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LITHUANIAN SOIL QUALITY CRITERIA BASED ON THE HEAVY METAL LEVELS, AND THEIR APPLICATION IN URBAN TERRITORIES WITH DIFFERENT INDUSTRIAL IMPACT

Ričardas TARAŠKEVIČIUS[1], Rimantė ZINKUTĖ[1]

Abstract. Following the Lithuanian hygienic norm, a topsoil quality was evaluated for Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, and Zn in public-residential micro-zones of four Lithuanian towns with a different industrial impact. A general evaluation took into account maximum permitted concentrations of the elements and the maximum danger coefficient K_0, as well as the total contamination index Zd. That last one was related to the element background values, reflected the combined pollutants effect, and in this way, predetermined the final result. In urban public-residential zones, this index depends mostly on Zn, Pb, Ag, Cu and Sn contents.

The topsoil geochemical quality in these zones depends not only on concentration of pollution sources, but also on the time-span of urbanisation, and density of the population. The increase of theses factors leads to a development of less favourable conditions. The topsoil quality is the least favourable in the central part of the largest city (Vilnius), followed by medium town (Šiauliai), and finally by two small towns (Joniškis, Mažeikiai). The higher topsoil enrichment with more elements-pollutants in Joniškis than in Mažeikiai can be explained by differences in historical development (Joniškis is older than Mažeikiai) and a disturbance of the soil cover in Mažeikiai during the construction works. Therefore, in old and densely populated public-residential districts the monitoring of urban soils is urgent.

Key words: urban soil, heavy metals, maximum permitted concentrations, total contamination index.

Abstrakt. Zgodnie z litewskimi normami jakości ornej warstwy gleby, oceniono zanieczyszczenie gleb przez Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V oraz Zn na terenie osiedli mieszkaniowych w czterech litewskich miastach, będących pod różnorodnym wpływem przemysłu. Przy ogólnej ocenie jakości warstwy glebowej uwzględniono nie tylko maksimum dozwolonej koncentracji pierwiastków i wartość maksymalnego współczynnika zagrożenia K_0, ale także, w celu lepszego określenia miejsc o niekorzystnych właściwościach, indeks całkowitego zanieczyszczenia Zd, który jest związany z wartością tła geochemicznego pierwiastków. Indeks Zd terenów miejskich – osiedli mieszkaniowych – zależy głównie od zawartości Zn, Pb, Ag, Cu i Sn.

Geochemiczna jakość warstwy glebowej na tych terenach zależy nie tylko od skupienia źródeł zanieczyszczeń, ale także od długotrwałości urbanizacji i gęstości zaludnienia. Podwyższenie tych wskaźników prowadzi do powstania niekorzystnych warunków. Najmniej korzystne warunki zaobserwowano w centralnych częściach największych miast (Vilnius), następnie w średniej wielkości miastach (Šiauliai), a najlepsze w dwóch najmniejszych miastach (Joniškis, Mažeikiai). W Joniškis górna warstwa glebowa była bardziej wzbogacona w pierwiastki zanieczyszczające, niż w Mažeikiai, co można wytłumaczyć różnicami w historycznym rozwoju tych miast (Joniškis jest starsze od Mažeikiai) oraz zaburzeniem struktury gleb w Mažeikiai podczas prac budowlanych. Potrzebny jest zatem systematyczny monitoring gleb miejskich, zwłaszcza na obszarze starych i gęsto zaludnionych dzielnic.

S[3]owa kluczowe: gleby miejskie, metale ciężkie, maksimum dozwolonej koncentracji pierwiastków, indeks całkowitego zanieczyszczenia.

[1] Institute of Geology and Geography, T. Ševčenkos 13, 03223 Vilnius; e-mails: Taraskevicius@geo.lt, Zinkute@geo.lt

INTRODUCTION

Heavy metal levels in different environmental components, influenced by industrial and other pollution sources, are the most important indices of the urban quality. The geochemical mapping in urban territories was carried out because heavy metals accumulated in a topsoil (Birke, Rauch, 1994; Pasieczna, 2003). It was expedient to compare element contents in the topsoil with their limit values, i.e. levels, which could not be exceeded without risk to a human health and/or to the environment. The Swedish guideline values, available on the internet, may be as an example (http://www.internat.environ.se/).

