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Soil Contamination in One of Preschools Influenced by Metal Working Industry

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***Abstract*. The aim of research was to estimate the present impact of drill plant or other pollution sources on soil anomalies of the preschool area and to reveal the depth of penetration of pollutants. Soil samples from 9 cores in the territory of the preschool were taken from 5 depth intervals: 0-0.5 m, 0.5-1.0 m, 1.0-1.5 m, 1.5-2.0 m and 2.0-3.0 m. Total number of samples was 45. Each sample was sieved to <2 mm fraction, milled and homogenised with binder before pressing 2 pellets. All pressed pellets were analysed by energy-dispersive x-ray fluorescence for determination of the contents of harmful chemical elements As, Ba, Cr, Cu, Mo, Ni, Pb, Sn, V, Zn and major elements Al, Ca, K, Fe, Mg, Na, P, S. Si, Ti. Samples where maximum permitted concentrations of Mo, Pb, Sn are exceeded occur not only in the uppermost layers, but also in the deeper layers. The highest median contents of most harmful chemical elements, except V and As, are in the uppermost 0.0-0.5 m layer and decrease with depth until 2.0-3.0 m or 1.5-2.0 m. To eliminate the influence of soil clay content in different samples, normalisation of concentration coefficients by the median of Al, K and Ti concentration coefficients was used. The depth of penetration is largely influenced by lithological composition of soil and is much deeper in sandy soil without layers enriched in clay.**

***Keywords* – harmful chemical elements, metal working, preschools, soil contamination.**

I INTRODUCTION

Urban topsoil is inevitably polluted by harmful chemical elements [1, 2, 3, 4]. Children attending preschools are especially sensitive to this contamination [5]. Therefore the areas of preschools are important objects of urban geochemical investigations. In Lithuania they are carried out taking into account national hygienic norm for maximum permissible concentrations (MPC) of harmful chemical elements in soil [6]. Previous research of topsoil contamination in 49 preschool playgrounds located in 7 districts of Vilnius city has shown that 21 of them had moderately hazardous to hazardous levels of contamination and that Zn was the dominant soil contaminant, because the harmful chemical elements according to the number of areas where their MPC values were exceeded were arranged as follows: Zn(13)>Pb(5)>Ag(2)>Cu, Sn, Mo (1) [7]. The only area where MPC of Mo is exceeded is in Naujamiestis district. Previous investigations of Vilnius topsoil contamination by harmful chemical elements have shown that this district is one of the most heavily polluted [8]. The reason is that powerful metal-working, radio and electrical engineering plants operated in it in the 20th century. Drill plant was one of them which formed contrasting anomalies of Mo, Cr, Co, Cu, V, Ni, also Ba was its specific pollutant. Drill plant is still operating though production volume has decreased. One of the preschools of this district is located close to this plant.

The aim of this research was to estimate the present impact of drill plant or other pollution sources on soil anomalies of the preschool area and to reveal the depth of penetration of pollutants.

II MATERIALS AND METHODS

Soil samples from 9 cores in the territory of the preschool which is close to drill plant (Fig. 1) were taken from 5 depth intervals: 0-0.5 m, 0.5-1.0 m, 1.0-1.5 m, 1.5-2.0 m and 2.0-3.0 m. Total number of samples was 45.

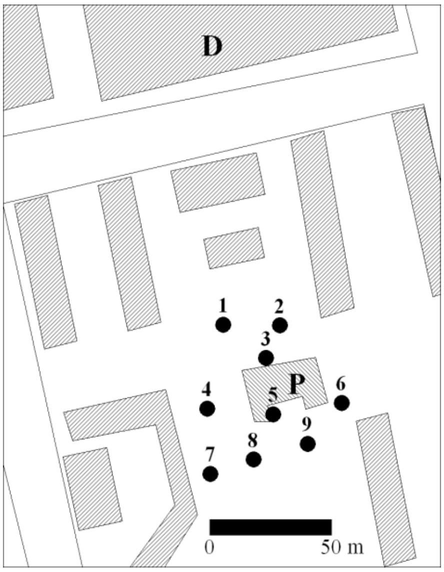

Fig. 1. Location of drill cores in preschool area. Note that P means preschool, D drill plant and black circle with the number above indicates location and number of core.

