Geochemical studies for environment in the Institute of Geology of Lithuania

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The problem of near-surface air quality but mainly the concentration of heavy metals in urban areas is actual up to now. Traditional methods of air quality assessment by using stationary or mobile air analysis stations often have not yielded desirable results. The main reason is that air composition is a quickly changing system. That is why continuous investigations of air quality are needed. In addition, a more dense network of observation stations is necessary, but this system is very expensive. Besides, the determined spectrum of metals is narrow. That is why the relevant information about the air quality during a longer period is very scarce.

One of the non-traditional ways of solution of this problem is the geochemical exploration of snow cover in spring. It is especially effective in those countries where it lies for a longer period of time. In this respect the winter of 1995–1996 in Lithuania was very favourable. The snow cover formed in November of 1995 did not thaw until spring (end of March, 1996). This enabled to collect 51 samples of snow in Alytus from the area of almost 34 km^2 before the beginning of intensive thaw. A nearly regular grid of sampling points was chosen on scale 1 : 100,000. The pattern of the town was also taken into account.

Each snow sample consisted of 9 sub-samples that were collected from 9 sites (20 x 20 cm, total area was about 0,36 km^2) to the bottom of the snow cover. The snow was collected to polyethylene bags and transported to the laboratory of the Institute of Geology. It was immediately placed in plastic buckets and thawed at room temperature. The volume of each thawed water sample ranged from 21 to 25 litres. Later, it was filtered using FILTRAK-91 (very dense filter paper for all the fine and finest precipitates).

The collected dust was mineralised together with a filter, and weighed. It was analysed by DC Arc Emission Spectrometer (DC ARC ES) for Ag, Al, B, Ba, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, P, Pb, Sc, Sn, Sr, Ti, V, W, Y, Zn and Zr. It enabled making maps of elemental distribution in dry fall-outs (in micrograms of elements per gram of dust), and evaluating the intensity of atmospheric load (grams of elements in square kilometre per day). This could be accomplished because the time of snow cover exposition, dust concentration per square unit, and concentration of elements in dust were known.

The filtrate was analysed by AAS for Cr, Cu, Mn, Ni, Pb and Zn („Varian 400" equipment). This enabled to prepare supplementary maps of distribution of dissolved fraction in snow water (in milligrams per cubic meter of snow water). Thus, atmogeochemical evaluation of the study area near Alytus was realised.

Some of the obtained are as follows:

1. Median concentration of Pb in dust collected from snow (1,300 mg/kg) exceeded its baseline (12.8 mg/kg) in topsoils of Alytus by 102 times, Ag (4.7/0.074) — 100, Zn (1,600/18.9) — 85, Cu (355/6.88) — 52, Ni (340/10.7) — 32, Sn (54/1.83) — 30, V (570/26.5) — 22, Mo (6.8/0.563) — 12, Cr (200/28.2) — 7.1, P (3,000/529) — 5.7, Co

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(14/3.34) — 4.2, B (46/19.1) — 2.4, Sr (148/71.8) — 2.1, Ba (600/303) — 2.0, Mn (680/344) — 2.0 times.

2. The intensity of atmospheric load in Alytus (34 km^2, dry fall-outs) reached 1,070 g for P, 620 g for Zn, 440 g for Pb, 312 g for Mn, 226 g for V, 187 g for Ba, 127 g for Ni, 111 g for Cu, 71.2 g for Cr, 54.6 g for Sr, 19.5 g for Sn, 16 g for B, 5.3 g for Co, 2.58 g for Mo, 1.97g for Ag.

3. Median concentration of Zn in dissolved fraction of snow-water was 43.3 mg (per cubic meter), Pb — 10 mg, Cu — 4.63 mg, Ni — 4.15 mg, Cr — 2.91 mg, Mn — 0.23 mg, Cd — 0.21 mg.

The second of the main ways for evaluating the quality of dwelling medium is the pedogeochemical analysis of topsoil which reflects the integral technogenical loading of pollutants including atmogenical one. The real structure of contamination is determined with detailed mapping. The isolines in monoelement and multielement pedogeochemical maps are drawn in relation to: 1) the local level of geochemical background, and 2) the sanitary and phytotoxic limits. Topsoil samples are analysed for Ag, As, B, Ba, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Nb, Ni, P, Pb, Rb, Sc, Sn, Sr, Th, Ti, V, Zn, Zr, Y, Yb, U, W. In 1998, additional samples have been examined. They included more than 7,000 topsoil samples from the Vilnius area, over 60 industrial and municipal solid waste landfills (scale 1 : 2,500–1 : 10,000), high industrialised dwelling districts (scale 1 : 10,000–1 : 15,000) and the remaining part with recreational zones (scale 1 : 25,000–1 : 50,000). Since 1995, Hg and Cd have also been determined in topsoils of Vilnius. Particularly harmful elements such as Ag, Cd, Cr, Cu, Hd, Mo, Ni, Pb, Sn, and Zn contributed from 80 to 90% to the most intensive multielement pedogeochemical anomalies. The selected results of geochemical investigations of the dwelling districts of Vilnius: Zverynas, Snipiskes and Zirmunai, are presented in tab. 1.

