ECOLOGICAL-GEOCHEMICAL STATE OF TOPSOIL AND WATER SEDIMENTS IN ŠIAULIAI

Ekoloģiski-ģeoķīmiskais aramkārtas un ūdens nogulumiežu stāvoklis Šauļos

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Abstract

Ecological-geochemical state of topsoil and water sediments in Šiauliai was evaluated taking into account total contents of 14 hazardous elements (Pb, Zn, Cu, Sn, Ag, Ni, Mo, Cr, Co, Mn, V, B, Sr, Ba) in a complex way – both according to their total contamination index and their standards (existing State standards and phytotoxic concentrations in soil used in European countries). The fraction < 1 mm of samples was analysed by atomic emission spectrophotometry. Topsoil composite samples (110 in all) were taken approximately from each square kilometre and classified into 4 groups according to functional micro-zones. The number of samples from water sediments (Talša and Ginkūnai lakes, Kulpė and Violė rivers) was 13. Even 54.5% topsoil samples were characterised by unsatisfactory final ecological-geochemical state (30% of them had bad state). Topsoil of industrial functional micro-zones had the worst state. It was followed by topsoil of residential, then by topsoil from social-residential micro-zones. Topsoil from the territories of recreation or protected areas had the best quality. Ecological-geochemical state of water sediments in Ginkūnai and Talša lakes and in Kulpė or Violė rivers was very bad or bad.

Keywords: *ecological-geochemical state, urban territories, metal pollution, topsoil, lake sediments, river sediments.*

Introduction

One of the aims of the program "Urban environmental quality and its change" was to evaluate ecological-geochemical state of topsoil and water sediments in Šiauliai, i.e. their suitability for life, work and recreation of people. The spatial variability of topsoil state and its dependency on functional micro-zones also had to be analysed. Similar investigations have been carried out in other countries [1]. For such evaluation the total contamination index Zc or various standards can be used. The existing State standard for element content in soil [2] defines maximum permitted concentration (MPC) of element and gives the corresponding values for total contents of Mn, V, Pb and Mn + V which are determined according to the general sanitary limiting indication, i.e. the influence on soil self-purification and biological activity. While samples have been taken also from cultivated topsoil, the phytotoxic concentrations (Fk) used in European countries can be taken into account [3]. When they are exceeded, the elements have negative influence on plants, because their physiological processes are disturbed and the amount and quality of plant production deteriorates [2]. Though there are no special State standards for element contents in water sediments, the limit values (LV) for classifying sewage sludge into three categories [4] can be applied for water sediments. Also their total contamination index Zc can be used for evaluation.

Methods

Complex samples (their total number was 110) consisting from several sub-samples were taken in 2002 from the upper (0-10 cm depth) soil layer approximately from each square kilometre and classified into 4 groups according to functional micro-zones (A – social-residential, B – residential, C – industrial and D – recreational). The number of samples from water sediments (Talša and Ginkūnai lakes, Kulpė and Violė rivers) was 13. Besides, one sample was taken from Violė tributary for local background determination and one in Mūša for determination of the influence of pollution from the whole Šiauliai. All samples were air-

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dried, sieved through nylon sieves (choosing fraction < 1 mm). After organic matter mineralisation at 450^0 C and mechanical pulverisation they were analysed by DC arc emission spectrophotometry for determination of the total contents of Li, B, Ga, P, Mn, Ti, V, Cr, Co, Ni, Cu, Zn, Pb, Mo, Ag, Sn, Zr, Y, La, Yb, Sc, Sr, Ba. International reference materials OOKO 153 and OOKO 151 were used for quality control.

Both total contamination index Zc and standards for total contents of elements were taken into account for more integrated assessment. The evaluation was based only on 14 hazardous elements, for which at least one standard value (MPC, Fk or LV) is defined (Table 1). Most of them belong to class I, III or III of toxicity [5].

Table 1.