Each sample was sieved to <2 mm fraction, milled and homogenised with binder before pressing 2 pellets. All pellets were analysed by energy-dispersive x-ray fluorescence (Spectro XEPOS equipment with TurboQuant calibration method) for determination of the contents of harmful chemical elements As, Ba, Cr, Cu, Mo, Ni, Pb, Sn, V, Zn and major elements Al, Ca, K, Fe, Mg, Na, P, S. Si, Ti. The median value from two pressed pellets of each sample was calculated. The laboratory participates in International Soil-analytical Exchange (ISE) program of Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) [9]. ISE samples were used for re-calibration of the element contents using linear, power and second order polynomial functions, for some elements the average from two re-calibrated values.

III RESULTS AND DISCUSSION

The contents of most harmful chemical elements, except Mo, Pb and Sn, do not exceed maximum permitted concentrations (MPC) for soil [6]. The samples where MPC values of Mo (5 ppm), Pb (100 ppm), Sn (10 ppm) are exceeded occur not only in the uppermost layers (Mo in core No 1, Sn in core No 5), but also in the deeper layers: at the depth 0.5-1.0 m in core No 7 (Sn) and core No 8 (Pb and Sn), at the depth 1.0-1.5 m of core No 9 (Sn) (Table 1).

TABLE 1.

THE CONTENTS OF CHEMICAL ELEMENTS (PPM) IN DEPTH INTERVALS OF CORES.

NOTE. THAT MAXIMUM CONTENT OF CHEMICAL ELEMENT IN EACH CORE IS IN BOLD AND MAXIMUM IN ALL CORES IS UNDERLINED.