Tab. 1. The selected results of ecogeochemical investigations of topsoil in the dwelling districts of Vilnius

Element	Zverynas			Snipiskes			Zirmunai		
	Md	I_{md}	Ex_p	Md	I_{md}	Ex_p	Md	I_{md}	Ex_p
Ag	0.18	**2.9**	4.0	0.19	**3.3**	3.7	0.18	**2.6**	1.9
Cd	0.42	**2.4**	–	0.43	**2.4**	–	0.19	**1.9**	–
Cr	37	**1.6**	2.2	31	**1.4**	1.9	30	**1.5**	3.4
Cu	14	**2.0**	4.0	18	**2.4**	2.6	17	**2.1**	5.9
Hg	0.12	**4.7**	18	0.16	**6.0**	21	0.09	**3.1**	10.0
Mo	0.93	**1.6**	0.4	0.89	**1.4**	1.5	0.88	**1.4**	3.4
Ni	15	**1.7**	–	12	**1.4**	0.7	14	**1.6**	1.9
Pb	39	**3.0**	10	39	**2.4**	13	43	**3.1**	12.5
Sn	3.6	**2.0**	0.4	3.7	**2.0**	0.3	3.0	**1.6**	0.3
Zn	120	**5.7**	24	130	**6.0**	22	68	**2.9**	6.5
I_{multi}		**21.1**			**19.7**			**13.2**	

Notes: md — median value (in mg/kg); I_{multi} — median level of loading calculated in relation to the level of local geochemical background; Ex_p — the number of observations that exceed the phytotoxic limit (in %) relative to the total number of observations in the investigated area

A short description of the study Vilnius area.

Zverynas: total area (S) — 2.6 km^2, number of topsoil samples (n) — 224. Lack of industrial infrastructure, private gardening prevails there. Industrial facilities (mainly food plants) are situated on its outskirts.

Snipiskes: S — 2.96 km^2, n — 270. Private gardening is intermingled with many-stored houses. There is some transport and different industrial enterprises between residential areas.

Zirmunai: S — 5.7 km^2, n — 321. Many-stored houses are prevailing. There are a lot of transport and mechanical and electrical engineering enterprises. The base of former motorised military sub-unit is located in the centre.

The analysis of the total contamination index (I_{multi}), calculated by summing up the median level of loading for each element (I_{md}), showed that the highest level of pollution was in topsoil of Snipiskes and Zverynas; and the lowest one was recorded in Zirmunai. The main cause is that in residential districts of gardening type the prevailing pollution resulted from the local private municipal wastes. The contamination caused by enterprises was observed at a small distance from them. The structure and origin of pedogeochemical anomalies generally depends on peculiarities of industrial enterprises, road transport, people activity and historical aspects.

The highest pollution level was detected in soils of mechanical and electrical engineering facilities, roads (and their repair plants) of the Vilnius area.

The results of detailed mapping of industrial soils have been closely connected with the type of production (tab. 2).

Tab. 2. Level of topsoil loading in the areas of different type of industrial facilities

Element	Industrial facility production							
	boring instruments n = 62		electrical measuring instruments n = 85		motor repairs n = 82		bakery's goods n = 46	
	I_{md}	Ex_p	I_{md}	Ex_p	Imd	Ex_p	Imd	Ex_p
Ag	**3,2**	–	**32.6**	53	**1.7**	–	**1.6**	–
As	**3.2**	34	**1.5**	7.1	**1.9**	2.4	**1.1**	–
B	**0.94**	4.8	**0.93**	–	**1.2**	–	**1.2**	–
Ba	**2.5**		**1.1**		**1.7**		**1.6**	
Co	**18.7**	79	**1.6**	3.5	**1.8**	1.2	**1.7**	–
Cr	**42.3**	56	**2.8**	33	**2.8**	24	**1.4**	–
Cu	**13.4**	65	**17.9**	82	**6.5**	35	**1.8**	2.2
Mn	**1.9**	23	**1.4**	1.2	**1.4**	2.4	**1.2**	–
Mo	**408**	100	**11.1**	78	**6.0**	46	**2.3**	–
Ni	**11.4**	63	**2.8**	16	**2.7**	6.1	**1.4**	–
Pb	**4.4**	23	**4.8**	25	**7.2**	55	**2.0**	–
Sn	**5.8**	3.2	**6.1**	9.4	**3.8**	7.3	**2.3**	–
V	**16**	79	**1.1**	1.2	**1.0**	–	**1.1**	–
W	**782**		**16.6**		**8.2**			
Zn	**5.3**	21	**8.6**	48	**7.3**	32	**4.9**	15
I_{multi}	**1374**		**98**		**41.2**		**12.6**	