Parameters (mg/kg) for evaluation of ecological-geochemical state of topsoil and water sediments

	Standards				Background values			
Elements and their class of toxicity [5]	MPC (HN 60-1996) [2]	Fk [3]	Category II sludge ($LV_1 – LV_2$) [4]	Category III sludge [4]	Top-soil [6]	River sedi-ments	Lake sediments (20-30% of organic matter) [7]	Lake sediments (30-40% of organic matter) [7]
Pb (I)	32	100	140–500	>500	14.8	35.3	21.3	21.1
Zn (I)	-	300	300–2000	>2000	25.9	86.1	62.5	**67.0**
Cu (II)	-	100	75–600	>600	9.7	19.8	14.4	10.5
Ni (II)	-	100	50–300	>300	13.5	27.6	15.2	14.5
Cr (II)	-	100	140–400	>400	34.1	68.9	30.4	28.2
Co (II)	-	30			5	6.9	5.4	5.1
Mo (II)	-	5			0.68	0.86	1.08	**1.25**
B (II)	-	100			28.4	38.7	33	30.6
Mn (III)	1500	1500			371	862	828	387
V (III)	150	100			37	31.9	29.2	**30.0**
Ba (III)	-	-			391	715	383	314
Sr (III)	-	-			86.9	172	110	89
Sn	-	50			2.01	2.58	2.92	2.86
Ag	-	2			0.067	0.215	0.091	**0.095**
Mn+V	1000+100	-						

Total contamination at site **i** by Pb, Zn, Cu, Sn, Ag, Ni, Mo, Cr, Co, Mn, V, B, Sr, Ba index is calculated according to the formula: $Zc_i=\Sigma Kk_{ij}–n+1$, where summing is according to **j**, Kk_{ij} is concentration coefficient of element **j** at point **i** and n=14 is the number of elements (when $Kk_{ij}<1$, it is accepted that $Kk_{ij}=1$). Element concentration coefficients Kk_{ij} were calculated by dividing element content in sample by its background value. Background values for topsoil were taken from Middle Venta soil region [6]. For lake sediments they depended on the percentage of organic matter in sample [7]. Not general or regional background values [6, 8, 9, 10] but local background values were used for river sediments. They were determined in sample taken in Violė tributary outside town territory. The main role for evaluation was given to Zc. According to Zc categories for polluted soil [5] or water sediments [11] samples with good, satisfactory, medium, bad or extremely bad basic ecological-geochemical state can be revealed (Table 2). Zc categories in soil are related to population health indices, while in water sediments to concentration of hazardous elements in water. This assessment was adjusted taking into account the exceeding of MPC, Fk or LV. Soil is very polluted, when the content of chemical substance or element 2 times exceeds MPC, and polluted, when it exceeds MPC 1–2 times [2]. According to this principle, general sanitary ratios Rgs and

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phytotoxic ratios Rph were determined for each topsoil sample (element content in sample divided by its MPC or Fk, respectively). According to their maximum values general sanitary and phytotoxic state of topsoil was evaluated in the same way: it was estimated as bad, if max(Rgs)>2 or max(Rph)>2, medium, if max(Rgs) (or Rph) were within the interval (1,2), and satisfactory, if max(Rgs)≤1 or max(Rph)≤1. Final ecological-geochemical state of topsoil was evaluated as the worst from three states (basic, general sanitary and phytotoxic). Special variable ST was calculated indicating this final state. The set of its possible values is the following: 1, 2, 3, 4, 5 (Table 2).

Table 2.

Evaluation of topsoil and water sediment quality according to Zc

Pollution level (category)	Topsoil Zc	Water sediments Zc	Ecological-geochemical state
Acceptable	< 8	< 5	Good (G), ST=1
	8–16	5–10	Satisfactory (S), ST=2
Medium dangerous	16-32	10–30	Medium (M), ST=3
Dangerous	32-128	30–100	Bad (B), ST=4
Most dangerous	> 128	> 100	Extremely bad (E), ST=5

Basic ecological-geochemical state of water sediments was also evaluated according to Zc categories (Table 2). It was adjusted according to categories of wastewater sludge (determined according to Pb, Cr, Cu, Ni, Zn contents): sediment samples of category III were attributed to extremely bad ecological-geochemical state, while of category II – to bad state. Assessment of samples of category I was not adjusted, i.e. realised only according to Zc. In this way final ecological-geochemical state of sediments was determined.