No	H (m)	Zn	Pb	Cu	Sn	As	Mo	V	Cr	Mn	Ni	Ba	Al	K	Ti	Si
1	0.0-0.5	**156**	**50.2**	**18.6**	5.64	**5.94**	**5.75**	13.1	**26.8**	395	10.0	**290**	18615	12571	1099	303806
1	0.5-1.0	74.1	39.5	15.3	**9.44**	<3.0	1.18	12.7	17.2	**402**	7.2	251	18319	12725	1012	**390491**
1	1.0-1.5	48.1	18.3	10.0	6.26	4.14	0.70	18.0	16.7	366	8.2	276	25442	14729	1133	389035
1	1.5-2.0	29.3	11.6	7.2	<1.5	3.04	1.29	**35.9**	18.6	382	8.2	251	21235	13905	1027	325045
1	2.0-3.0	25.8	8.4	9.0	<1.5	<3.0	0.58	26.8	24.1	287	**11.9**	287	**30659**	**19736**	**1707**	336369
2	0.0-0.5	**47.8**	**18.0**	**9.2**	**7.06**	**3.10**	0.92	16.1	15.7	242	6.3	**277**	23380	15683	1208	417779
2	0.5-1.0	34.0	11.7	5.8	1.61	<3.0	0.68	5.9	13.6	234	5.4	251	25301	14814	1022	426738
2	1.0-1.5	19.3	8.9	4.6	<1.5	3.16	0.22	22.1	14.9	**412**	6.6	254	20946	13962	987	**445658**
2	1.5-2.0	18.7	8.6	4.7	2.46	<3.0	**1.08**	**29.7**	12.4	368	5.8	224	16746	12265	808	334550
2	2.0-3.0	24.3	9.4	8.3	1.74	3.04	0.39	19.3	**21.6**	284	**10.2**	270	**29416**	**19038**	**1536**	340417
3	0.0-0.5	33.6	17.6	11.9	1.94	<3.0	0.43	23.9	18.5	374	7.4	235	19468	12435	1134	**431559**
3	0.5-1.0	**39.6**	**22.5**	**18.2**	**5.57**	3.10	0.85	**24.2**	20.7	379	9.1	245	22456	13735	1250	394720
3	1.0-1.5	25.1	10.4	8.7	<1.5	3.23	**2.60**	18.8	24.5	**435**	9.6	231	23285	13400	1405	396312
3	1.5-2.0	28.2	10.4	9.5	<1.5	**5.14**	1.39	21.6	19.5	433	9.7	251	20846	12832	1368	381849
3	2.0-3.0	26.8	9.1	8.2	<1.5	<3.0	1.59	24.9	**26.1**	320	**12.3**	**303**	**34018**	**20520**	**1833**	311901
4	0.0-0.5	**66.9**	**39.0**	**17.6**	**7.00**	**3.96**	**1.21**	16.3	**21.8**	**339**	**10.5**	**293**	**25737**	16046	**1323**	369979
4	0.5-1.0	35.6	20.4	8.9	3.23	<3.0	1.05	**18.6**	11.5	314	6.4	286	21730	15614	1125	389081
4	1.0-1.5	17.2	14.8	5.6	2.27	<3.0	0.98	11.8	14.5	193	5.2	289	22009	**18243**	1103	427784
4	1.5-2.0	14.9	10.4	4.4	<1.5	<3.0	0.87	9.7	12.2	192	5.8	265	19557	16250	962	**441474**
4	2.0-3.0	17.2	9.0	4.4	<1.5	<3.0	1.21	14.9	13.6	258	6.2	254	18863	14030	827	416460
5	0.0-0.5	**71.7**	**51.8**	**28.5**	**12.8**	**3.47**	**1.37**	16.7	**18.4**	**256**	**7.6**	248	**19127**	14150	**929**	399541
5	0.5-1.0	32.7	31.0	15.2	6.01	<3.0	1.21	6.0	11.9	194	4.7	234	14738	11810	680	443247
5	1.0-1.5	7.3	7.2	2.6	3.30	<3.0	1.16	3.6	9.0	87	3.0	**282**	17853	**18323**	474	452389
5	1.5-2.0	14.5	6.0	5.6	<1.5	<3.0	0.77	**19.1**	9.0	168	4.1	199	12381	10271	751	457619
5	2.0-3.0	7.4	3.5	1.8	<1.5	<3.0	**1.37**	11.6	10.8	122	2.9	180	10545	9860	559	**471354**
6	0.0-0.5	**185**	**36.6**	**20.2**	**8.81**	**8.61**	**3.50**	21.2	21.3	329	10.0	250	20153	12793	1021	313584
6	0.5-1.0	73.1	28.8	15.7	3.49	6.00	1.56	**26.9**	**25.1**	469	**11.0**	241	**24747**	13832	1405	381440
6	1.0-1.5	44.2	16.7	9.7	2.33	4.02	1.45	18.3	21.6	469	9.0	**270**	23279	13201	1298	400678
6	1.5-2.0	28.5	12.1	8.5	2.40	<3.0	0.53	9.2	13.3	326	6.2	234	18341	12424	888	**431832**
6	2.0-3.0	38.6	12.8	9.1	<1.5	5.32	0.70	23.7	**25.1**	**481**	9.8	252	24229	**14950**	**1426**	327501
7	0.0-0.5	68.0	35.6	21.3	7.79	**8.35**	1.70	13.9	**19.1**	333	7.6	272	15083	11788	830	366659
7	0.5-1.0	**69.6**	**38.5**	**22.4**	**14.8**	3.66	1.13	**16.9**	14.4	**422**	**8.2**	**313**	19182	14655	1037	377802
7	1.0-1.5	11.7	7.8	3.6	2.59	<3.0	0.80	0.4	9.3	157	3.9	290	**19237**	**16841**	995	438927
7	1.5-2.0	8.7	5.9	3.5	3.11	<3.0	**2.04**	8.7	14.0	147	4.3	266	15164	15331	1083	**460029**
7	2.0-3.0	20.0	6.6	5.9	3.68	<3.0	0.95	16.6	16.0	308	5.9	192	15153	10719	**1465**	451661
8	0.0-0.5	120	42.2	17.6	4.25	**3.78**	**1.81**	25.0	18.9	**304**	**10.8**	269	**19006**	13576	1049	389581
8	0.5-1.0	154	60.6	**19.8**	12.5	3.60	1.42	13.7	**21.5**	303	7.5	**291**	18956	**13888**	1018	408364
8	1.0-1.5	**40.1**	**131**	12.4	**29.4**	<3.0	1.26	5.3	11.0	221	4.9	244	17225	13832	886	404453
8	1.5-2.0	22.5	15.6	6.0	6.38	<3.0	1.13	9.9	14.0	214	4.4	228	15920	12231	963	454526
8	2.0-3.0	14.3	6.7	4.2	1.81	<3.0	0.77	**20.1**	13.9	217	3.8	162	9209	8942	**1372**	**468398**
9	0.0-0.5	81.1	29.2	19.7	7.12	<3.0	**1.98**	11.2	**21.0**	276	**9.0**	**278**	**22082**	**14541**	**1096**	373890
9	0.5-1.0	92.2	63.9	19.6	12.4	**4.08**	1.05	14.1	15.8	277	7.2	247	18478	13434	999	397904
9	1.0-1.5	**95.3**	**71.7**	**33.1**	**104**	<3.0	1.13	**18.9**	15.7	**295**	6.9	265	16278	12730	981	408410
9	1.5-2.0	38.0	34.2	14.9	9.23	<3.0	1.08	7.3	9.9	243	4.5	234	15126	12111	758	430331
9	2.0-3.0	8.3	3.9	3.1	<1.5	<3.0	0.77	10.1	9.0	136	2.8	161	9506	8544	512	**465123**

