Pedogeochemical Accumulating Associations of Education and Learning Institutions and Sport Stadiums in Klaipeda

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Abstract

The aim of the research was to reveal the main peculiarities of pedogeochemical accumulation on the territories of 51 schools and 27 football stadiums in the seaport Klaipeda (Lithuania). Energy dispersive X-ray fluorescence and optical atomic emission spectrophotometry were used for determining the total contents of Ag, Al, As, B, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Th, Ti, Tl, U, V, W, Zn, Zr. in topsoil. It is established that the right-bank central part of the city, where there are shipment storehouses and where the main shop of galvanic batteries works operated until 1989, is the most plentiful in toxic chemical elements. There is close relationship of accumulating associations with shipment storehouses of the seaport (Cr, Sn, Sr, Ag ir Pb) and urban development (Ag, Pb, Cu, Zn, Cr, Sn, Mo, Sr, P, S). The galvanic batteries works is not identified as the main pollution source of the city environment. Parallel pedogeochemical research has shown that the average content of Cl around the schools is 3.4 times higher than on the playing surfaces of the neighboring stadiums, of Zn 2.0 times, of S 1.4 times, of Cu 1.3 times, of Pb, Br, B, Mg, Ag 1.2 times of Cr, Sn, P 1.1 times higher, respectively.

Key words: heavy metals, galvanic batteries, urban topsoil, schools, football stadiums

Introduction

Before starting the monitoring of soil cover in Klaipeda, the exploratory geochemical investigations were done in 2006. The samples from the cover of football stadiums of the city and from the territories of education and learning institutions (schools) were among different other samples. Stadiums and schools, which are usually side-by-side, differ according to accumulation of pollutants. Besides the influence of contamination with atmospheric fallout, the surroundings of schools are also directly affected by other types of pollution arising from motor vehicles, which are parked alongside the schools, from construction materials of surrounding buildings and other urban or social activity. Meanwhile the stadiums can usually be influenced only by atmospheric pollution transfer or lawn fertilizers.

The aims of this research were the following: 1) to determine local geochemical background and its peculiarities in comparison with median element contents in Lithuania and Europe, 2) to distinguish chemical elements which determine contamination level and characterise the peculiarities of their distribution on the territory.

These was a hypothesis about the possibility of the influence of the former galvanic batteries works (GBW), which was one of the greatest factories in the former Soviet Union, operated in the seaport Klaipeda from the middle of the XXth century till 1989. Basing on analysis of 20 topsoil samples taken in 1991 on the territory of the first workshop of GBW, the pollutants were arranged according to their descending average concentration coefficients $K_{k,av}$ as follows: Hg($K_{k,av}$ = 193; maximum determined content was 16.9 mg/kg), Zn(93; 13600), Cu(30; 499), As(29; 1525), Sn(27; 377), Mn(24; 13870), Ni(17; 2087), Pb(12; 840), Ag(10; 3,9), Mo(4.8; 17,6), Sr (6.3; 1526), Co(3.4; 43), Ba(2.4; 6980), Cr(2.1; 245). According to other 15 topsoil samples taken at the same time on the territory of the second workshop of GBW the elements were arranged as follows: Hg($K_{k,av}$ = 70; maximum value was 5.5 mg/kg), Zn(4.1; 752), Mn(3.6; 2590), Ni(1.8; 44), Sr(1.6; 377). For other elements $K_{k,av}$ were lower than 1.5.

Materials and Methods

Topsoil samples were collected from a depth of 0-10 cm from the territories of 51 school and from the cover of the lawn of 21 stadium and were a composite of 20 to 30 sub-samples. These samples were dried and sieved to < 1 mm, then split and randomised

