity growth and on competitiveness changes in particular industries.

 

The EU industrial structure is a series of studies which focus on the competitiveness of the EU economy from a sectoral perspective (see last EU industrial structure issue). It provides insights into the performance of each industry and helps to explain the competitiveness of the

EU economy as a whole. These studies apply the same set of indicators to all sectors. This allows the comparison of performance across sectors. Industrial Policy and Economic Reforms Papers are written by the staff of DG Enterprise and Industry or experts working in association with them. This publication series aims to raise awareness and stimulate the debate in the areas of industrial policy, business environment and economic reforms [1].

**3. Economic crisis**

The bursting of the American subprime mortgage bubble and the bankruptcy of a major American investment bank in September 2008 triggered a dramatic collapse of the global financial system. A meltdown of financial markets could only be avoided through massive interventions by central banks and governments. On financial markets, decisive action coordinated at the European level also showed that a well coordinated response ensures that the outcome can be significantly more than the sum of its parts. Business confidence around the world has plummeted, and so has consumer confidence. Orders have been cancelled on a large scale, export markets around the world have shifted into reverse gear and investment and consumption growth has slowed significantly or even turned negative. In the face of the economic crisis, many businesses have preferred to wait until the dust has settled and the financial market crisis has been resolved, before risking taking on new business opportunities.

**4. Intellectual property rights**

Intellectual property rights (IPR) are important contributors to European competitiveness. These rights, including patents, trademarks, design rights and copyrights, can serve as incentives for research and development, for innovation, and can help users identify trusted producers. We develop policies to help make European businesses aware of these rights and to assess the impact and effectiveness of the use of these rights. We co-ordinate with national administrations and trading partners on these subjects. To this end, DG Enterprise and Industry has launched projects that include support to national intellectual property offices improving their business support services about IPR (IPeuropAware), and a pilot project to help small and medium-sized businesses facing IPR problems in, or arising from, China (China IPR SME Helpdesk).

**5. European standards**

Standardisation is the voluntary process of developing technical specifications based on consensus among all interested parties (industry including Small and Medium-sized Enterprises (SMEs), consumers, trade unions, environmental Non Governmental Organisations (NGO), public authorities, etc). It is carried out by independent standards bodies, acting at national, European and international level. While the use of standards remains voluntary, the European Union has, since the mid-1980s, made an increasing use of standards in support of its policies and legislation. Standardisation has contributed significantly to the completion of the Internal Market in the context of 'New Approach' legislation, which refers to European standards developed by the European standards organisations.Furthermore, European standardisation supports European policies in the areas of competitiveness, Information and Communication Technologies (ICT), innovation, interoperability, environment, transport, energy, consumer protection, etc. Standardisation is an excellent tool to facilitate international trade, competition and the acceptance of innovations by markets. A key challenge for European standardisation is to strengthen its contribution to the competitiveness of Small and Medium-sized Enterprises (SMEs). Standardisation supports market-based competition, so as to achieve objectives such as the interoperability of complementary products and services, or to provide agreed test methods and requirements for health, safety, organisational and environmental performance. Through the development of European standards and the withdrawal of conflicting national standards, standardisation has played a leading role in the achievement of a Single Market for goods. Standardisation also has a public interest dimension, in particular with regard to the issues of health, safety, security and of the environment. For this reason, the European Union has an active standardisation policy, which promotes standardisation in support of better regulation, and as an instrument for the competitiveness of European industry. This policy is centred upon the recognised European standardisation system, and a partnership to implement the 'New Approach'.

## 6. Innovation

In a remarkably short time, economic globalisation has changed the world's economic order, bringing with it new challenges and opportunities [2] . Europe cannot compete in this new environment unless it becomes more innovative and responds more effectively to consumers' needs and preferences. The European Union possesses extraordinary potential for innovation. Europe has a longstanding tradition of producing breakthrough inventions; it has a wealth of creative people and can build on its cultural diversity. It has laid the foundations for one of the largest single markets in the world, where innovative products and services may be commercialised on a large scale. Historically it has a strong and responsible public sector, which should be capitalised on. The European Commission is formulating, influencing and, where appropriate, implementing policies and programmes to increase Europe's innovativeness. The Commission is trying to make sure innovation is thoroughly understood and approached comprehensively, thereby contributing to greater competitiveness, sustainability and job creation.

**6.1. Innovation - Facts, figures and analysis -** to make sure implemented innovation policies yield tangible results, the European Commission makes use of a number of tools enabling it to collect data on innovation performance in Europe.


These facts, figures and analyses provide insight into the strengths and weaknesses of national innovation systems in EU member states and other countries. They also help in understanding specific drivers and barriers to innovation at sector level. The data includes assessments of innovation performance, policy responses, innovation policy governance and innovation policy trends across Europe.

**6.2. Innovation Policy [1,2] -** about helping companies to perform better and contributing to wider social objectives such as growth, jobs and sustainability. There are many policy tools available to achieve this, ranging from establishing supportive framework conditions (e.g. human resources, an internal market, intellectual property) to facilitating access to finance, policy benchmarking and enabling collaboration or stimulating demand, for instance, through regulation, standards and public procurement. The rationale for European innovation policy is strongest where it is oriented toward addressing the most significant challenges facing society today. The main current Community innovation policy is the "Broad-based innovation strategy for the EU". It points the way to accompanying industry-led and society-driven innovation with competitiveness and public policies at all levels as a key element of the renewed Lisbon strategy for growth and jobs.

The strategy singles out ten priority actions in a roadmap for action at national and European levels. The Commission plans in particular to encourage the emergence of "lead markets", where public authorities facilitate industry-led innovation by creating the conditions for a successful market uptake of innovative products and services in a focused way in areas such as e-health, internal security, eco-innovation and eco-construction.

**6.3. Future EU Innovation Policy** The December 2008 European Council called for a European Plan for Innovation. As a first step the Commission presented possible short term actions in response to the economic crisis and an assessment of achievements made under the Broad Based Innovation Strategy, accompanied by reviews of the Lead markets Initiative, innovation in services, financing innovation in SMEs and the effectiveness of innovation support measures. This provided the basis for consultations (see below) and debate on the directions and possible measures to be included in a European plan for innovation that could be presented in autumn 2010. The reflections on future innovation policy are an integral part of the Europe 2020 strategy.