Basing on previous investigations of drill plant, also its nearest surroundings [10], much higher contents of harmful chemical elements, especially siderophiles were expected. Most probably, there are several reasons. Possibly, the contamination level markedly decreases with distance from pollution source or lower production volume and environmental protection measures in drill plant result in rather satisfactory situation of the territory of preschool. Besides, it has been shown [11] that the contents of most harmful chemical elements earlier determined by OAES are higher than respective contents determined presently by EDXRF. According to the radio of respective medians the harmful chemical elements can be arranged as follows: V(2.48)>Ni(1.91)> Mo(1.75)> Zn(1.71)> Mn(1.70)> Cr(1.58)> Cu(1.56)> Pb(1.37)> Ba(1.01). The sequence shows that mainly the estimates of the contents of siderophiles by EDXRF equipment are significantly lower. This regularity can explain why large and contrasting anomalies of Mo are now hardly noticeable, except one sample in the uppermost layer of core No 1. However, the following facts confirm that the influence of drill plant still exists: 1) maximum contents of Mo and Cr are in surface layer of core No 1; 2) maximum content of V is in the 1.5-2.0 m layer of this core. Namely this core is the closest to drill plant and namely these elements are specific pollutants of this plant.

The highest median contents of most harmful chemical elements, except V and As, are in the uppermost 0.0-0.5 m layer and are as follows in ppm: 71.7 for Zn, 36.6 for Pb, 18.6 for Cu, 7.06 for Sn, 1.70 for Mo, 19.1 for Cr, 9.02 for Ni, 329 for Mn and 272 for Ba. For Zn, Pb, Cu, Sn, Mo they gradually decrease with depth until 2.0-3.0 m, for Cr, Ni, Mn, Ba only until 1.5-2.0 m depth where they are the lowest. On the other hand, the highest median contents of V (19.3 ppm) and As (4.18 ppm) are in the lowermost layer 2.0-3.0 m. However, increase of the content of harmful chemical elements can be related not only to anthropogenic activity, but also to natural reasons, first of all to increase of clay content in soil. It has been shown that major elements Al, K and Ti are good indicators of clay content in urban soil [12]. In some of the cores (No 1, No 2, No 3) the lowermost layer has the highest contents of Al, K, Ti, meanwhile in other cores (e.g. No 4, No 9), on the contrary, it has the lowest contents of these clay indicators. Unequal clay content is the first obstacle for precise estimation of contamination level. Another obstacle for the aim of this research is that the new background values based on EDXRF measurements are not yet estimated for different types of natural soil.

Quaternary sediments comprise soil parent rocks in Lithuania. Vilnius is located at the boundary between the sediments formed during penultimate glaciation (Medininkai) and sediments of the last glaciation. Great part of Vilnius soil was formed on sandy sediments. The preschool is located in the area which is at the boundary between marginal glaciofluvial sediments of Medininkai glaciation represented by various sand and glaciofluvial sediments of Baltija glaciation represented by fine sand [13]. Since the dominant sediments are sandy, their background values are supposed to be much lower than of sandy loamy or loamy soil as it was shown on the basis of OAES results [14]. Therefore the lower quartile values were chosen in this research as approximate estimate of background. First of all the concentration coefficients of chemical elements were calculated dividing their content in sample by respective background value. Then the median of Al, K and Ti concentration coefficients was calculated in each sample. This value serves as an estimate of sample enrichment in clay (EC). Aiming to obtain more precise estimate of contamination level, the enrichment factors of harmful chemical elements were calculated by dividing their concentration coefficients by respective enrichment in clay.