Results and discussion

Zc of the greater part (64.5%) of topsoil samples taken from the town territory was acceptable, though in the rest 35.5% of samples it exceeded the permissible level: 21.8% of them belonged to the category of medium contamination and 13.6% to dangerous one. No extremely dangerously polluted samples were found, as the territories of industrial enterprises were not investigated. Meanwhile Zc of the greater part (84.6%) of investigated sediment samples was not acceptable, most of them (61.5%) could be attributed to dangerous level of pollution and two samples (from Ginkūnai and Talša lakes) – even to extremely dangerous level. According to average Zc basic ecological-geochemical state of urban topsoil was not far from medium (14.7), while of water sediments (64.7) it was bad. Phytotoxic state of most (74.5%) topsoil samples was satisfactory, though there was rather great part of samples with medium (20.9%) or bad (4.5%) state. However, general sanitary state of more than half (53.6%) topsoil samples was unsatisfactory, even 27.3% among them were characterised by bad state. Such state was predetermined by lead pollution originating from vehicles. Only 45.5% of topsoil samples were characterised by good or satisfactory final ecological-geochemical state and even 54.5% by unsatisfactory (including 30% of samples with bad state) (Table 3). The sequence of topsoil pollutants according to average accumulation was the following: Zn>Pb>Cu>Sn>Ag>Sr>Cr>Mo (Table 4). The largest territory with unsuitable final ecological-geochemical state of topsoil included the centre of town (Fig. 1).

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Table 3.

Ecological-geochemical state of topsoil and water sediments in Šiauliai

Objects of assessment	Number of samples	Average Zc	Ecological-geochemical state, % of samples				
			Good	Satisfactory	Medium	Bad	Extremely bad
Topsoil of all territory							
A	11	7.6	63.6	0.0	27.3	9.1	0.0
B	31	15.1	38.7	9.7	22.6	29.0	0.0
C	46	21.2	19.6	0.0	30.4	50.0	0.0
D	22	4.2	86.4	0.0	13.6	0.0	0.0
A+B+C+D	110	14.7	42.8	2.7	24.5	30.0	0.0
Topsoil of the central territory							
A	2	13.8	0.0	0.0	100.0	0.0	0.0
B	1	19.7	0.0	0.0	0.0	100.0	0.0
C	3	21.0	0.0	0.0	0.0	100.0	0.0
D	1	7.9	0.0	0.0	100.0	0.0	0.0
A+B+C+D	7	16.9	0.0	0.0	42.9	57.1	0.0
Former military territory of Zokniai							
A+B+C+D	11	11.6	36.4	0.0	27.3	36.4	0.0
Water sediments							
Lake sediments	9	69.9	11.1	0.0	0.0	11.1	77.8
River sediments	4	40.6	0.0	0.0	0.0	25.0	75.0

Table 4.

Accumulation of hazardous elements in topsoil and water sediments

Objects	Descending sets of element average concentration coefficients													
All topsoil (A+B+C+D)	**Zn 5.60**	**Pb 3.49**	**Cu 2.82**	**Sn 2.13**	**Ag 1.76**	**Sr 1.60**	**Cr 1.56**	**Mo 1.43**	Mn 1.20	Ni 1.19	Co 1.17	Ba 1.04	B 0.91	V 0.88
Topsoil of micro-zones D	**Zn 1.75**	**Sr 1.33**	Cu 1.29	Pb 1.21	Cr 1.18	Sn 1.12	Ni 1.05	Ag 1.00	Ba 0.98	Mo 0.97	Co 0.97	Mn 0.95	V 0.91	B 0.90
Topsoil of micro-zones A	**Zn 3.32**	**Pb 2.15**	**Cu 1.58**	**Sn 1.48**	**Sr 1.47**	Co 1.23	Mn 1.22	Cr 1.17	Ag 1.14	Mo 1.11	Ni 1.05	V 0.99	B 0.95	Ba 0.79
Topsoil of micro-zones B	**Zn 6.80**	**Pb 2.72**	**Ag 2.47**	**Cu 2.44**	**Sn 1.89**	**Sr 1.62**	**Cr 1.56**	**Mn 1.31**	Co 1.26	Mo 1.22	Ni 1.17	Ba 1.13	B 1.03	V 0.98
Topsoil of micro-zones C	**Zn 7.17**	**Pb 5.41**	**Cu 4.11**	**Sn 2.94**	**Mo 1.86**	**Cr 1.83**	**Ag 1.80**	**Sr 1.75**	**Ni 1.30**	Mn 1.24	Co 1.19	Ba 1.08	B 0.83	V 0.78
All sediments	**Cr 26.11**	**Ag 14.29**	**Zn 7.19**	**Pb 4.85**	**Ni 3.59**	**Cu 3.13**	**Sr 1.99**	**Sn 1.93**	**V 1.55**	**Mo 1.52**	Ba 1.15	Co 0.80	B 0.80	Mn 0.70
Talša lake sediments	**Cr 24.87**	**Ag 16.13**	**Zn 7.30**	**Pb 4.34**	**Ni 3.28**	**Cu 2.36**	**Sn 1.76**	**Mo 1.71**	**V 1.68**	**Sr 1.62**	**Ba 1.38**	Co 0.84	Mn 0.71	B 0.57
Ginkūnai lake sediments	**Cr 90.70**	**Ag 59.23**	**Zn 6.87**	**Pb 6.06**	**Ni 4.41**	**Sn 4.02**	**Cu 3.23**	**Ba 2.24**	**V 1.88**	**Sr 1.59**	Co 1.13	Mo 1.02	Mn 0.74	B 0.63
Kulpė river sediments	**Cr 28.44**	**Zn 10.67**	**Pb 9.71**	**Ag 5.31**	**Cu 4.62**	**Sr 4.38**	**Ni 3.57**	**Sn 2.25**	V 1.29	Mo 1.24	B 0.89	Ba 0.81	Co 0.65	Mn 0.63
Violė river sediments	**Zn 5.00**	**Cu 2.59**	**B 1.85**	**Mo 1.67**	**Ni 1.53**	Sn 1.19	V 1.19	Pb 0.94	Cr 0.70	Co 0.52	Ag 0.40	Sr 0.36	Mn 0.27	Ba 0.11
Mūša river sediments	**Cr 14.86**	**Ni 9.90**	**Ag 8.72**	**Cu 7.32**	**Zn 4.36**	**Sn 1.78**	**V 1.71**	**Mo 1.58**	B 1.23	Mn 0.89	Pb 0.72	Co 0.67	Sr 0.67	Ba 0.42