Public consultation on Community innovation policy seeks to follow up the findings of the Commission Communication "Reviewing Community innovation policy in a changing world" and two previous consultations, one on the effectiveness of innovation support in Europe and one on design as a driver ofuser-centred innovation. It will serve as an input to the preparation of a new European innovation plan, as called for by the European Council. Business Panel on future European innovation policy and its blog consultation has been established by DG Enterprise and Industry to provide inputs from a business perspective on priorities for future EU innovation policy. From 7 July to 31 August 2009, the panel was holding an open online consultation on its ideas and proposals through the Innovation Unlimited blog.

**6.4. Innovation - Knowledge and Technology Transfer**

Generating new knowledge and turning it into new products and services is important to maintaining and enhancing Europe's competitiveness. It is fundamental that researchers and industry work closely together and maximise the social and economic benefits of new ideas. Transforming research results into new commercial products is a complex process, involving a broad range of stakeholders. It is not enough to simply increase public investment in research; it is important to create a framework to facilitate the process of knowledge transfer by removing the barriers which hinder collaboration between research and industry in order for Europe to operate as a single market for knowledge. In its broad-based innovation strategy, the Commission has identified the importance of improving the transfer of knowledge between public research institutions and third parties, including industry and civil society organisations, as one of ten key areas for action [3].

**6.5. Innovation - ICT and other key technology enablers**

In today's economy, it is clearer than ever that information and communication technology (ICT) is the most important driver of innovation and competitiveness. In addition to ICT, other key enabling technologies are more and more revolutionising the products and services on offer as well as the way business is conducted in Europe and this revolution will continue in the future. The Enterprise and Industry Directorate-General pursues a range of policies to enhance the use of ICT and the deployment of other key technology-enablers that advance the economy, create innovation and deliver sound competitiveness benefits. Learn more about our activities in this area by visiting the pages of this website related to ICT for Competitiveness & Innovation.

## Summary

Innovation and Innovation Union - The European Commission's "Innovation Union" has been presented. It sets out a strategic approach to innovation. This Europe 2020 flagship will boost Europe's research and innovation performance by speeding up the process from ideas to markets. The Commission proposes a series of actions to put innovation at the heart of EU economy and society for the benefit of companies and citizens. The new "Innovation partnerships" will generate breakthroughs in areas of concern for the citizens such as climate change, energy efficiency and healthy living. The success will depend on the commitment of all actors involved in innovation cycle.


## References


1. Petrova D., Management on firm – theory and practices, monograph, Education „EKC – PRES" – Gabrovo, Bulgaria, 2010, ISBN 978-954-490-112-7
2. Petrova D., Higher productivity of labor and competitive power on firm used motivation of staff through involvement in concept oriented change processes, 38th IGIP Symposium – $Q^2$ of $E^2$, Quality and Quantity of Engineering Education, September 6-9, 2009, Graz, Austria, Fachhochschule der Wirtschaft CAMPUS 02 – Graz, ISBN: 978-3-85295-035-8, pp. 291-299
3. www.europe.com

# COMPARATIVE ANALYSIS OF HEMP FIBER GROWN IN YEAR $2010^{TH}$

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**Abstract.** *Annually increasingly all over the world is observed growing tendency to reduce the production of various products containing non-renewable component and replace them with natural fiber raw materials for textile and non-textile products as well. One of such raw materials is hemp. This paper discusses comparative study results of testing local genotype „Purini" and commercial available ES registered industrial hemp variety „Bialobrzeskie" (Poland) fibers which were grown in Latvia, year $2010^{th}$. Studies have been carried out for small fiber bundles to determine the durability properties of hemp fiber.*

**Keywords:** *hemp fibres, distribution, durability cycles, hemp variety, hemp line.*

## Introduction

Hemp is classified as environmentally friendly natural fiber in processes of cultivation, processing, hemp products exploitation and liquidation. Hemp production easily biodegradable and disposable requires relatively little fertilizer in comparison with other fiber crops, and, having few natural predators, it needs little or no treatment with pesticides [1].

Throughout the life cycle of hemp cultivation, processing and consumption of technical products and the elimination in the end of life-cycle, energy consumption is lower than the others, particularly on petroleum-based fibers designed products. Hemp benefits the environment and the rural economy while providing a sustainable alternative source of fiber for paper, textiles, nonwovens and other purposes. With few insect enemies and little competition from weeds, hemp is good candidate to produce a high-quality, sustainable grown fiber for using in manufacturing of nonwoven products as well as other materials. Hemp also is vital to maintaining air by removing carbon dioxide and returning oxygen [1;2].

In Latvia fiber hemp areas for industrial uses have been started only since year 2008 in following volumes: 5 ha in year 2008, 140 ha in year 2009 and 72 ha in year 2010 [3].

In order to move forward successfully is need to solve a range of issues related to hemp growing agro-technical problems, pretreatment, processing, use of field selection/ expansion, advanced, cost-effective technologies at all stages of development, as well as appropriate methodologies for properties testing of raw materials for intermediates and final product specifications development.

In many applications of products obtained from hemp fiber which are subjected to cyclical deformations in processing and use of processes, which over time leads to the exercise of a function of withdrawal - which shortens the product life cycle, usage efficiency.

Riga Technical University current studies of hemp fiber physical and mechanical properties testing methodology approbation and development [4;5;6;7;8] directed towards full spectrum of properties exploration, the effective selection of test parameters in order to make the testing process less time consuming, but at the same time provide adequate exploitation properties prediction.

## Materials and methods

***Object of investigation.*** Hemp fibers used in this study were obtained from hemp stems harvested from a trial plot at Agriculture Science Centre of Latgale - local dioeciously variety "Purini" and ES registered monoecious industrial hemp variety „Bialobrzeskie" in Vilani district, Latvia. In order to extract fibres from retted „Bialobrzeskie" hemp stems slightly modified flax scutching line was used. Hemp fibers in growing process were cultivated with active nitrogen fertilizer doses by looking at 2 options: 1) with no additional fertilizer (N0), 2) with active nitrogen 100 kg/ha (N100).

***Methods.*** Durability tests for small fiber bundles of genotypes „Purini“ and „Bialobrzeskie” were carried out on pulsator UB-5 [7, figure 1] till samples full degradation with frequency 250 $min^{-1}$. Small fiber bundles for experiments were obtained by mechanical separation. Under microscope were selected 0,04 mm thin fiber bundles and pasted into the millimeter paper with the fibres clamping length 20 mm [7, figure 1]. Total amount of made and tested samples: a) variety "Purini" – 100 samples with no additional fertilizer (PN0), b) variety "Purini" – 100 samples with active nitrogen 100 kg/ha (PN100) and c) variety „Bialobrzeskie” - 100 samples with no additional fertilizer (BN0). All samples were tested under the same circumstances – with amplitude 0,25 mm and load 0,7 grams.

