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METALS IN TOPSOIL OF THE TERRITORIES OF INDUSTRIAL ENTERPRISES OF ŠIAULIAI AND ITS ENVIRONS

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Abstract. An investigation of the temporal changes of topsoil contamination by non-ferrous metals Cu, Zn, Pb, Sn, Ag and ferrous metals Cr, Mo, Ni, Co, V was done on the territories of 5 industrial enterprises in Šiauliai (2 tanneries, 2 radioelectronical plants and 1 metal processing plant) and in their nearest surroundings. Comparison was based on the total contents of these elements determined by the same OAES analytical method in a fraction <1 mm of samples taken at the same sites in 1989 and 2003. Due to possibility of topsoil to accumulate heavy metals, its level of contamination has mostly increased or at least remained the same. It has decreased only in those territories where the soil cover was disturbed or changed. Due to the influence of other pollution sources, including traffic or household, the changes of the topsoil contamination in the surroundings of enterprises were not always related to the changes of the topsoil contamination on their territories. Ferrous metals prevail only in tanneries, while the non-ferrous ones in other plants and in all surrounding territories. The absolute growth of the contamination by the non-ferrous metals is everywhere higher in comparison with the ferrous metals.

Key words: urban topsoil, ferrous metals, non-ferrous metals, radioelectronics, tanning, metal working.

Abstrakt. Przeprowadzono badania czasowych zmian kontaminacji gleby przez metale nieżelazne Cu, Zn, Pb, Sn, Ag i żelazne Cr, Mo, Ni, Co, V na obszarze 5 zakładów przemysłowych w Šiauliai (2 farbiarnie, 2 fabryki radioelectroniczne and 1 zakład przetwarzania metali) oraz w ich najbliższym sąsiedztwie. Porównania oparto na całkowitych zawartościach tych pierwiastkow określonych przy pomocy tej samej procedury analitycznej OAES we frakcji <1 mm w próbkach pobranych w tych samych miejscach w latach 1989 i 2003. Wskutek możliwości akumulacji metali ciężkich w glebie, poziom kontaminacji gleb znacznie wzrósł lub przynajmniej pozostał na tym samym poziomie. Obniżył się tylko w obszarach, gdzie przykrycie gleby zostało uszkodzone lub zmienione. Z racji wpływu innych źródeł zanieczyszczeń jak ruch uliczny czy gospodarstwa domowe, zmiany kontaminacji w glebie w okolicy badanych zakładów nie zawsze wiązały się ze zmianami kontaminacji na ich terenie. Metale żelazne przeważają tylko w farbiarniach, podczas gdy nieżelazne – w innych fabrykach i na otaczajacym obszarze. Bezwzględny wzrost kontaminacji metalami nieżelaznymi jest wszędzie wyższy aniżeli metalami żelaznymi.

S³owa kluczowe: gleba miejska, metale żelazne, metale nieżelazne, radioelektronika, farbiarstwo, przetwórstwo metali.

INTRODUCTION

Pollution by heavy metals is one of the well-known human induced hazards. An occupational exposure to heavy metals is proven (Lazutka *et al*., 1999; Palus *et al*., 2003). Also the urban population can be at risk of their influence on health. Not only intensive traffic and household pollution but also industrial enterprises predetermine elevated contents of hazardous elements in urban environment. As the topsoil accumulates heavy metals, it is often analysed for their contents in urban territories of the world (Madrid *et al*., 2002; Pasieczna, 2003). The main part of investigations on heavy metal pollution by stationary

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sources was devoted to smelters (Meyer *et al*., 1999; Klumpp *et al*., 2003). Also petroleum refineries (Bosco *et al*., 2005), cement factories (Işikli *et al*., 2006) or other huge pollution sources were analysed. They are often placed outside urban territories. Meanwhile the investigation of industrial enterprises within the boundaries of the cities is even more important, because they are often close to residential districts. The research for comparison of the peculiarities of different types of industrial pollution in the urban territories is not abundant and has been done mainly by IMGRE specialists in Moscow (Sayet *et al*., 1990).

In Lithuania such a research was started in Šiauliai during geochemical investigations in 1989 (Taraškevičius, 1994). That revealed that the main pedogeochemical anomalies were related to industrial enterprises. The following five of them were analysed: two tanneries "Elnias" (E) and "Stumbras" (S), two radioelectronical plants "Nuklonas" (N) and "Tauras" (T) and one metal working plant "Vairas" (V). The tanneries (Zinkutė *et al*., 2005) are the oldest among these enterprises (the enterprise on the territory of E was founded in 1877, while on the territory of S in 1898), metal processing plant V is younger (founded in 1948), and radioelectronical plants are the youngest (e.g. T was founded in 1963).

