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DISTRIBUTION OF HEAVY METALS IN UPPER LAYERS OF SOIL FROM VILNIUS SITES EXPOSED TO DIFFERENT TYPE OF POLLUTION

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Abstract. The distribution of total contents of non-ferrous metals Cu, Zn, Pb, Sn, Ag and ferrous metals Cr, Mo, Ni, Co, V in 3 depth layers 0–5 cm (A), 5–10 cm (B) and 10–25 cm (C) of the nearer (at 20 m distance) and further (at 70 m distance) zones of metal processing area (M) and transport area (T) revealed that the input of non-ferrous metals to total contamination in both areas is greater than that of the ferrous metals. The ferrous metals (especially Mo) play an important role in zones of the metal processing area and Cu is specific element of trolleybus traffic pollution in the transport area. Pollution in zones of the metal processing area extends to a larger distance and causes more dangerous soil contamination. A distribution of pollutants in upper depth layers of the soil depends on the organic matter content.

Key words: urban soil, heavy metals, residential districts, metal processing, traffic.

Abstrakt. Rozkład całkowitej zawartości metali nieżelaznych Cu, Zn, Pb, Sn, Ag i metali żelaznych Cr, Mo, Ni, Co, V w trzech warstwach na głębokości 0–5 cm (A), 5–10 cm (B) and 10–25 cm (C) w bliskiej (odległość 20 m) i dalszej (odległość 70 m) strefie obszaru przetwórstwa metali (M) i rejonie transportu (T) pokazuje, że wpływ metali nieżelaznych na całkowitą kontaminację w obu obszarach jest większy aniżeli metali żelaznych. Metale żelazne (zwłaszcza Mo) odgrywają dużą rolę w strefach obszaru przeróbki metali. Cu jest pierwiastkiem charakterystycznym dla rejonu zanieczyszczenia ruchem trolejbusów na obszarze transportu. Zanieczyszczenie w strefach przeróbki metali rozciąga się na dużych odległościach i powoduje niebezpieczną kontaminację gleby. Rozkład składników zanieczyszczeń w górnej warstwie gleby zależy od zawartości materii organicznej.

S[3]owa kluczowe: gleba miejska, metale ciężkie, obszary zamieszkałe, przeróbka metali, ruch uliczny.

INTRODUCTION

Due to many different processes, a urban soil is a highly complex and heterogeneous mixture of many contributing materials and associated contaminants. It is exposed to various pollution sources including industrial enterprises and traffic. The same elements – pollutants can have different origin, e.g. the urban dust research revealed that Pb and Zn can be derived both from industrial and traffic sources (Yongming *et al*., 2006). Although spatial distributions of Pb, Cu and Zn present an abrupt division between the urban and rural samples (Biasioli *et al*., 2006), the clarification of the input of industry and traffic to urban anomalies of these elements is much more complicated. Moreover, the input of both pollution sources is variable in time. Due to different reasons the industrial pollution decreases at present in many cities of the world, meanwhile traffic pollution increases. However, the soil in those urban areas that have been or still are centres of industrial activity contains a legacy of anthropogenic chemicals deposited in the soil environment (Hooker and Nathanail, 2006). They can pose potential risks to human health via a number of possible exposure pathways, including soil ingestion. Such situation occurs in Vilnius, where the volume of the industrial production is lowered at present and the volume of traffic has grown up. Still there are some industrial enterprises operating in residential quarters of this city. One of them is the plant of drills in

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Naujamiestis district (Taraškevičius, Zinkutė, 2005). The aim of the quoted research was to analyse the distribution of heavy metals in upper layers of soil in this area exposed mainly to the industrial pollution and to compare it with the area exposed mainly with the complex traffic pollution (trolleybusses, busses, trucks, cars).

Investigations of element contents in a soil profile or in several layers are more informative as compared to the sampling of the surface soil. For example in urban territories of Poland two depth intervals of soil (0–0.2 m and 0.4–0.6 m) were analysed, the lower one reflected a chemical composition of rocks and the upper one – urban-industrial and transportation activities (Pasieczna, 2003). Sampling from different soil layers or horizons also enables to find out a historical pollution during various human activities, i.e. weapon making, smelting (Alexandrovskaya, Alexandrovskiy, 2000; Zhang *et al*., 2005) or to make assumptions about their vertical migration (Hawkins *et al*., 1995). More detailed sampling of the upper layers of the soil (until 25 cm depth) seems to be appropriate to find out both present and historical pollutions of the last century as well as to speculate about the accumulation or the possible vertical migration of elements.