For the treatment of the results used descriptive methods of mathematical statistics – statistical basic values (Average, Mode, Median, Standard Deviation, Maximum, Range, Standard Error, Confidence Level, Relative error, Kurtosis, Skewness), distriburion analysis.

## Results and discussion

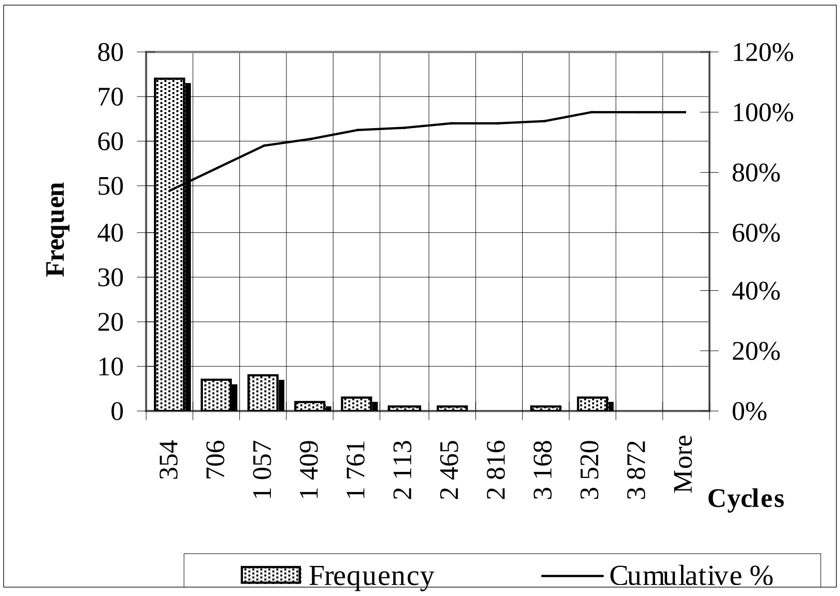


*Fig.1.* **Histogram of cycles till breaking (sample PN0)**

As seen from graph (Fig.1) almost 80 % of samples durability does not exceed 354 cycles. Histograms of other two experimental ranges (PN100 and BN0) show similar assimetry.

For methodology development descriptive statistics parameters are calculated including all measurements (table 1). As examination of histograms shows that only a few measurements exceed 2000 cycles, the same statistic parameters are calculated under durability mesurements if experiment become interupted after 2000 cycles (Table 2).

From graphs of Fig. 1 are seen that average values for variants PN0 and BN0 become lower as influence of few large values removed. But confidence level of these two variants become lower too. Measurements of variant PN100 do not include extrem high cycle values and as a result average and confidence level is the same in both cases (Fig.1).

*Table 1.*

**Main statistic parameters of samples under examination till *full degradation***

| | **P N100** | **P N0** | **B N0** |
|---|---|---|---|
| Average | 123,83 | 396,38 | 271,78 |
| Mode | 2 | 2 | 20 |
| Median | 20 | 70 | 30 |
| Standard Deviation | 305 | 738 | 756 |
| Maximum | 1 990 | 3 520 | 5 320 |
| Minimum | 2 | 2 | 1 |
| Range | 1 988 | 3 518 | 5 319 |
| Standard Error | 30,48 | 73,78 | 75,63 |
| Confidence Level (95,0%) | 59,75 | 144,61 | 148,24 |
| Relative error | 48% | 36% | 55% |
| Kurtosis | 20,00 | 7,57 | 29,19 |
| Skewness | 4,21 | 2,72 | 5,12 |

*Table 2.*

**Main statistic parameters of samples under examination till *2000 cycles***

**< 2000 cycles**

| | **P N100** | **P N0** | **B N0** |
|---|---|---|---|
| Average | 123,83 | 344,88 | 211,18 |
| Mode | 2 | 2 | 20 |
| Median | 20 | 70 | 30 |
| Standard Deviation | 305 | 557 | 427 |
| Maximum | 1 990 | 2 000 | 2 000 |
| Minimum | 2 | 2 | 1 |
| Range | 1 988 | 1 998 | 1 999 |
| Standard Error | 30,48 | 55,67 | 42,73 |
| Confidence Level(95,0%) | 59,75 | 109,11 | 83,75 |
| Relative error | 48% | 32% | 40% |
| Kurtosis | 20,00 | 2,58 | 8,89 |
| Skewness | 4,21 | 1,89 | 2,99 |

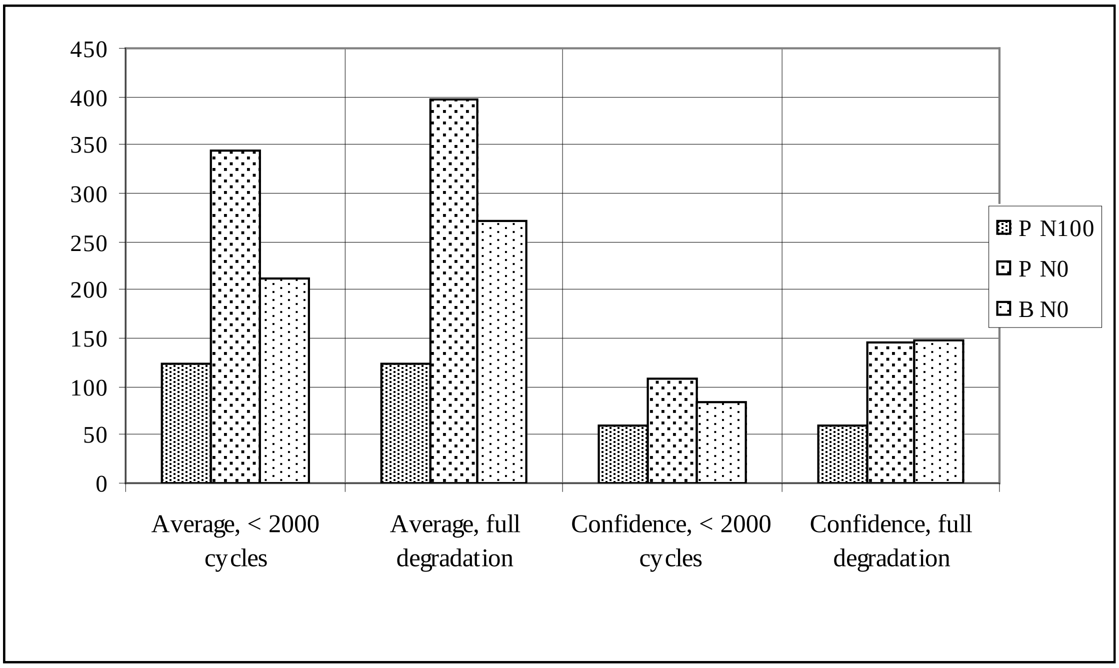


*Fig. 2.* **Average values of durability cycles and corresponding confidence intervals**