The aim of this research was to evaluate the topsoil quality as far as Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, and Zn contents were concerned, in the public-residential micro-zones of the four Lithuanian towns (Vilnius, Šiauliai, Mažeikiai, and Joniškis), characterised by a different industrial impact, to reveal main pollutants in this group and to analyse the relationship between characteristics of these towns and the topsoil geohygienic quality.

The towns under research differ from each other. The capital, Vilnius, is the largest centre of industry and motor transport in Lithuania. Metalworking, electrical engineering, production of food and building materials are the main types of the industry, there. Šiauliai is the fourth town in Lithuania, with metalworking (production of bicycles), electrical engineering (production of TV sets, electrical engineering equipment and devices), tanning and footwear enterprises. Mažeikiai has in its northern part an electrical engineering plant and a huge oil refinery, and on the northwestern one – a power plant built in 1980. Joniškis is the district centre, but the industry has been not much developed there, except for food industry and a repair of agricultural machines.

Vilnius was founded in 1323, Šiauliai in 1524, and Joniškis in 1616. More intensive development of Mažeikiai started in 1869. The total number of population in Vilnius is about 553,000, in Šiauliai – 133,800, in Mažeikiai – 45,300 (the eighth town in Lithuania), and in Joniškis – 11,300. The average population density in Vilnius is 1,380 people/km^2, in Šiauliai – 1,650 people/km^2, in Mažeikiai – 3,250 people/km^2, and in Joniškis – 1,150 people/km^2. In the central part of Vilnius, it exceeds 6,000 people/km^2 and in its peripherals is about 1,030 people/km^2. The high density in Mažeikiai is a result of its recent development. In 1959, only 7,957 people lived there, and the average population density was that time equal to 740 people/km^2.

METHODS

Complex samples composed of several sub-samples were taken from the upper soil layer (0–10cm depth). A sampling scale was different (Table 1). Sampling sites were classified into different land use micro-zones, in Vilnius also into two groups (6 central districts mapped in detail and 15 peripheral districts).

All samples were air-dried. Fraction <1mm, after having been burned to ash at 450^{0}C, and mechanically pulverised, was analysed by DC Arc Emission Spectrophotometry for determination of the total contents of Ag, B, Ba, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sn, V, and Zn. Since 1997, the participation in *the International Soil-Analytical Exchange* subprogram, organised by the Wageningen University, ensured the quality of analytical results.

In the present research, only the topsoil from public-residential micro-zones was evaluated, because these areas were characterised by the highest population density and because the Lithuanian hygienic norm (HN 60-2004, 2004) was intended for agrarian, recreational, and residential territories. A complex evaluation was carried out taking into account *maximum permitted concentrations* (MPC) of the above-mentioned heavy metals and their *coefficients of danger* K_0, and *total (additive) contamination index* Zd of the same elements.

MPC are concentrations, which have no direct or indirect (through plants, air or water) influence on human health (HN 60-2004, 2004). For each element, the *coefficient of danger* in comparison with its MPC was calculated according to the formula $K_0 = C/MPC$, where C is the determined content of the element. Then, the maximum K_0 was chosen. The higher this coefficient was, the greater could be the danger caused by contaminated soil. A category of danger could be: allowable (A),

Table 1

Information on sampling in four Lithuanian towns

Territory	Abbreviation	Scale	Total number of samples	Number of samples from public-residential micro-zones
Six central districts of Vilnius *	V-6	1:7500–1:15 000	2272	1406
Peripheral districts of Vilnius	V-15	1:100 000	261	129
Šiauliai	S	1:100 000	110	42
Mažeikiai **	M	1:10 000–1:25 000	428	192
Joniškis	J	1:25 000	108	45

* – detailed description in Taraškevičius, 2000, ** – detailed description in Kadūnas *et al*., 2001

when K_0 <= 1, medium dangerous (MD), when K_0 = 1–3, dangerous (D), when K_0 = 3–10 or extremely dangerous (ED), when K_0 >10.

Except for MPC, the *total (additive) contamination index* Zd was calculated at each site according to the formula: $Zd = \Sigma Kk_j - n+1$, where the sum was in accordance with j, Kk_j was *concentration coefficient* of j^{th} element at the site, and n was the number of contaminating elements. The concentration coefficient Kk was a ratio of the element content at the site to the background value. The Zd index revealed a common deviation of chemical elements pollutants from the background. Investigations in Russia (Revich, Sayet, 1989) and in Vilnius (Krasilščikovas *et al*., 1988) have shown that the Zd index was related to the sick children rate. According to Zd, the recommended categories of danger caused by the contaminated soil are as follows: Zd<16 – allowable (A), Zd = 16–32 – medium dangerous (MD), Zd = 32–128 – dangerous (D), and Zd>128 – extremely dangerous (ED).