OBJECTS AND METHODS

Two urban residential areas were chosen for sampling in 2004. One of them is a metal processing area (M) located near the plant of drills and affected by its pollution. It is characterised by less intensive traffic load (only private cars). Formerly it was also affected by pollution of electrical engineering plant located at about 250 m distance. The other area (T) is in the district, where there are almost no industrial enterprises, but which is characterised by an intensive traffic load (trolleybuses, busses, trucks, cars) along the street. In each area soil samples were taken at four sites: the first pair of sites located at a closer distance (20 m) from the respective pollution source (i.e. either plant, or street), the next pair of sites at further distance (70 m). These pairs of sites were chosen for calculating average element contents in nearer zones (M1 and T1) or further zones (M2 and T2) affected by respective pollution sources. In each site the samples were taken from three soil depth layers: 0–5 cm (A), 5–10 cm (B) and 10–25 cm (C). Besides, all the samples were composite and consisted of 5 incremental samples taken from respective layers at points along the line (the distance between adjacent points was 1 m).

The samples were dried at room temperature and screened through nylon sieves with 1 mm diameter. After ashing at 450°C the screened part was ground. The samples were analysed by AOES in laboratory of the Institute of Geology and Geography in Vilnius for determination of total contents of a large group of elements. The following 13 elements were analysed in detail: Cu, Zn, Pb, Sn, Ag, Cr, Mo, Ni, Co, V, Mn, B, Ba. Since 1997 the laboratory has been successfully participating in "International Soil-analytical Exchange" organised by Wageningen University (Taraškevičius, Zinkutė, 1999). Their concentration coefficients (Kk) were calculated as well as several additive contamination indices: Zg (a general according to all 13 elements), Znf (a partial of non-ferrous metals Cu, Zn, Pb, Sn, Ag) and Zf (a partial of ferrous metals Cr, Mo, Ni, Co, V). The background values for most elements were taken as estimated before (Taraškevičius, 2000).

RESULTS AND DISCUSSION

According to median Zg values all three depth layers of the M area belong to the category of dangerous contamination (32<Zg<128) and only the deepest layer C in the nearer zone M1 belongs to medium dangerous category (16<Zg<32) (Fig. 1). Meanwhile, the T area is less contaminated: according to the median Zg, only the depth layers of the nearer zone T1 belong to the medium dangerous category and the layers of the further zone T2 to allowable (Zg<16). The Zg values in each depth layer of each zone are higher in the M area compared to respective layers and zones of the T area. The same concerns Zf values (Fig. 2). For Znf values the only exception is the deepest layer C of the nearer zone of the T area, where Znf is higher than in respective C layer of the M1 zone (Fig. 3). In all soil depth layers, except for the deepest layer C of M1 zone, there exists the higher contamination by the non-ferrous metals in comparison with ferrous, i.e. Znf>Zf (Fig. 4). However, in the M1 zone the Zf percentage from the sum Znf+Zf is higher than that in the T1 zone and it exceeds 40. That fact indicates that the

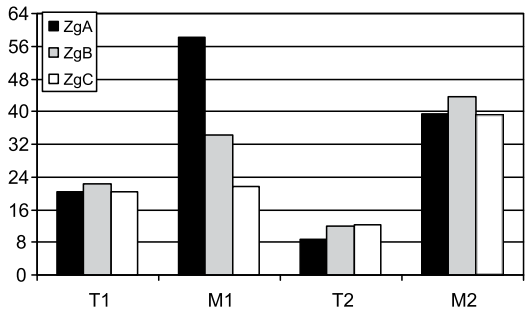

Fig. 1. Distribution of general additive index of contamination in upper (ZgA), middle (ZgB) and lower (ZgC) layers of soil

T1 – nearer zone of transport area, M1 – nearer zone of metal processing area, T2 – further zone of transport area, M2 – further zone of metal processing area

ferrous metals play the more important role in the pollution of the metal processing plant than in the traffic pollution (Fig. 5). In both areas, the Zf values of respective soil depth layers in the nearer zone are higher that those in the further zone (Fig. 2). Meanwhile for Znf (Fig. 3) and Zg (Fig.1) values this is not always a rule, because in B and C layers of the M area the opposite relationship is observed. This might be explained by the influence of pollution by Pb and Sn from a parking place which is near the M2 zone as well as probably by the former pollution by Ag from the electrical engineering plant. An obvious decrease in Zg, Znf and Zf values in deeper layers is noted only in the M1 zone (Figs. 1–3). In other zones the differences of additive contamination indices of different layes are not high. Sometimes slightly higher values are observed in deeper layers (B or even C). This might be explained by heterogeneous samples and especially – by differences in the organic matter content. The contents of Mo, V, Zn, Ag and Sn in all depth layers and the contents of Cr, Ni, Co and Pb in the A layer of M1 and M2 zones are higher than in respective layers of the T1 and T2 zones (Fig. 6). However, the content of Cu in all depth layers of T1 zone is higher when compared to respective layers of the M1 zone indicating that this element is a specific pollutant of the trolleybus transport (copper wires). Similar results when comparing industrial and road traffic pollution were obtained in Turkey with a high level of Pb and Cu in samples collected from urban roadsides (Çelik *et al.*, 2005). According to decreasing Kk>2 values in the A layer of the M1 zone, the elements are arranged as follows (Fig.7): Zn (22) > Mo (18) > Pb