In most cores (except No 6, No 7) the maximum value of EC coincides with maximum value of Al/Si which is well known indicator of clay content. Pearson correlation coefficient between these variables is 0.921 and is significant ($p<0.001$) indicating that dividing by EC might give more precise estimation of contamination level. Enrichment factors (EF) exceeding 1.3 can be used as indicators of anthropogenic pollution [15]. Likewise, EC>1.3 values can be used as indicators of increased clay content.

There are obvious differences between the cores according to layers with maximum EC values: in cores No 1, No 2 and No 3 they are in the lowermost layer, in cores No 4, No 5, No 8 and No 9 in the uppermost, in cores No 6 and No 7 in the intermediate layers. The cores No 5, No 7, No 8 and No 9 are sandy, meanwhile in other cores the enriched in clay layers exist at different depth.

Overall maximum EF values of the greater part of harmful chemical elements are in the uppermost layers: of Mo and Cr they are in core No 1 which is the closest to drill plant indicating that the latter is pollution source of preschool, of Zn in core No 6 which is close to the street and might be influenced by traffic, of Ni in core No 8, of As and Ba in core No 7. However, overall maximum values of 5 other harmful chemical elements are in deeper horizons: either at the depth of 1.0-1.5 m or at the depth 1.5-2.0 m.

Approximate depth of penetration of pollutants can be estimated according to EF>1.3 values. In the closest to the drill plant core No 1 the maximum depth of penetration is 1.5-2.0 layer for V, Mn, Ni and Zn. All 4 upper layers are sandy, meanwhile the lowermost is enriched in clay and is probably waterproof. For Pb, Cu, Sn the depth of penetration is not so deep: only until 1.0-1.5 m. These elements are not specific pollutants of drill plant. Maximum values of most pollutants in core No 1 are in the uppermost layer or at 0.5-1.0 m depth, the only exception is V.

The lowermost layer of cores No 2 and No 3 is also mostly enriched in clay, so maximum depth of penetration also does not exceed 2 m. However, there are some differences between these cores. The uppermost layer of core No 2 is slightly enriched in clay, so only some of pollutants (V, Mo, Mn, Sn, partly Zn) penetrate deeper. On the contrary, in core No 3 the upper layer is sandy and the next two are slightly enriched in clay, so maximum EF values are usually not in the surface layer, but deeper.

In core No 4 the uppermost layer is mostly enriched in clay, also the third layer at 1.0-1.5 m depth is slightly enriched in clay. Therefore maximum depth of penetration does not exceed 1 m, besides, maximum EF values of most pollutants (except V) are in the uppermost layer.

In cores No 5, No 7, No 8 and No 9 there are no layers enriched in clay, so maximum penetration of pollutants is the deepest, for some of them until 2.0-3.0 m depth, despite the fact that the highest EC value is in the uppermost layer.

In core No 6 the uppermost layer is sandy and the layer 0.5-1.0 m is mostly enriched in clay. Therefore maximum EF values of pollutants, except Mn, are in the uppermost layer. Despite the fact that there are two deeper layers (1.0-1.5 m and 2.0-3.0 m) with EC>1.3 in this core, penetration of pollutants is deeper, the maximum depth of penetration for Zn, Cr, Mn is 2.0-3.0 m. Most probably, either the layers are not quite waterproof (other than 1.3 value should be selected for distinguishing layers enriched in clay), or the layers were disturbed by digging for installation of the service-pipes, or contamination origin is different: not from atmosphere and infiltration, but from underground pipelines or contamination from borer.

IV CONCLUSION

Samples where maximum permitted concentrations of Mo, Pb, Sn are exceeded occur not only in the uppermost layers, but also in the deeper layers. Whatever is the reason of pollution, the depth of penetration is largely influenced by lithological composition of soil and is much deeper in sandy soil without layers enriched in clay.

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