In this research, the regional soil background values (Kadūnas *et al*., 1999) were the basis for Kk and Zd calculation. For Joniškis, Mažeikiai and Šiauliai, they were adjusted in the way, which had been described earlier (Taraškevičius, Zinkutė, 2003). The general (G) evaluation of each site soil quality was obtained by choosing the most dangerous category.

RESULTS AND DISCUSSION

In all towns, the Zn content in soil is exceeding MPC in most of sites, i.e. this element predetermines unfavourable quality of the soil (Table 2). Unlike Vilnius, in Mažeikiai and Šiauliai, it is followed by Ba. Barium is also among few elements, which exceed MPC in arable rural land (Zinkutė *et al*., 2005). This is partly because the background values of Ba are much closer to MPC compared to other elements (Table 3). A comparison of the Vilnius peripheral districts with the central districts indicates that the role of chalcophiles in deterioration of soil quality increases in more densely populated areas. They are most probably related to the transportation influence (Taraškevičius, Šiaudinienė, 2001). These results are in agreement with the previous investigation of arable land zones: unlike in rural areas, where Ba and B sometimes exceed their MPC, in urban areas (represented by Joniškis and Šiauliai), the chalcophiles are main elements exceeding their MPC (Zinkutė *et al*., 2005).

Table 2

Percentage of topsoil samples from public-residential micro-zones of the towns with MPC values exceeded

Joniškis		Mažeikiai		Šiauliai		Vilnius-15		Vilnius-6	
Zn	2.2	Zn	3.6	Zn	11.9	Zn	7.8	Zn	18.1
Ag	–	Ba	1.0	Ba	4.8	Sn	4.7	Sn	16.2
B	–	Cr	0.5	Cr	2.4	Ba	3.1	Pb	14.8
Ba	–	Sn	0.5	Pb	2.4	Ag	2.3	Ba	12.7
Co	–	Ag	–	Sn	2.4	Cu	2.3	Ag	6.5
Cr	–	B	–	Ag	–	Pb	2.3	Mo	4.6
Cu	–	Co	–	B	–	Cr	0.8	Cu	3.8
Mn	–	Cu	–	Co	–	B	–	Cr	1.4
Mo	–	Mn	–	Cu	–	Co	–	B	0.5
Ni	–	Mo	–	Mn	–	Mn	–	Mn	0.3
Pb	–	Ni	–	Mo	–	Mo	–	V	0.3
Sn	–	Pb	–	Ni	–	Ni	–	Ni	0.2
V	–	V	–	V	–	V	–	Co	0.1

V-15 – peripheral districts of Vilnius, V-6 – central districts of Vilnius

A relatively high percentage of samples with Cr exceeding MPC in public-residential zones of Šiauliai, can be explained by the influence of tanneries and galvanic shops of the bicycle production plant (Taraškevičius, Gregorauskas, 1993). Due to the influence of various types of industry, the number of elements exceeding their MPC is the greatest in Vilnius, especially in its central districts, which are not only affected by the industry but also are much older and much more densely populated.

The arrangement of the elements in accordance with their median values of Kk reflects their input to the Zd index (Table 4). Zn is the main pollutant in public-residential districts of all towns, i.e. there is an obvious correspondence between the main element exceeding its MPC and the element with the highest accumulation level. The pollution of Zn can be related to the transport or the corrosion of roofs. Unlike Zn, the accumulation level of Ba is relatively low, though it often exceeds its MPC in most of the urban public-residential areas. In all towns, except for Mažeikiai, Zn (as for to Kk) is followed by a group of other chalcophiles (Pb, Cu, Sn and Ag). They are indicators of the transport and household pollution.

The sequence of the accumulation of elements in Mažeikiai does not follow a general regularity, because Co and Ni follow Zn; also the accumulation of V and Cr is relatively high. This fact reflects the negative influence of the Mažeikiai oil refinery and the power plant onto the town. Though, they are not very dangerous, because neither Ni, nor V exceed their MPC in public-residential town districts (Table 3), and their Kk are not high (Table 4), they are well reflected in a general elevated baseline of the Mažeikiai surroundings (Kadūnas *et al*., 2001). The Kk of greater part of chalcophiles (Pb, Ag, and Sn) are even lower, indicating that most public-residential territories were settled not long ago, their soil cover was often disturbed during the construction activity and has not yet accumulated higher contents of heavy metals. The heavily polluted territories in Mažeikiai are not in public-residential districts. They are located near the industrial or infra-structural constructions.