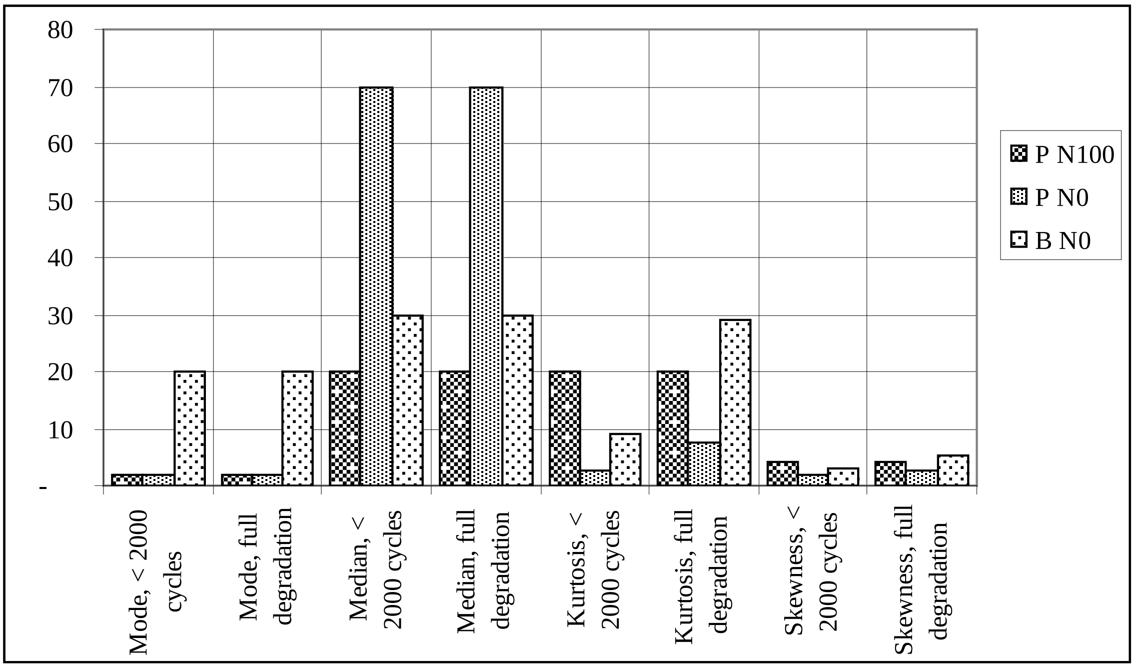


*Fig. 3.* **Comparative parameters of distribution of durability cycles**

Some of hemp durability distribution parameters such as mode and median do not change their values in cut experiment, but values of parameters which characterize deviation from normal distribution form for variants PN0 and BN0 decrease.

If samples tested till 2000 durability cycles, some samples extreme values are excluded, because they leave little impression on the product performance for the fact that the product performance more directly determines less resistant fiber resistance to repetitive deformations. As a result, durability distribution is closer to normal distribution, which is more predictable (Fig.3, Table 2).

*Table 3.*

**Main statistic parameters of samples under examination till *1000 cycles***

| < 1000 cycles | P N100 | P N0 | B N0 |
|---|---|---|---|
| Average | 105,93 | 266,18 | 169,98 |
| Mode | 2 | 2 | 20 |
| Median | 20 | 70 | 30 |
| Standard Deviation | 217 | 365 | 284 |
| Maximum | 1 000 | 1 000 | 1 000 |
| Minimum | 2 | 2 | 1 |
| Range | 998 | 998 | 999 |
| Standard Error | 22 | 36 | 28 |
| Confidence Level (95,0%) | 42,52 | 71,46 | 55,63 |
| Relative error | 40% | 27% | 33% |
| Kurtosis | 8,56 | - 0,13 | 3,29 |
| Skewness | 2,94 | 1,23 | 2,08 |
| ***Cover full degradation of fibers bundle*** | ***97%*** | ***87%*** | ***93%*** |

In the third table shown statistical characteristics, obtained by testing samples only up to 1000 tensile cycles, testifies that the distribution center parameter - arithmetic average slight decrease because maximal values shifts it as statistical parameter. The median remain on the same level, suggesting that the effect of little resistant fiber parts are perceived, are covered at least 85% of the fiber bundles durability.

From all graphs and tables are seen that from durability point of view, the best characteristics present fiber bundles of the variant PN0. Low characteristics of PN100 could be related to the fact that high doses of nitrogen weakens the cellulose cell walls, thereby reducing fibers ability to withstand repeated tensile deformations of this variety.

## Summary

Hemp fiber samples verifications by durability tests useful to suspend by reaching a certain number of cycles. Probable 1000 cycles in quite aggressive regime, can be enough to effectively compare options/ lines/ varieties of the durability point of view, thereby reducing the test work time-consuming.

The obtained results show that PN0 of the durability point of view is more desirable and is perspective for a local variety of hemp fiber development. However further studies on the effects of nitrogen doses on this line of hemp fiber durability and other mechanical properties required, whereas the cultivation of free nitrogen creates a range of agronomic and economic problems.

**References**

1. Robinson, R. The great book of hemp. The complete Guide to the Environmental, Commercial, and Medicinal Uses of the World's Most Extraordinary Plant. ISBN 0-89281-541-8. 1996, p. 247.
2. Norton, A. J. Murphy, Callum, R. Hill, A. S. Newman, G. The life cycle assessments of natural fiber insulation materials. Proc. of the 11th International Conference on Non-conventional Materials and Technologies (NOCMAT 2009), Bath, UK, 2009.