The aim of this research was to compare the changes in the topsoil heavy metal contamination in the territories of these enterprises and around them in 2003 and in 1989 and to reveal the influence of different types of pollution and the time-span of industrial activity on the topsoil contamination level.

METHODS

Repeated sampling of the topsoil in 2003 was done in some of the sampling sites of 1989 both from the territories (t) of the enterprises and from their nearest surroundings (s) with residential quarters. Total number of samples was 128. They were taken from the upper 10 cm thick layer of the soil and were complex, i.e. they consisted of several increments taken at some meters distance from the central sampling site. The samples were dried at room temperature and screened through nylon sieves with 1 mm diameter. After aching at 450°C the screened part was ground. Later, the samples were analysed by optical atomic emission spectrophotometry (OAES) in laboratory of the Institute of Geology and Geography in Vilnius aiming at determination of the total contents of large group of elements. Since 1997 the laboratory participates in "International Soil analytical exchange" subprogram organised by Wageningen University (Taraškevičius, Zinkutė, 1999). The following 13 elements were analysed in detail: Cu, Zn, Pb, Sn, Ag, Cr, Mo, Ni, Co, V, Mn, B, Ba. Their concentration coefficients (Kk) were calculated as well as several additive contamination indices: Zg (a general index according to all 13 elements), Znf (a partial index of non-ferrous metals Cu, Zn, Pb, Sn, Ag) and Zf (partial of ferrous metals Cr, Mo, Ni, Co, V).

RESULTS AND DISCUSSION

Though some of the enterprises (E) have reduced their production volume or various new enterprises (especially motor transport repair) were established on their territories (N), the increase of topsoil median Zg is obvious on the territories of the greater part of them, except for Vt and Et (Fig. 1). According to this index all the enterprises now belong to the dangerous category of topsoil contamination (32<Zg<128), meanwhile in 1989 only 3 of them (Vt, Tt and the older tannery Et). The younger tannery St falls to the medium dangerous category (16<Zg<32). The reason is that heavy metals accumulate in the topsoil. Only in the case of a metal processing plant (Vt), where a great part of the territory has been dug, the median Zg has decreased and therefore cannot reflect the history of contamination of the area. In Et there are no changes due to actual shutdown of production. The highest growth of Zg median (9.9 times) was in Nt, followed by St(1.6) and finally Tt(1.2), i.e. in both radioelectronical enterprises and the younger tannery (that corresponds to the present increase of a production volume there). An assumption that the influence of the time-span of industrial activity is lower than the influence of its type may be accepted based on the intensive growth of the topsoil contamination on the territories of the youngest radioelectronical enterprises as well as high contamination level of metal processing plant. On the other hand, the higher contamination

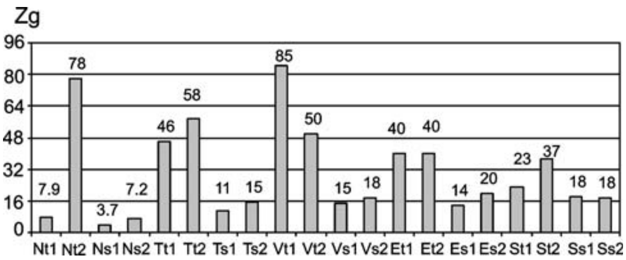

Fig. 1. TTara kevi iuyzWar zawa h ddt iei rek of topsoil contamination Zg on the territories of the enterprises and their surroundings

Nt1 – "Nuklonas" territory in 1989, Nt2 – "Nuklonas" territory in 2003, Ns1 – "Nuklonas" surroundings in 1989, Ns2 – "Nuklonas" surroundings in 2003, Tt1 – "Tauras" territory in 1989, Tt2 – "Tauras" territory in 2003, Ts1 – "Tauras" surroundings in 1989, Ts2 – "Tauras" surroundings in 2003, Vt1 – "Vairas" territory in 1989, Vt2 – "Vairas" territory in 2003, Vs1 – "Vairas" surroundings in 1989, Vs2 – "Vairas" surroundings in 2003, Et1 – "Elnias" territory in 1989, Et2 – "Elnias" territory in 2003, Es1 – "Elnias" surroundings in 1989, Es2 – "Elnias" surroundings in 2003, St1 – "Stumbras" territory in 1989, St2 – "Stumbras" territory in 2003, Ss1 – "Stumbras" surroundings in 1989, Ss2 – "Stumbras" surroundings in 2003

level of the older Et compared to the younger St indicates that for the enterprises of the same profile the role of the time-span of operation is important. Finally the environmental protection measures also influence topsoil contamination level. Despite a continuation of the production in "Stumbras" and "Tauras", the increase of the median Zg in their territories is not so high as in Nt, where many different small enterprises were established after the closure of the radioelectronical plant.