Most of the elements have the higher accumulation level in the more densely populated central Vilnius districts comparing with its peripheral ones, and the sequence of elements according to relative accumulation level indicates the role of the motor transport related chalcophiles: Ag (2.63) > Pb

Table 3

Limit values and regional background values for the towns [mg/kg]

Elements	Limit values				Background values for:				Average ratio MPC/background
	Sweden	Finland	Lithuania	Canada (agric.)	Joniškis	Mažeikiai	Šiauliai	Vilnius	
Ag	–	–	**2**	20	0.054	0.068	0.063	0.066	32.2
B	–	–	**50**	–	28.9	22.4	29.9	21.3	2.0
Ba	–	600	**600**	500	326	291	377	305	1.9
Co	30	50	**30**	50	5.19	3.08	5.23	3.7	7.3
Cr	120	100	**100**	64	39.7	26.6	34.6	24.3	3.3
Cu	100	100	**100**	63	9.48	8.9	8.1	6.8	12.2
Mn	–	–	**1500**	–	360	284	395	436	4.2
Mo	–	5	**5**	10	0.58	0.58	0.78	0.64	7.9
Ni	35	60	**75**	50	11.3	10.7	13.5	9.6	6.8
Pb	80	60	**100**	140	14.5	13.1	12.4	15	7.3
Sn	–	50	**10**	50	2.09	2.20	1.90	1.95	4.9
V	120	50	**150**	130	41.5	32.0	30.4	25.7	4.8
Zn	350	150	**300**	200	31.8	23.7	34.2	24.9	10.7

Table 4

Descending sequences of median concentration coefficients (KKMed) of chemical elements in topsoil of public-residential territories of Lithuanian towns

Joniškis		Mažeikiai		Šiauliai		Vilnius, peripheral districts		Vilnius, central districts	
Element	KKMed	Element	KKMed	Element	KKMed	Element	KKMed	Element	KKMed
Zn	**2.38**	Zn	**1.64**	Zn	**3.14**	Zn	**3.99**	Zn	**5.46**
Pb	**2.34**	Co	**1.33**	Pb	**2.39**	Cu	**2.00**	Ag	**4.67**
Cu	**1.65**	Ni	**1.30**	Cu	**2.21**	Ag	**1.77**	Pb	**3.44**
Ag	**1.54**	Cu	1.27	Sn	**1.57**	Pb	**1.65**	Cu	**2.72**
Sn	**1.49**	V	1.26	Ag	**1.41**	Sn	**1.47**	Sn	**2.25**
Mo	**1.48**	Cr	1.22	Mn	1.21	Ba	**1.35**	Mo	**1.58**
Cr	1.25	Pb	1.17	Cr	1.21	Cr	**1.35**	Ni	**1.47**
Ba	1.23	Mn	1.16	V	1.19	Mo	**1.30**	Ba	**1.42**
Ni	1.22	Ba	1.14	Co	1.18	Ni	**1.30**	Cr	**1.39**
Mn	1.16	B	1.12	Ni	1.08	Mn	1.28	V	1.04
V	1.05	Mo	1.11	Ba	1.01	V	1.23	B	1.00
Co	0.97	Ag	1.10	B	0.96	B	1.15	Co	0.98
B	0.86	Sn	1.07	Mo	0.92	Co	1.05	Mn	0.98

KKMed>1.3 are in bold

(2.09) > Sn (1.53) > Zn (1.37) > Cu (1.36) > Mo (1.21) > Ni (1.13) > Ba (1.05) > Cr (1.02).

The geohygienical evaluation of the topsoil in the investigated areas (their abbreviations are given in Table 1), in accordance with the maximum coefficient K_0, revealed the following sequence: J<M<V-15<S<V-6 (Fig. 1). Meanwhile, according to Zd and general geohygienical evaluation, the obtained sequence was slightly different: M<J<V-15<S<V-6 (Fig. 1).