3. Ministry of Agriculture of Latvia, Department of Agriculture and Rural Development. Data about flax and hemp industry in Latvia, 2010. Latvijas Industriālo kaņepju asociācija (LIKA), http://lathemp.lv/wp-content/uploads/2010/11/ZM_Lini_Kanepes_Konference.pdf. ZM dati.
4. Baltina I., Strazds G., Zamuska Z. Latvian Hemp Fiber Quality. Scientific Journal of RTU. 9. series., Materiālzinātne. - 4. vol., 2009, p. 9.-15.
5. Baltina I., Zamuska Z. Effects of Late Hemp Straw Harvesting on Fiber Quality. Scientific Journal of RTU. 9. series., Materiālzinātne. - 5. vol., 2010, p 194-198.
6. Freivalde L., Kukle S., Ulme A. Comparative Analysis of Hemp Fiber Durability. Scientific Journal of RTU. 9. series., Materiālzinātne. - 5. vol., 2010, p 134-138.
7. Freivalde L., Kukle S., Puriņa B., Stramkale V. Durability Properties of Hemp Fibres. In: Proceedings of the 5th International Textile Clothing and Design Conference Magic World of Textiles. ISSN 1847-7275, Dubrovnik, Croatia, 2010, p.83-86.
8. Stramkale V., Freivalde L., Kukle S. Analysis of the renewable fibres properties and uses in scale of Latvia// University of Ljubljana, Faculty of Natural Sciences and Engineering, Department of Textiles, ISBN 978-961-6045-80-3, Ljubljana, Slovenia, 2010, p. 300. – 325.

**Kopsavilkums**

*Katru gadu visā pasaulē arvien vairāk tiek novērota augoša tendence samazināt dažādu produktu ražošanu, kas satur neatjaunojamas izejvielas un aizstāt tās ar dabīgo šķiedru izejmateriāliem, kā tekstila, tā arī netekstila produktiem. Kaņepes ir viens no šādu izejvielu avotiem. Šajā referātā aplūkoti salīdzinošo pētījumu pārbaužu rezultāti vietējā genotipa "Pūriņi" un tirdzniecībā pieejamas, ES reģistrētās rūpnieciskās šķirnes kaņepju "Bialobrzeskie" (Polija) šķiedras, kas audzētas Latvijā, Latgales Lauksaimniecības zinātniskajā centrā 2010.gadā. Pētījumi veikti kaņepju šķiedru ilgizturības īpašību noteikšanai un analīzei, testiem pakļaujot mazus primāro šķiedru kūlīšus.*

# CONCRETE SAWING WASTE RECYCLING AS MICROFILLER IN CONCRETE PRODUCTION

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**Abstract.** *The main idea of the presented work is to find the ways of recycling the sawing waste/sludge in production of the new concrete. The aim of the study is to examine application of the dust-water suspension as micro filler in self-compacting concrete. In the process of sawing concrete elements a lot of dust waste is produced, the average amount being approximately 0.5-1% of the total amount of concrete. To avoid dust pollution in a production plant the sawing process is accompanied by a water stream, as a result, concrete dust as dust-water suspension is stored in special reservoirs. Recycling of such concrete dust suspension and its utilization as a material pose a significant challenge.*

**Keywords**: *concrete sawing waste, sludge water, compressive strength.*

## Introduction

A lot of concrete waste is produced in the process of sawing concrete elements in the plants that manufacture pre-cast reinforced concrete. Technologically the process of sawing is accompanied by a water stream to avoid dust pollution and enhance sawing efficiency. Concrete saw waste (that is called *sludge*) is stored in special reservoirs for further utilization. The average amount of produced waste is about 0.5-1% of the total amount of concrete. The information about utilization of the saw sludge is pretty scarce; with the increasing volumes of concrete production it is turning into a serious environmental issue. The information, which is generally available, is about the waste water and water sludge containing residual cement from concrete mixing plants and agitator trucks [1,2]. Usually waste water is divided into two fractions as shown in Figure 1; one is a relatively clean fraction and it is called clarified water, whereas the other one is sludge water containing cement solids and other fine concrete particles. Clarified water can be used as mixing water in new batches, thus replacing some part of the water from town water supply sources. Due to the large amount of suspended matter and high alkalinity untreated sludge water cannot be legally discharged into urban sewers (Borger et al., 1994). It is stated in standard that the amount of the solid content in sludge water should contain less than 3% of cement content by weight, when used as mixing water. The sludge water with 3% of sludge solid content ratio can be used up as mixing water if the constant amount of ready-mixed concrete is produced every day [3]. However, since the ready-mixed concrete is an order-made product, fine particles in unused sludge water settle out. The settled material is usually dehydrated, and this is called sludge cake. Most of the sludge cake is discharged to the controlled landfills, because the settled material falls under the category of dirty mud according to standard. The total disposal cost of sludge cake is very high [3]. With the growing demand for ready mixed concrete, the disposal of sludge water is becoming an increasing environmental concern [4, 5]. Each working day approximately 700–1300 l of wash water is required for a single concrete truck [6]. Since it is very difficult to treat the sludge cake as concrete material because of its high water content (70% by weight), the process of drying and crushing is introduced to make pulverized dry sludge from the sludge cake. Significant challenge is to recycle this concrete dust suspension with 95% of particles smaller than 0,063mm, and some with size <2mm and use it as a material.

It has been found that fine-filler effects and a reduction of the actual water/cement ratio due to the fine solids content of sludge water lead to a reduction in concrete capillary water absorption and porosity, and possibly improve the durability of the concrete [6].