The Zg levels in the surroundings of all the enterprises are lower than on their territories but they have also increased (Fig. 1). In 1989 only the median Zg value of Ss was of medium dangerous level, while in 2003 also of Es and Vs. The highest growth of median Zg values is observed in Ns (1.9 times). It is followed by Es(1.5), Ts(1.4), Vs(1.2) and Ss(1.02). The highest increase of Zg in Ns corresponds to the highest growth of the median Zg on the territory of "Nuklonas". This fact as well as the growth of Zg both in Tt and Ts confirms the existence of the influence of the industrial pollution on surrounding territories. However, this might be not the only reason, because the growth of Zg in Es cannot be explained by the influence of "Elnias" tannery (Et contamination level remained similar), but rather by the traffic pollution.

According to the descending median Zg values the arrangement of the territories of the enterprises has changed from Vt(85) > Tt(46) > Et(40) > St(23) > Nt(7.9) in 1989 to Nt(78) > Tt(58) > Vt(50) > Et(40) > St(35) in 2003 indicating a significant variation of industrial pedogeochemical anomalies during 14 years. Meanwhile the arrangement of the surroundings of the enterprises was rather similar: Ss(18) > Vs(15) > Es(14) > Ts(11) > Ns(3.7) in 1989 and Es(20) > Ss(18) ≈ Vs(18) > Ts(15) > Ns(7.2) in 2003. The latter can be explained by multiple pollution sources (including traffic and household) affecting the surroundings of the enterprises.

The median Znf values on the territories of electrical engineering and metal working plants both in 1989 and 2003 were higher than those median Zf values, whereas the tanneries were characterised by the opposite relationship (Fig. 2). The median Znf values also exceeded median Zf values in all surroundings of different type enterprises (Fig. 3). The growth of Znf values in 2003 compared to 1989 is obvious everywhere, except for Vt with a disturbed soil cover. The median values of Zf on the territories of the enterprises in 2003 were also higher when compared with 1989, except for the above-mentioned Vt and also Et, where the leather processing with a characteristic relationship Zf > Znf actually terminated. The median values of Zf have mostly grown also in the surroundings of the enterprises, but Vs and Ss. A decrease of Zf in Ss territory as well as the lower contamination of "Talša" lake near it, can be explained by the efficiency of nature protection measures in chromium tanning introduced in "Stumbras" (Zinkutė *et al.*, 2005). In case of the increasing Zg values, the absolute growth of the median Znf values everywhere was higher than that of the median Zf ones.

The highest input percentage of the non-ferrous metals to the topsoil contamination is in the territories of electrical engineering plants (>60%). It is even higher than in surroundings of respective enterprises (Fig. 4). This input on the territory of metal processing plant is slightly lower than 60% and on the territories of both tanneries – the lowest (<50%). The input of non-ferrous metals has grown up in all surroundings of the enterprises reflecting the increase of the traffic pollution. It has also risen in most of the territories of the enterprises, but Tt and Vt, where the input percentage of the ferrous metals has increased probably due to multiple metal working sources including a forge.

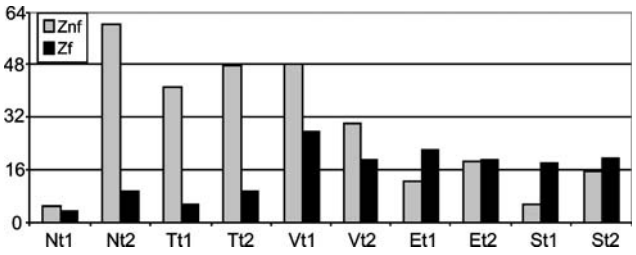

Fig. 2. Temporal changes of median additive indices of topsoil contamination by non-ferrous metals Znf and by ferrous metals Zf on the territories of the enterprises (explanations are in Fig. 1)