before submitting them for analysis. Real total contents of Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Th, Ti, Tl, U, V, W, Zn and Zr were measured by EDXRF equipment Spectro Xepos using screening analysis of turboquant methods, meanwhile of Ag, B and Co values by optical atomic emission spectrophotometry (OAES) using spectrograph DFS13 at the Institute of Geology and Geography (IGG) of Nature Research Centre, Vilnius. All samples were analysed twice and mean values of results were used for data analysis. Relative standard deviations RSD of double measurements of samples were within the intervals 20-30% for U, Sb, W, Se and Tl, 10-20% for As, V, Ag and Cl, 5-10% for Th, S, Cu, Sn, Mo, B and Cr, 3-5% for Br, Y, Na, Ni, Zr, Ga, Pb, Co, Nb and 0.8-3% for Rb, Sr, Fe, Si, K, Mn, Zn, Al, Ti, Ba, Ca, Mg and P. Quality control and improving of laboratory results has been performed since 1998 for OAES and since 2007 for EDXRF by participation in "International Soil-analytical exchange" (ISE) program organised by Wageningen University (Houba et al., 1996). More than 50 ISE reference samples and other certified reference materials were used for the recalibration of results.

More than a half of the contents of Sb, Se, Tl, U, W were below double value of their detection limit and the concentrations of Al, Fe, Ga, Y, K, Nb, Rb, Si, Sr, Th, Ti, V, Zr were within the near interval of their local background concentrations Cf. Therefore the greater part of these elements will not be analysed. Only 14 trace elements Ag, As, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V and Zn listed in HN 60:2004, also important elements of geosphere and biosphere Al, Fe, K, Mg, Na, P, S, Si, Sr and elements Cl, Br, B, S, Na which are specific to sea aerosols were selected for this research.

The local background values C_f were calculated as the third median value from the set of analytical results of 20 topsoil samples not located in the centre of the city after 2 consecusive eliminations of the measured values outside the interval (M-2S, M+2S), where M is the consecutive median and S is consecutive standard deviation.

The additive soil contamination index Z_{s14} was calculated by summing up concentration coefficients K_k of 14 chemical elements Ag, As, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V and Zn listed in Lithuanian hygienic norm HN 60:2004 (Lithuanian, 2004). The coefficients of danger K_0 were also calculated using the values of maximum permitted concentrations CP and methods presented in HN 60:2004. General danger of contaminated soil was estimated by choosing more dangerous from two categories: either according to Z_{s14} or according to K_0.

Spearman rank correlation coefficients were analysed between the contents of the elements forming anomalies (except for Hg) and the distances from two workshops of GBW, location sites of shipment storehouses and Memelburg castle, i.e. the site where development of the city started.

Principal component analysis with varimax normalised rotation was used for distinguishing of associations.

Results and Discussion

Local geochemical background Cf (Table 1) is distinguished by more than 3 times higher values of Sn, 2.1 times higher S, 1.9 times higher Zn, 1.6 times higher Pb and P, 1.5 times higher Ca, 1.4 times higher Mg, 1.3 times higher Cu, 1.2 times higher Mo and Ni, 1.1 times higher Na in comparison with agricultural soils of Lithuania (Reimann et al., 2003). Median contents of elements presented in geochemical atlas of Lithuania (Kadenas et al., 1999) also confirm relative enrichment of local background of Klaipuda Cf in the following elements: Zn (2.2 times), P (1.7), Pb (1.4), Sn (1.3), Cu (1.1).

In comparison with agricultural soils of Northern Europe (Table 1), the topsoil of schools (MD_{Sc}) and stadiums (MD_{At}) located in the city centre is distinguished by higher median contents of the following elements (respective enrichment factors are in parentheses): Zn (5.8 for MD_{Sc} and 2.1 for MD_{At}), Cl (5.4, 1.4), Sn (3.9, 5.1), Pb (3.1, 3.3), Cr (2.7, 1.2), S (2.6, 2.1), Cu (2.5, 1.6), Ca (2.1, 1.0), Mg and Ni (1.3, 0.9), P (1.3, 1.1), Si (1.1, 1.2).