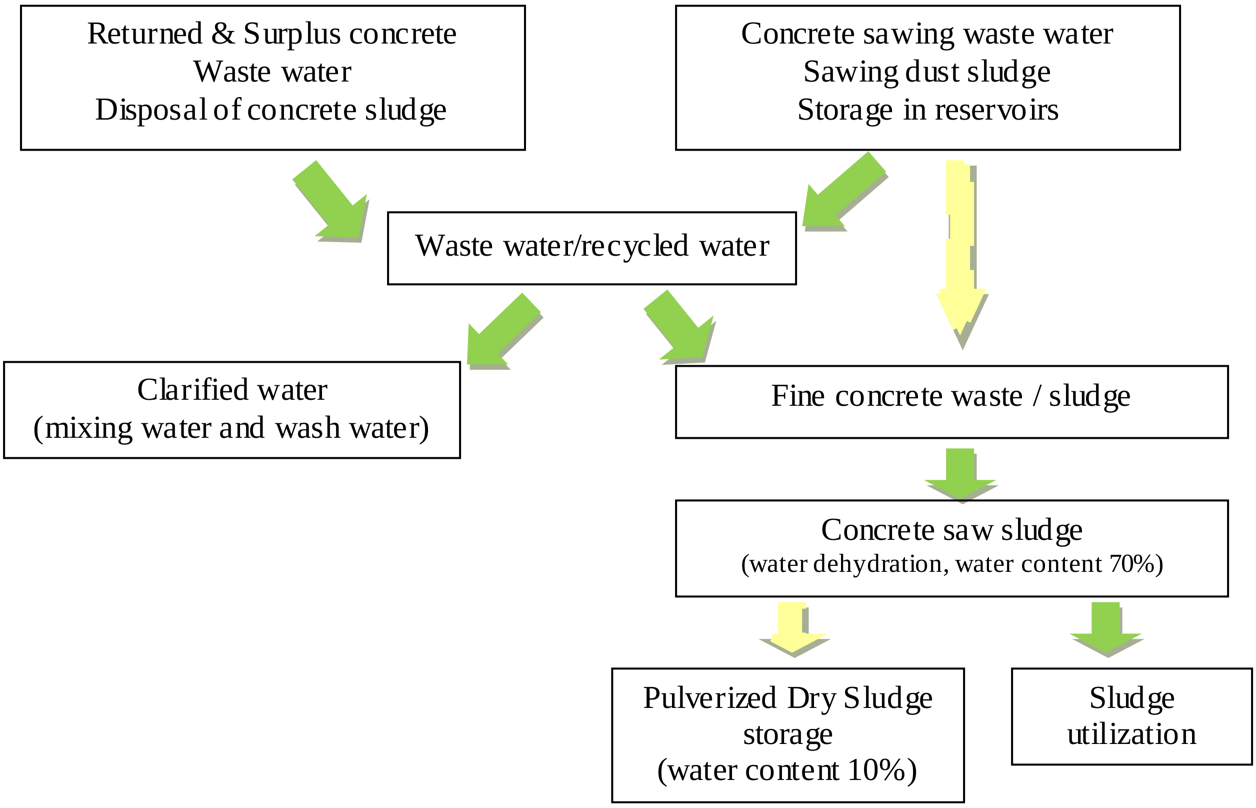


*Fig. 1.* **Effective use of concrete sludge**

Concrete mixed with the sludge water containing residual cement tends to exhibit a shorter setting time and lower flowability [7]. Nevertheless, the complete recycling of sludge water has been considered in concrete mixing plants because of the great benefit in terms of disposal cost reduction and environmental conservation [7, 8, 9].
It is necessary to investigate strategies for managing the effective use of concrete sludge. The main idea of the presented work is to find the ways of recycling concrete sawing waste sludge in production of the new concrete. The material used in mixes is sludge water suspension originally taken from the source in a concrete plant to avoid additional costs of material drying and grinding. Ways of how to utilize sludge water in mixes containing both an additive and an admixture will be researched in the future.

## Materials and methods

### *Basic properties of concrete saw sludge (SL)*

Material used in this research is a waste by-product saw sludge from a pre-cast reinforced concrete plant which needs an efficient way of recycling. Proper use of this waste would prevent landfills from further storage of this kind of waste. Samples of concrete sawing sludge (SL) for experimental work were collected at a pre-cast concrete plant. The origin of the waste material is the sawing sludge created during cutting of the hardened reinforced concrete panels with the help of the diamond disc with the stream of water. The waste thus obtained represents fine concrete particles suspension, which consistency is that of a paste.

The following basic characteristics of the sawing sludge were determined:

| | |
|---|---|
| Moisture (water) content: | 70% of the mass (deviations 69 – 71 %) |
| Dry material content: | 30% of the mass |
| Sludge bulk density: | 1240 kg/m$^3$ |
| Dry particle density: | 2650 kg/m$^3$ |
| Amount of particles smaller than 0.063 mm: 98% | |

Particle grading analysis was performed with the help of laser diffraction in water environment. The results indicated the presence of fine particles with a wide size range: 0.3 - 50 μm (Fig. 2), the average particle diameter being 8.3 μm.

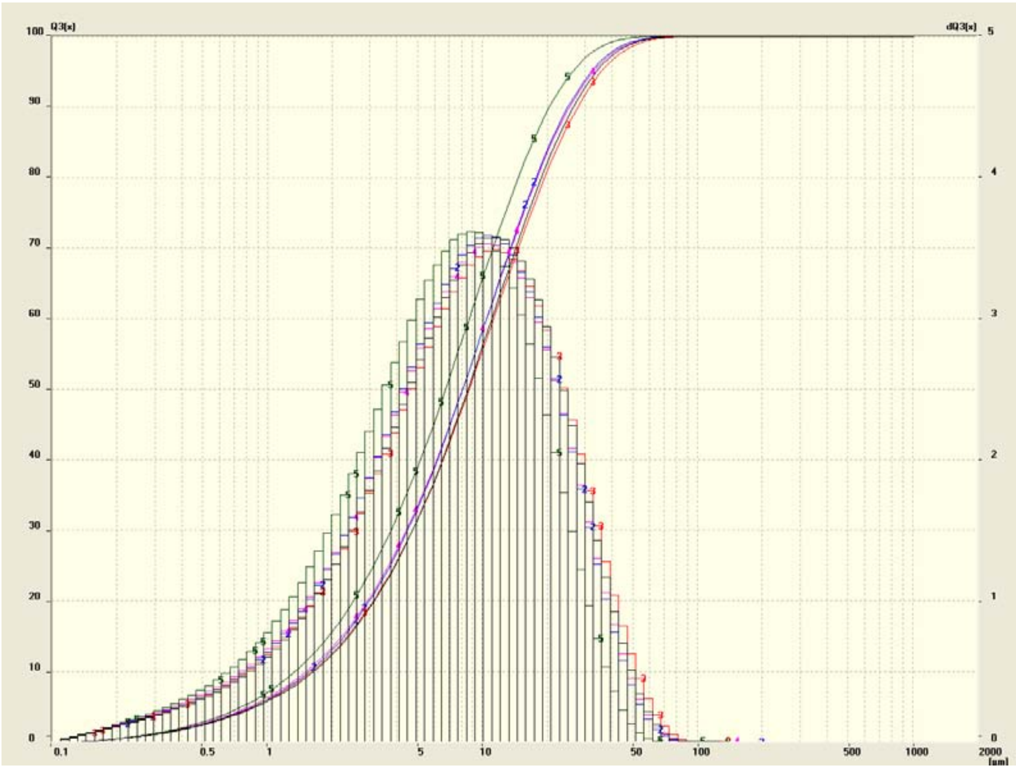


*Fig.2.* **Particle size distribution diagram (by laser diffraction method)**

***Experimental methods***

During the experiment self-compacting concrete (SCC) with various amounts of cement and micro fillers was produced in the laboratory. Local commercially available materials were used as fine and course aggregates. Dolomite powders (D), silica fume (SF) and concrete saw sludge (SL) were used as micro fillers.