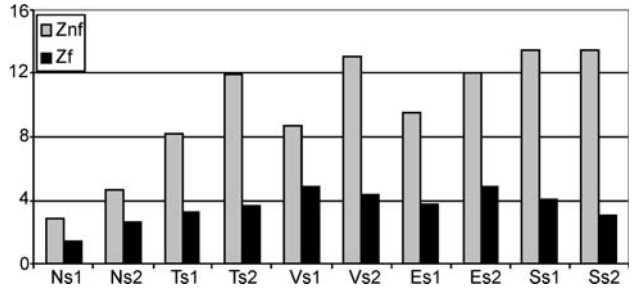

Fig. 3. Temporal changes of median additive indices of topsoil contamination by non-ferrous metals Znf and by ferrous metals Zf in surroundings of the enterprises (explanations are in Fig. 1)

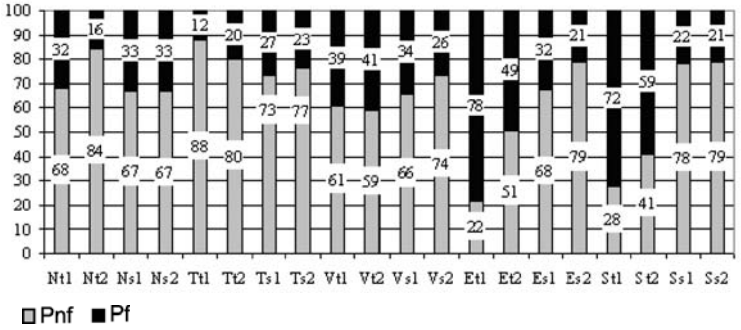

Fig. 4. Temporal changes of the input percentage of ferrous (Pf) and non-ferrous (Pnf) metals to topsoil contamination on the territories of the enterprises and their surroundings (explanations are in Fig. 1)

Table 1

Temporal variability of accumulating associations on the territories of the enterprises

Nt1	Cu>Mo>Sn>Ag>Zn>Cr
Nt2	**Cu>Sn>Zn**>Mo>**Ag>Pb**>Cr>Ni
Tt1	**Sn>Cu>Pb>Zn>Ag**>Mo>Ni>Cr
Tt2	**Cu>Sn>Zn>Pb**>Mo>Ni>Cr>**Ag**>Mn>Ba>V>Co
Vt1	**Cu**>Ni>Mo>**Zn**>Cr>**Pb>Sn>Ag**>Ba>Mn>Co
Vt2	**Cu**>Ni>**Zn**>Cr>**Pb**>Mo>**Sn>Ag**>Ba>Co>Mn
Et1	Cr>**Zn**>Mo>**Pb>Cu>Sn**>Ni
Et2	Cr>**Zn>Cu>Pb**>Mo>Ni>**Sn**
St1	Cr>**Pb>Cu>Zn**>Mo>**Sn**
St2	Cr>**Zn>Cu>Pb**>Mo>**Sn**>Ni>Mn>Co

Explanations are in Figure 1

Unlike the metal processing plant and radioelectronical plants, the accumulating associations of tanneries contain only 4 non-ferrous metals (without Ag) and are characterised by the highest Cr accumulation (Table 1). Though both the metal processing plant and the radioelectronical plants are similar according to their highest accumulation of Cu (or Sn), they differ in the ferrous metals: Ni is the main pollutant in the metal processing plant, while Mo – in the radioelectronical plants.

The accumulating association of "Vairas" was very wide already in 1989 and included 11 elements. The same elements were accumulating in 2003, while the accumulating associations in the radioelectronical plants and the "Stumbras" tannery grew up in 2003 when compared to 1989 that confirms the increase of their contamination. The widest accumulating association is characteristic of "Tauras" in 2003. This can be partly the influence of the adjacent metal processing plant and multiple pollution sources.