Notes: n — number of analysed topsoil samples; other explanations are in tab. 1; Cd and Hg were not analysed

Industrial facilities manufacturing boring and electrical instruments are located close to one another. It can be assumed that pollutants coming from individual sources overlap. The factor analysis results show that characteristic for each enterprise group of elements (with greatest I_{md} — tab. 2) generally contributes to the total variability of chemical elements, which is reflected by loading of the main factor (tab. 3). The number of elements in groups corresponding to factors 2, 3, ... is much smaller. In generally they do

Tab. 3.

Boring instruments production:
Factor 1 (**55.0%** — coefficient of factor variable — in per cent): V_{97} (97 — multiplied by 100 correlation coefficient with the factor) — Cr_{97} — Ni_{94} — W_{92} — Co_{87} — As_{80} — Mo_{75} — Sn_{70} — Mn_{62} — Ga_{44} — Ba_{41} — ...;
Factor 2 (**14.1%**): Zn_{85} — Cu_{80} — B_{80} — Pb_{79} — Ag_{66} — Ga_{54} — Sn_{53} — Ba_{45} — Mn_{44} — Co_{37} — ...;
Electrical measuring instruments production:
Factor 1 (**44.8%**): Sn_{90} — Cu_{88} — Zn_{87} — Ag_{86} — Ni_{85} — Cr_{82} — Pb_{68} — B_{56} — Mo_{43} — Co_{36} — ...;
Factor 2 (**14.2%**): W_{88} — Mo_{84} — V_{73} — Co_{70} — Ga_{40} — P_{32} — B_{31} — ...;
Factor 3 (**8.1%**): Mn_{86} — Ga_{60} — P_{59} — As_{53} — V_{51} — Ba_{33} — ...;

not reflect the type of the facility production, but the character of surrounding sources of contamination.

In the contaminated places, the biogeochemical accumulation of chemical elements is high. It is closely linked not only to the soil geochemistry, but also to bioavailability of the elements, and probably to the level of air pollution. The agricultural activity in these areas should be limited.

The variety of plants in the area of one of the municipal waste landfills in Vilnius enabled to analyse the possibility of technogenical biogeochemical accumulation of elements. This was accomplished by collected **meadow grass** from 3 sites:

a) at the top of municipal solid waste landfill,
b) at its foot,
c) in the surrounding area,

as well as **Caucasian plums** from 3 sites:

a) on the slope of the landfill,
b) in botanical gardens of Vilnius university,
c) in out-of-town garden.

At the same time **topsoil** was investigated within 3 levels of the landfill:

1) at the top,
2) on the slope,
3) at the foot,

as well as in the neighbourhood. Each investigated object was characterised by 16 samples analysed for Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, P, Pb, Sn, Sr, V, Zn using DC Arc ES.

The set of elements with anomalous concentrations in soils from the top of the landfill includes Cu (average loading index I_{av} relative to natural concentration in soils is 10), Ag (I_{av} = 7.8), Zn (6.3), Cr (2.6), Pb (2.5), Sn (2.5), Mo (1.2), Ni (1.2), Sr (1.2). I_{av} of the other elements are close to 1. Total average multielement index of soil pollution $I_{multi, av}$ is 27. The set of elements on the slope of the landfill includes Ag (I_{av} = 29), Zn (25), Cu (11), Sn (4.3), Pb (4.0), Cr (2.0), Mo (1.9), Ni (1.6), B (1.2), Sr (1.2) and $I_{multi, av}$ is 72. The set of elements in soils at the foot of the landfill includes Sn (I_{av} = 66), Zn (32), Ag (28), Cu (26), Pb (12), Mo (6.1), Cr (3.4), Ni (3.2), P (1.9), Ba (1.5), Sr (1.4), B (1.3), Co (1.2), $I_{multi, av}$ is 172. It is natural that total level of contamination is increasing from the top of the landfill downward to its foot. It is clear because precipitation washes out toxical elements that migrate downward to the bottom of the landfill.