Concrete components were batched and then mixed in the laboratory drum mixer during 4 minutes. For examination of the material properties standard testing sample 100×100×100mm cubes were produced. Concrete mixtures were cast into the oiled steel moulds without vibrating. Two days later the samples were dismantled. Standard curing conditions (temperature 20±2$^o$C, RH > 95±5%) were provided during the process of hardening. Sample compressive testing was performed after the 3, 7 and 28-days ageing period. Compression testing machine with the accuracy of ±1% was used, the rate of loading was 0.7 MPa/sec (according to LVS EN 12390-3:2002 standard).

Modern methods of mix workability testing such as cone flow and V-funnel methods were applied. Compressive strength of the concrete was obtained after 2, 7 and 28 days of standard curing period [10-14]. Water absorption tests were carried out.

## Results and discussion

***Mix compositions***

During the first stage of experimental work three SCC mixes with the cement content 360 kg/m$^3$ were prepared. Mix SF-1 contained silica fume as micro filler. D mix contained dolomite powder. Mix SL-1 contained only concrete sludge as micro filler, with the same content of fine particles that was recalculated to dry powder. Concrete sludge waste was used as dust/water suspension paste.

During the second stage of experimental mixing high strength SCC mixes with cement content 450 kg/m$^3$ were produced. Mix SF-2 and SL-2 contained silica fume and saw sludge paste accordingly as micro fillers. Mix 50/50 was created with silica fume being dispersed in water-sludge suspension in the proportion 1/1 to dry material. Compositions of the mixes and properties of fresh concrete mixes are summarized in Table 2.

*Table 2.*

**Mix compositions and properties of fresh concrete (cement content 360 kg/m$^3$)**

| Mix composition: | SF-1 | D | SL-1 | SF-2 | 50/50 | SL-2 |
|---|---|---|---|---|---|---|
| Portland cement I CEM 42.5 N | | 360 | | | 445 | |
| Gravel 2/8mm | | 450 | | | 410 | |
| Gravel 8/16mm | | 450 | | | 410 | |
| Sand 0/2mm | | 830 | | | 790 | |
| Silica fume | 60 | | | 90 | 45 | |
| Dolomite powder | | 60 | | | | |
| *Saw sludge, moisture content 70%* | | | *200* | | *150* | *300* |
| Saw sludge, recalculated to dry matter | | | 60 | | 45 | 90 |
| Super plasticizer | 7.0 | 7.0 | 7.0 | 10 | 10 | 11 |
| Water, incl. sludge water | 193 | 187 | 204 | 190 | 201 | 233 |
| Water / Cement ratio | 0.54 | 0.52 | 0.57 | 0.43 | 0.45 | 0.52 |

**Properties of fresh concrete:**

| | | | | | | |
|---|---|---|---|---|---|---|
| Cone flow, mm | 510 | 595 | 510 | 510 | 510 | 490 |
| Time 500 mm, sec | 3.7 | 3.2 | 3.4 | 5.6 | 5.9 | 2.5 |
| V-funnel time, sec | 5.6 | 18.5 | 6.9 | 8.7 | 9.1 | 5.9 |

Water dosage in concrete mixtures was selected in order to provide the required SCC concrete flowability through a flow cone (cone flow in the range 500 ... 600 mm). The results of the experiment showed that concrete mixes with concrete saw sludge suspension used as micro filler require more water to achieve the fresh concrete properties that would be identical to the mixes with conventional micro fillers.

Compressive strength results of hardened concrete are summarized in Figure 3 and Figure 4. Results obtained for compressive strength indicate that SCC mix compositions filled with saw sludge (mix SL-1, SL-2) have the weakest strength properties. This phenomenon can be explained by the higher water content and higher value of water/cement ratio. Mixes with silica fume (mix SF-1, SF-2) have the highest compressive strength results; dolomite powder (D) recorded medium strength values.

The most interesting results were demonstrated by the 50/50 mix based on the composite micro filler containing 50% of silica fume and 50% of saw sludge fine particles. In 28 days, the compressive strength of that mix (86.9 MPa) was just 8% lower in comparison to the mix with silica fume (92.3 MPa) and 27% higher in comparison to the mix SL-2 with saw sludge (68.3 MPa). This mix may become one of the prospective options for upcoming research. Such satisfactory results can be attributed to improved micro particle packing property resulting from such micro filler combination.