In Nt the median Kk values of all elements from accumulating association have increased (Fig. 5), the accumulation level of most of these elements, except for Zn and Ag, has also increased in Ns and the growth of Cu and Cr was essential both in Nt and in Ns. Therefore the surrounding new residential quarters are obviously influenced by the earlier industrial pollution of "Nuklonas" and the subsequent pollution of small enterprises established in its territory. In Tt the median Kk values of most members of accumulating association also have grown up, except for the decrease in Sn and Ag, which most probably indicates the changes of technological processes of TV production (Fig. 5). Some contents (Mo, Cr, V and Co, also Zn) have increased in Tt essentially. Except for Mo, the contents of all these elements, also of Cu and Ni have grown up in Ts. As radioelectronics is mainly characterised by the non-ferrous metals, this can be related either to the changes of technological processes or to the influence of the adjacent multiple pollution sources in the central industrial

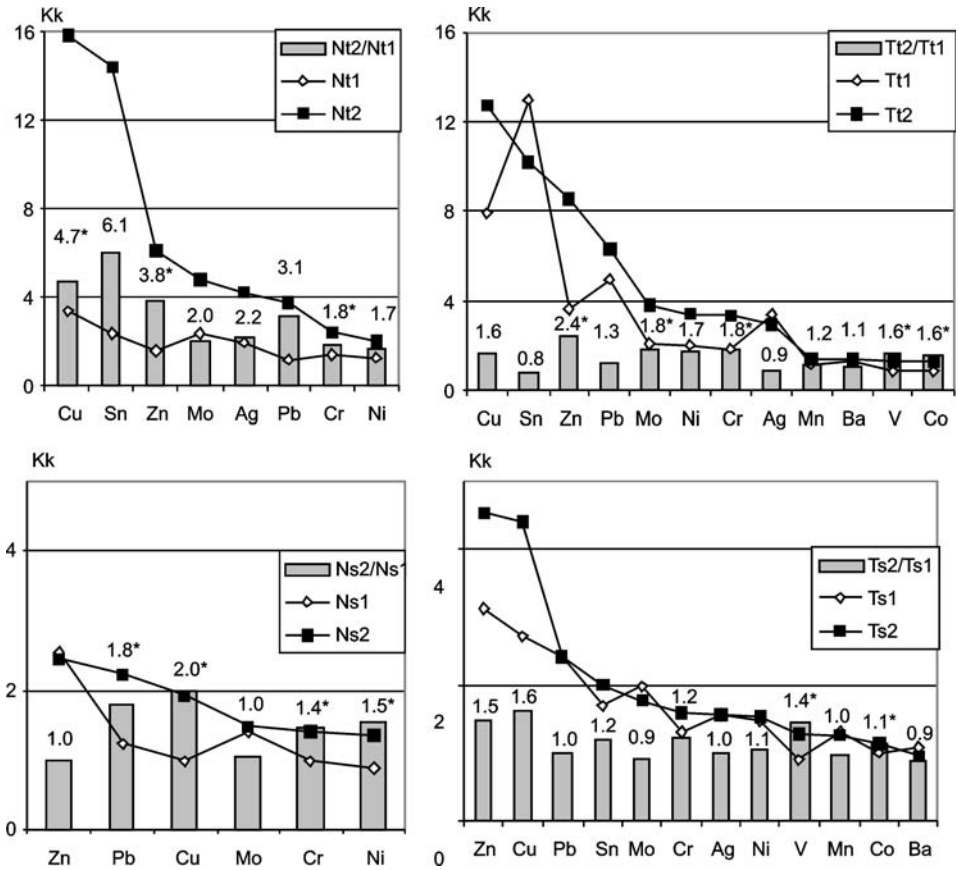

Fig. 5. Temporal changes of median Kk of elements in topsoil of radioelectronical plants and their surroundings

* – indicates essential growth, explanations are in Figure 1

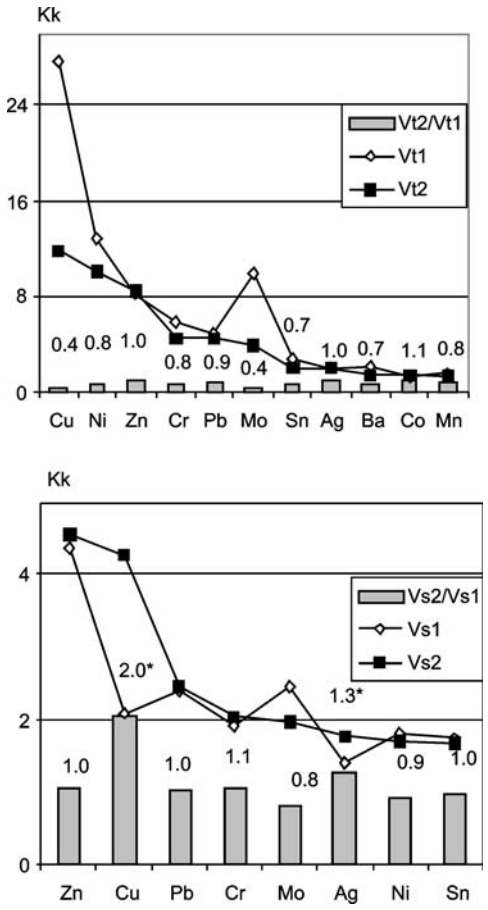

Fig. 6. Temporal changes of median Kk of elements in topsoil of metal processing plant "Vairas" and its surroundings