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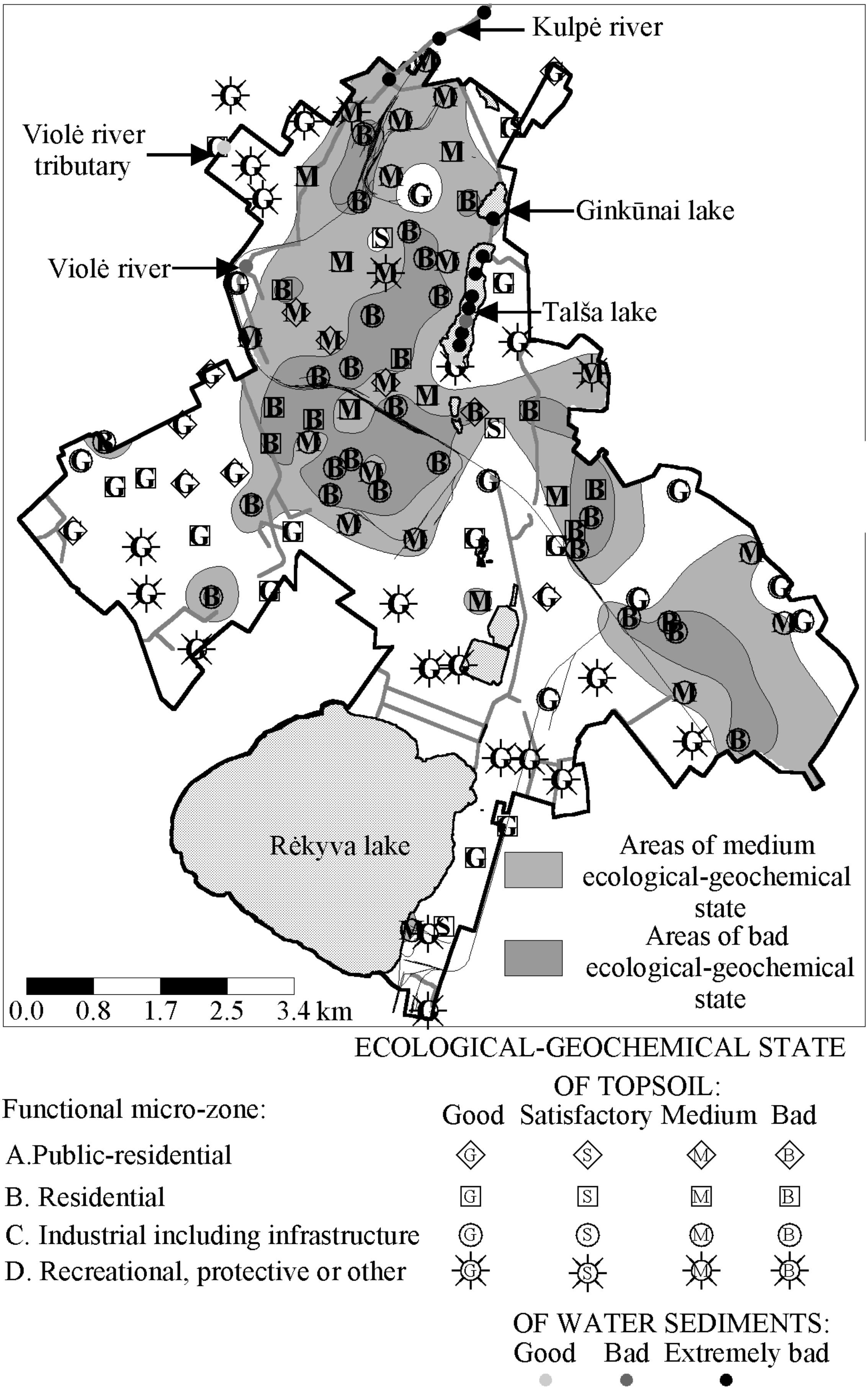