Factor analysis of data of 20 samples used for background estimation has shown that the elements Ni, Cr, Fe, Cu, V, Al, Co, Mg, Ti and K, which are indicators of clay and iron group minerals, are mostly related to the 1st factor (its input to total variation is 29.1%), their correlation coefficients are the highest ($r>0.5$), meanwhile Si, which is representative of sandy clastogenic soil, is their antagonist. The 2nd factor (17%) unites the elements K, Al, Ti of clay soil and Mg, their antagonists are biophylic elements P, Zn, S, Cu. Representatives Ca, Br, Mg and S related

to carbonates, which are antagonists to Si, are correlated with the 3rd factor (14.4%). The 4th factor (13.0%) reveals the group of elements Pb, Ag, Sn, Cu, (Zn) prevailing in technogenous anaomalies. Such grouping of elements is not accidental and shows that part of the elevated contents of Ag, Sn, Pb, Cu, Zn in conditions of ralative background might be determined by technogenic activity. Meanwhile part of elevated contents of other elements is determined by natural sorption of minerals (relationship with Al, K and Fe) or biogeochemical processes (relationship with P, S, Ca).

Table 1. Median values pedogeochemical parameters in topsoil of football stadiums and schools of the centre of Klaipeda.

Parameters	In city centre		Background	
	MD_{At}	MD_{Sc}	C_f	AS_{EU}
Ag	0.148	0.173	0.066	*0.071
Al	29875	25042	34966	47519
As	4.02	3.03	2.90	4.0
B	27.0	31.7	25.6	*26.6
Ba	354	370	335	404
Br	4.69	5.62	4.73	-
Ca	9700	**20554**	7824	9934
Cl	**113**	**429**	**99**	80
Co	4.9	4.4	4.5	5.3
Cr	**37.7**	**86.1**	33.0	32
Cu	**17.4**	**27.0**	10.7	11
Fe	11754	12685	13471	17065
K	15110	15133	**18118**	15605
Mg	3055	**4417**	**4024**	3437
Mn	280	302	297	426
Mo	0.86	0.72	0.67	*0.67
Na	5934	5771	5385	8977
Ni	**11.3**	**12.9**	**10.5**	9.9
P	**934**	**1047**	**918**	820
Pb	**56.4**	**52.7**	**21.1**	17
S	**541**	**661**	**439**	253
Si	**381974**	**366006**	**367083**	331387
Sn	**5.60**	**4.26**	**2.67**	1.1
Sr	**82.0**	**84.2**	**71.9**	68
V	24	25	27	39
Zn	**91**	**250**	**63**	43

Abbreviations. Median values in the centre of Klaipeda, in mg/kg: MD_{At} - in stadiums, MD_{Sc} - in schools, ASEU - in agricultural soils of Northern Europe (Reimann et al., 2003), C_f - local background value. When no data are given by Reimann et al. (2003), the median values from geochemical atlas of Lithuania (Kadunas et al., 1999) are given instead, they are marked by asterisk. Medians in Klaipeda which are higher than ASEU yra in bold.

No significant ($p<0.05$) negative Spearman rank correlation coefficients were revealed between the contents of elements in topsoil of the parts N2 and N3 (Fig.1) and the distance of sampling sites from location of the second workshop of GBW. On the contrary, significant positive relationships with this distances were found for Sn, Sr, Pb, Cu, Mo, Ag.

The K_k of chemical elements in topsoil of newer quarters of the city (N3), which were started to build since the middle of the second half of the XXth century and which are located to the west and southwest from the second workshop of GBW and the territory of free economic zone, in rare cases exceed 2. In all school or stadium territories on this peripheral part topsoil Z_{s14} does not exceed 16 and the values of coefficient of danger K0 do not exceed 1. Therefore topsoil state of stadiums and schools in this part of the city is estimated as permissible.

In the central left-bank topsoil of 2 schools belongs to moderately hazardous category, Zn, Cu and Pb contribute more than 50% to their Zs14. Moderately hazardous contamination category of 1 stadium is determined by Pb ($K_k = 6$; $1<K_0<3$).