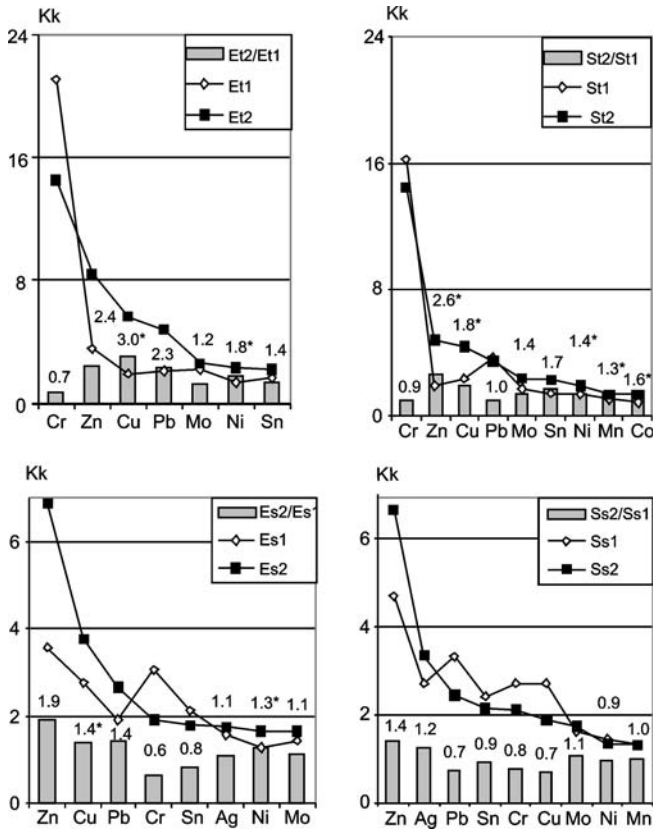

Fig. 7. Temporal changes of median Kk of elements in topsoil of tanneries and their surroundings

* – indicates essential growth, explanations are in Figure 1

district including metal processing plant. Though the growth of accumulation of these elements in Vt cannot be seen due to disturbed soil cover (Fig. 6), it can be assumed that this plant, which produces bicycles and prams and is involved in steel and aluminium processing, welding of steel frames and forks, painting and varnishing, is characterised by the higher content of the ferrous metals in emissions than radioelectronical plant. It is possible to assume that the northwestern winds can carry away the emissions of "Vairas" and they can reach Tt and Ts territories located to the southeast from the metal processing plant and cause the increase of ferrous metals there. An essential increase of the non-ferrous metals (Cu and Ag) and a slight increase of Zn, Pb, Cr in Vs can be caused both by the metal processing plant and by intensive traffic (Fig. 6). Both in Et and St, the accumulation level of Cr has decreased indicating the termination of production in "Elnias" and the efficacy of environmental protection measures in Cr tanning in "Stumbras" (Fig. 7). Meanwhile there was a growth of the contents of other elements from accumulating associations. A greater number of the elements with the essential growth of accumulation in St compared to Et can be explained by the increase of production volume in "Stumbras". The essential growth of Cu and Ni and increase of Zn, Pb, Mo both in Et and in Es is most probably related to the traffic.

CONCLUSIONS

The contamination level of heavy metals in the territories of industrial enterprises usually grows up , despite the decrease of the production volume or a change of the profile of the enterprises due to the possibility of their accumulate in the topsoil. It decreases only when the soil cover is disturbed or changed. The type of the industrial activity is more significant for the topsoil contamination level than the time-span. The increase of topsoil contamination level in the surroundings of the industrial enterprises is not always related to the changes of the topsoil contamination level in their territories, because it is affected by the traffic or the household pollution. The ferrous metals prevail only in tanneries, while in other plants and in all surrounding territories the dominance of the non-ferrous metals is obvious. The absolute growth of the contamination by the non-ferrous metals is everywhere higher than that of the ferrous metals.

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