The chemical composition of grass growing in different places of the landfill is also varied. The grass growing on the top of the landfill shows the following anomalous concentrations: Zn (average biogeochemical accumulation relative to natural concentrations in grass I_{av} = 5.0), Mo (3.2), Cu (1.7), P (1.6), Ag (1.3). Total average multielement index of biogeochemical accumulation $I_{multi, av}$ = 9. The anomalous elemental concentrations in grass growing at the foot of the landfill include Mo (I_{av} = 9.4), V (6.7), Ag (6.5), Cu (4.2), Mn (3.5), Ni (2.4), Pb (2.3), Cr (1.9), B (1.9), Ba (1.3), $I_{multi, av}$ is 31. The sequence of the elements in grass differs from that in soil due to diverse bioavailibility of elements. An increase of the total concentrations of elements is evident. The average geochemical accumulation coefficients showing the ratio of elemental-pollutants in the pulp of plums from the landfill and plums from the botanical gardens of Vilnius university exceed. They indicate a possible influence of the landfill on the fruit quality: Ag — 5.4, Cu — 4.5, Ni — 4.4, P — 1.8, Mn — 1.6, B — 1.5, Cr — 1.3, V — 1.2. The content of Zn in the pulp of plums is similar in both places, whereas of Pb and Mo is even lower within the landfill. It can be explained by the location of the botanical gardens near the large industrial district of Vilnius. The chemical composition of plums in the out-of-town garden is quite different. The concentrations of Pb and Zn exceeded even 5 and 1.8 times those from the landfill. As the garden is located near the highway this fact can be explained by atmospheric contamination from vehicle exhausts. Similarly, the content of B in the pulp of plums from versus out-of-town garden-plot the landfill was higher twice, Cu — 1.8, Mo — 1.6, Ni — 1.3, Ag — 1.3, Cr — 1.1.

The variety of plants growing within the municipal waste landfill enabled to evaluate separate species of vegetation as potential extractors of heavy metals for remediation of heavily contaminated soils. For this aim biogeochemical analyses of mixed meadow grass, touch-me-not with small

Tab. 4. Potential of biogeochemical accumulation of some species of plants

Element	Moss		Mixed meadow grass		Nettle		Touch-me-not	
	A_{aver}	A_{max}	A_{aver}	Amax	Aaver	Amax	Aaver	Amax
Ag	19.3	24.8	3.11	8.9	0.63	1.0	0.66	1.1
B	9.8	13.7	3.8	9.4	9.2	12.2	2.8	3.8
Ba	2.8	3.7	1.41	2.0	1.5	2.7	2.9	5.0
Co	2.8	3.9	0.6	1.8			0.33	0.6
Cr	10.0	53.6	0.4	0.8	0.12	0.5	0.35	0.6
Cu	48.8	62.8	20	32.7	11.2	14.4	5.2	7.9
Mn	1.6	1.8	1.8	3.6	0.09	0.1	0.64	1.2
Mo	18.7	28.4	37.8	60	28.7	43	4.71	6.6
Ni	5.2	6.4	0.6	1.5	0.28	0.6	0.64	1.1
P	33.2	40.8	23.8	28.1	23.1	27.2	18.1	27.2
Pb	24.2	38.8	0.9	2.1	0.43	0.8	2.1	3.4
Sn	32.6	102					0.51	0.8
Sr	4.5	4.9	2.3	3.1	4.3	4.7	2.2	3.1
Ti	1.4	1.9	0.14	0.5	0.02	0.04	0.13	0.24
V	3.7	4.5	0.76	3.2	0.15	0.2	79	1.2
Zn	86.9	126	10.2	54	7.6	14.2	3.1	6.5

Notes: A_{aver} — average index of biogeochemical accumulation calculated for the content of elements in ashes of plants relative to the level of local geochemical baseline in soils; A_{max} — maximum index of biogeochemical accumulation flowers, great nettle and moss were done. Sixteen parallel samples of each plant species were taken. They were mineralised by heating at a temperature of 400–450°C (tab. 4).

The concentrations of elements determined in ashes were compared with their baseline equivalents in uncontaminated soils. The investigations have shown that the moss has the greatest ability for bioaccumulating chemical elements. The meadow grass follows it. By continuous mowing and removing of the grass, toxicants can be eliminated from the contaminated soil.