From 11 schools and 4 stadiums located in central right-bank part (N1) the contamination category of 4 stadiums and even 5 schools is estimated as moderately hazardous, of 2 other schools, which are near the shipment storehouses, even as extremely hazardous. The latter ones are determined by K_0 values of Cr, which are higher than 10. The content of Cr exceeds its maximum permitted concentration CP given in HN 60:2004 in 8 schools and 1 stadium, Zn in 4 schools, Cu and Sn in 2 other schools. In most cases the moderately hazardous contamination category is determined by Cr content, this element is in accumulating associations together with Zn, Pb, Sn, Cu and Ag.

In central right-bank (N1) and central left-bank (N2) parts there was significant ($p<0.05$) positive relationship between measured contents of Cr, Cu, Sn and Pb and the distance of sites from the first workshop of GBW. However, comparison of element contents with the site distances from shipment storehouses has revealed significant negative correlation for Cr, Sn, Sr, Ag and Pb, which are not indicators of pollution of GBW.

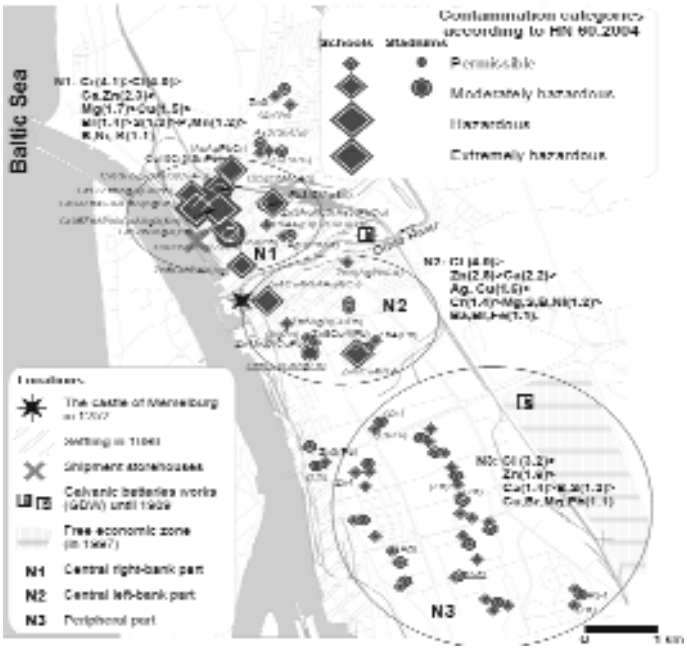

Figure 1. The associations of the contaminating elements in topsoil and the total contamination index Zs14 on the territories of schools and football stadiums of Klaipeda city.
Note. The associations of school territories are in regular font, meanwhile of stadiums are in italic and underlined. The number after the symbol of element indicates its concentration coefficient Kk, the elements with $2<K_k<3$ are in parentheses. For each part of the city the enrichment coefficients of schools in comparison with the side-by-side located stadiums are listed in bold.

The expansion of technogenous contamination of topsoil in the context of the whole city is closely related to its historical development, which is indicated by significant ($p<0.05$) negative correlation between the content of Ag, Pb, Cu, Zn, Cr, Sn, Mo, Sr, P, S and the distance from location of Memelburg castle.

Comparison of side-by-side schools and stadiums has shown that the content of Cl in schools exceeds the respective content in stadiums on the average 3.4 times, Zn 2.0 times, Ca 1.8 times, S 1.4 times, Cu 1.3 times, Pb, Br, B, Mg, Ag 1.2 times, Cr, Sn, P 1.1 times. This tendency is observed in all parts of the city.

Conclusion

Higher content of Sn, S, Zn, Pb, P, Ca, Mg, Cu, Mo, Ni, Na than in all Lithuania is the peculiarity of the local geochemical background. Anomalous high contents of trace elements, first of all of Cr are found near shipment storehouses and are not related to activity of the former galvanic batteries works. Accumulation of Ag, Pb, Cu, Zn, Cr, Sn, Mo, Sr, P, S is related to expansion of Klaip?da. Schools are more enriched in Cl, Zn, Ca, Cu, Pb, Br, B, Mg, Ag, Cr, Sn, P, Ba and Ni in comparison with side-by-side located stadiums.

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