The main difference is in the arrangement of Joniškis and Mažeikiai. On one hand, the topsoil enrichment in most elements in Joniškis is higher than in that in Mažeikiai, and can be explained by differences of their historical development. Mažeikiai is younger than Joniškis, and until recent it had a very low population density. Its residential districts soil cover was recently often disturbed and has not yet accumulated high pollutant contents. On the other hand, the number of elements exceeding their MPC is greater in Mažeikiai (Zn, Ba, Cr, Sn)

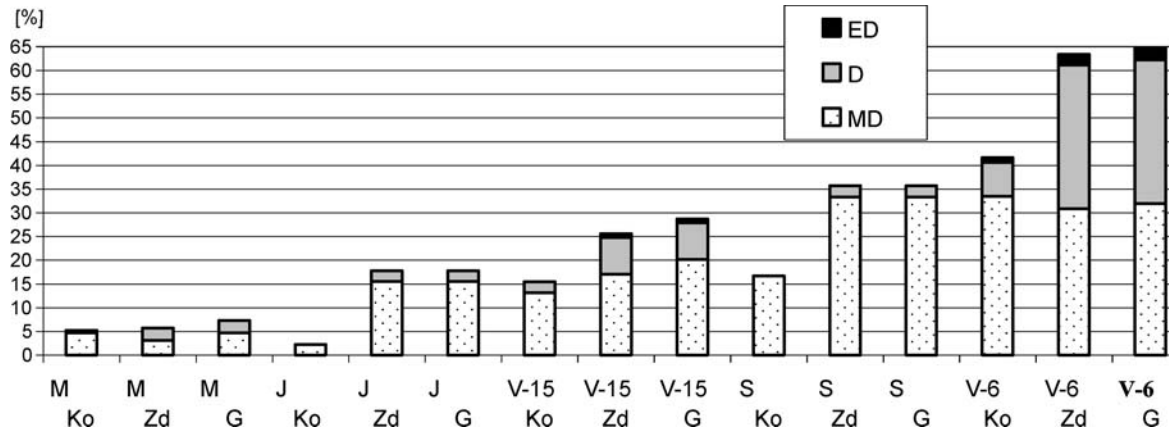

Fig. 1. Geohygienical evaluation of topsoil from public-residential micro-zones in 4 towns of Lithuania

Abbreviations of the territories (M, J, V-15, S and V-6) are given in the first row and are explained in Table 1, while the ways of geohygienical evaluation (Ko – according to maximum coefficient of danger, Zd – according to index Zd, G – general) are given in the second row. In all cases geohygienical evaluation of public-residential zones was expressed as cumulative percentage of sampling sites with topsoil contamination, which causes unfavourable conditions: MD – medium dangerous, D – dangerous, ED – extremely dangerous

compared to Joniškis (only Zn), because Mažeikiai is much more industrialised than Joniškis. In most sites in Mažeikiai, only one element exceeds its MPC and, therefore, Zd index is not necessarily very high.

Less favourable geohygienical conditions are existing in Šiauliai and Vilnius, compared with Joniškis and Mažeikiai, because the first two towns are older, more densely populated, and more industrialised than the other two. The arrangement of the territories in a sequence V-15<S<V-6 corresponds to the increase of the population density and duration of the urbanisation.

The 3 geohygienic evaluation, according to Zd, reveals a greater percentage of unfavourable sites, compared with its evaluation according to MPC. It seems that also general geohygienic evaluation is determined mostly by the Zd index. The evaluation of rural arable soil revealed the opposite regularity, i.e. that the role of Zd in general evaluation was less important (Zinkutė *et al*., 2005).

CONCLUSIONS

Results of the general geohygienic evaluation of the topsoil in the urban public-residential zones depend directly not only on concentration of regional or local pollution sources, but also on duration of territory urbanisation and density of its population. Their increase leads to less favourable conditions for the human health and for all the environment. These conditions depend also on the lifestyle and the type of pollution sources in the surrounding. The older and the more densely populated is the urban public-residential area, the more probable is that its topsoil is contaminated by heavy metals. In these zones, their Zd index depends mostly on chalcophiles Zn, Pb, Ag, Cu, and Sn, which usually are followed by Mo, Cr, Ni, and V, arranged in different order.

Therefore, in the old and densely populated areas, the topsoil monitoring and information sharing is necessary. In some sites, where the topsoil contamination level falls in dangerous or extremely dangerous classes, even the remediation is required. Similarity of the Lithuanian maximum permitted concentrations MPC to the limit values of other European countries and to the complex general geohygienic evaluation of topsoil, taking into account not only MPC, but also the Zd index, ensures that the sites with an unfavourable topsoil geohygienic quality are exposed in the urban public-residential territories.

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