Fig.1. Ecological-geochemical state of topsoil and water sediments in Šiauliai

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It included also industrial districts surrounding it: the mostly polluted central one at the railway (with “Tauras” TV-plant, “Vairas” bicycle plant, foundry, fuel station, garages, forge, storehouses, railway depot), the northern one Gubernija (with experimental mechanic plant, metal commerce enterprise, factory), the north-eastern one near Talša lake (with “Stumbras” leather processing plant, transport enterprise “Šiaulių autotransportas”, service station and garages) and the eastern one in the north-western part of Zokniai airport (with aviation repair plant having two galvanic facilities).

Three smaller anomalies were related to former “Nuklonas” TV-set plant in the southwestern part of Šiauliai, Rėkyva southern industrial district and southeastern part of Zokniai. According to average Zc ecological-geochemical state of topsoil in the centre of the city due to Pb pollution is worse and in surroundings of Zokniai is slightly better in comparison with the whole town. However, the percentage of topsoil samples (63.7%) attributed to not acceptable ecological-geochemical state in Zokniai is higher than in the whole town. The greatest accumulation of most pollutants (Zn, Pb, Cu, Sn, Sr, Cr, Mo, Ni) is in topsoil of industrial micro-zones, only Ag, Mn mostly accumulate in residential micro-zones (probably due to municipal pollution). Zn is the greatest polluter in all micro-zones (Table 4). Topsoil from industrial micro-zones has the most unsuitable ecological-geochemical state. It is followed by topsoil from residential and public-residential micro-zones. The pollution level of topsoil from recreation, protection or similar destination territories is the lowest.

Even 92.3% of taken sediment samples were characterised by generally not acceptable ecological-geochemical state (including 76.9% of samples with extremely bad state). Most of investigated sediments (except one sample in the southern part of Talša lake) were attributed to categories III or II of sewage sludge. Average Zc was greater in lake sediments (Table 3). Ginkūnai lake was polluted most of all (average Zc=171). It was followed by Kulpė river (63), Talša lake (57) and finally by Violė river (9). The sequence of sediment pollutants was larger than in topsoil and their arrangement was different (Table 4). Zc of sediments mostly depended on Cr, Ag, Zn, Pb, Ni, Cu. These elements were actively accumulating in Talša and Ginkūnai lakes and in Kulpė river, 5 of them (except Pb) predetermined pollution level even in Mūša river. Meanwhile bad ecological-geochemical state of Violė sediments was predetermined by Zn and Cu. The greatest concentration of Pb and Zn was observed in the central part of Talša lake, meanwhile of Ni and Cr in its northern part.

Conclusions

Long period of urbanisation, great industrialisation and intensive transport predetermined fair or bad quality of 54.5% topsoil samples mainly in central and northern part of Šiauliai. Topsoil of industrial functional micro-zones does not meet quality criteria. Pollution from metal processing plants can influence the neighbouring residential districts. Wastewater from leather processing plants and surface runoff from highly urbanised and industrialised territories predetermined extremely bad or bad quality of sediments in Talša, Ginkūnai lakes and in Kulpė and Violė rivers.

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