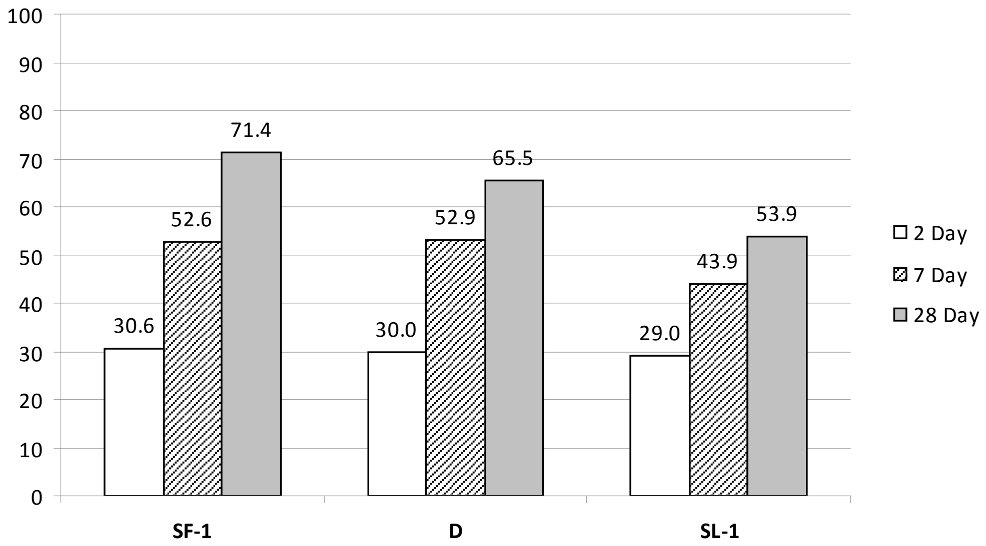


*Fig.3.* **Compressive strength results (cement content 360 kg/m$^3$)**

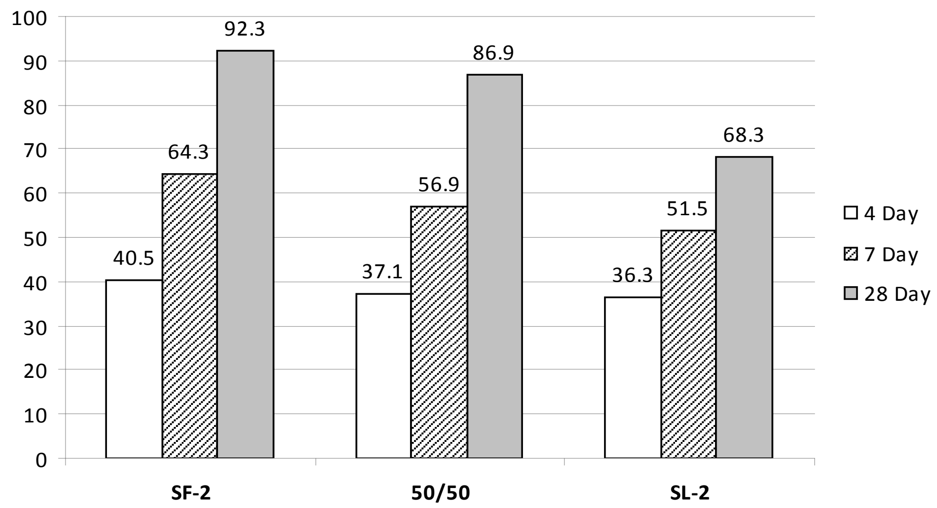


*Fig.4.* **Compressive strength results (cement content 450 kg/m$^3$)**

Water absorption was determined for three concrete mixes containing 360 kg of cement. The results are as follows:

| | |
|---|---|
| SF-1: | 1.3% |
| D: | 3.8% |
| SL-1: | 4.3% |

Mix with silica fume demonstrated the best result of 1.3%, whereas dolomite and sludge-filled concrete samples have higher value: 3.8 and 4.3 % accordingly.

## Conclusions

- Pilot SCC concrete mixes were made by adding concrete wet saw sludge as micro filler. The obtained results show lower physical and mechanical properties of the concrete compared to the mixes with silica fume and dolomite powder, as well as to the mixes with composite additives. Addition of wet sludge to concrete mix (without additional drying) significantly facilitates the use of sludge and provides good dispersion in concrete.
- Additional amount of water is required for the mixes with wet saw sludge to ensure concrete consistency of the mixes. Reduced compressive strength results (a decrease by 25% compared to silica fume mix) and increased water cement ratio were obtained. The mixes with silica fume showed lower water consumption, which corresponds to the data available in the literature, whereas higher water consumption results were demonstrated by the mixes made with wet saw sludge. This could be attributed to the angular shape of particles containing saw sludge.
- The mix with the combined micro filler 50/50 content (50% silica fume and 50% of the sludge particles) looks prospective; it showed satisfactory results on strength given a relatively small quantity of micro fume. Research in this direction should be continued as it can provide the silica fume saving effect while the waste from precast concrete plants can be utilized.
- Further sludge research should be done. One of the prospective options of sludge waste disposal: conduct research of the conventional concrete properties with the smaller content of sludge waste in concrete in the range of 1-10% to cement weight. Another research that would involve combined micro fillers containing conventional fillers and sludge waste filler in various combinations should be performed either.
- In general view, concrete sludge waste could be re-used in concrete production to prevent environmental pollution and disposal to landfills. Apart from the ecological factor deterioration of concrete mechanical and physical properties should be taken into account in application of concrete sludge waste; the benefits of utilization of this waste material should be carefully assessed.

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## Summary

Due to lack of information about utilization of concrete saw sludge worldwide and given the satisfactory results obtained in the present study, further investigation and research will be carried out in order to find feasible ways of recycling wastes from precast concrete plants.

### References

1. Chatveera, B., Lertwattanaruk, P., Makul, N. Effect of sludge water from ready-mixed concrete plant on properties and durability of concrete. Cement and Concrete Composites 28, 2006, p. 441–450.
2. Chatveera, B., Lertwattanaruk, P. Use of ready-mixed concrete sludge water in concrete containing an additive or admixture, Journal of Environmental Management 90, 2009, p. 1901-1908.
3. Sato, Y., Kiyohara, C., Chia-Ming, L. Studies on the effective use of concrete sludge - sludge water and pulverized dry sludge, Exploiting wastes in concrete: seminar 5, 1999, p. 37-46
4. Borger, J., Carrdsguillo, R., Fowler, D. Use of Recycled Wash Water and Returned Plastic Concrete in the Production of Fresh Concrete, J. of Advanced Based Materials, 1994, p. 267-274
5. Souwerbren, C. Re-use of wash water in the concrete industrial production circle without waste. European standard for mixing water and the re-use of wash water, proc., of the Conf., Concrete in the service of mankind, concrete for environmental and protection, edited by R.K. Dhir & T.D. Dyer, 1996, p.183-197

6. Sandrolini, F., Franzoni, E. Waste wash water recycling in ready-mixed concrete plants. Cement and Concrete Research 31, 2001, p. 485–489.
7. Su, N., Miao, B., Liu, F. Effect of wash water and underground water on properties of concrete. Cement and Concrete Research 32, 2002, p. 777–782.
8. Chini, A.R., Muszynski, L.C. Reuse of wastewater at concrete plants in Florida in the production of fresh concrete. Magazine of Concrete Research 53 (5), 2001, p. 311–319.
9. Paolini, M., Khurana, R. Admixtures for recycling of waste concrete. Cement and Concrete Composites 20, 1998, p. 221–229.
10. EN 12390-2:2002. Testing hardened concrete - Part: 2: Making and curing specimens for strength tests. LVS. Riga, 2002. 7 p.
11. EN 12390-3:2002. Testing hardened concrete - Part 3: Compressive strength of test specimens. LVS. Riga, 2002. 16 p.
12. Draft prEN 12350-8. Testing fresh concrete – Part 8: Self-compacting concrete – Slump-flow test. Brussels, 2007. 8 p.
13. Drafr prEN 12350-9. Testing fresh concrete – Part 9: Self-compacting concrete – V-funnel test. Brussels, 2007. 6 p.
14. 12730.3-78 "Бетоны. Метод определения водопоглощения" (Concretes. Method for determining water absorption)

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