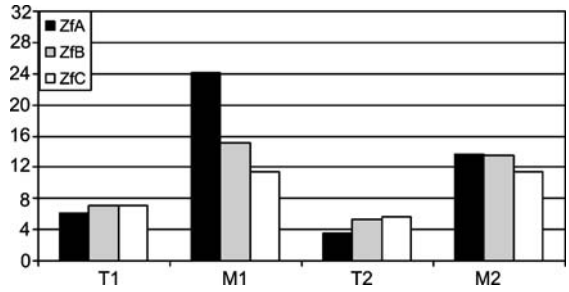

Fig. 2. Distribution of additive index of contamination by ferrous metals in upper (ZfA), middle (ZfB) and lower (ZfC) layers of soil

T1 – nearer zone of transport area, M1 – nearer zone of metal processing area, T2 – further zone of transport area, M2 – further zone of metal processing area

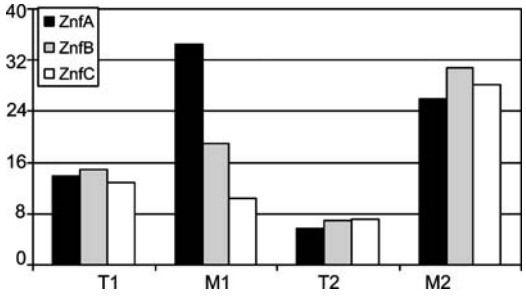

Fig. 3. Distribution of additive index of contamination by non-ferrous metals in upper (ZnfA), middle (ZnfB) and lower (ZnfC) layers of soil

T1 – nearer zone of transport area, M1 – nearer zone of metal processing area, T2 – further zone of transport area, M2 – further zone of metal processing area

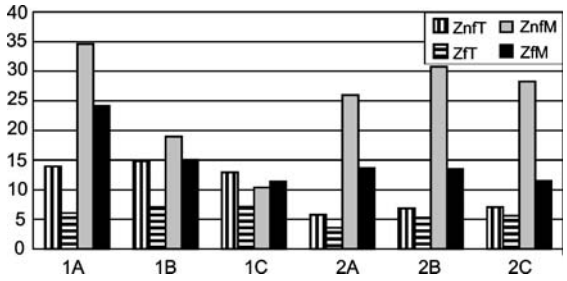

Fig. 4. Additive indices of contamination by non-ferrous and ferrous metals in different zones and layers of transport (T) and metal processing (M) areas

1A, 1B, 1C – upper, middle and lower layers of the nearer zone, 2A, 2B, 2C – upper, middle and lower layers of the further zone

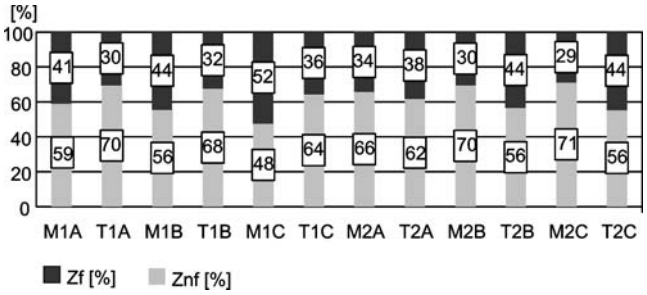

Fig. 5. The input percentage of ferrous (Zn%) and non-ferrous (Znf%) metals in different layers and zones of metal processing (M) and transport (T) areas

M1A, T1A – upper soil layer of the nearer zone in M and T areas, respectively; M1B, T1B – middle soil layer of the nearer zone in M and T areas, respectively; M1C, T1C – lower soil layer of the nearer zone in M and T areas, respectively; M2A, T2A – upper soil layer of the further zone in M and T areas, respectively; M2B, T2B – middle soil layer of the further zone in M and T areas, respectively; M2C, T2C – lower soil layer of the further zone in M and T areas, respectively

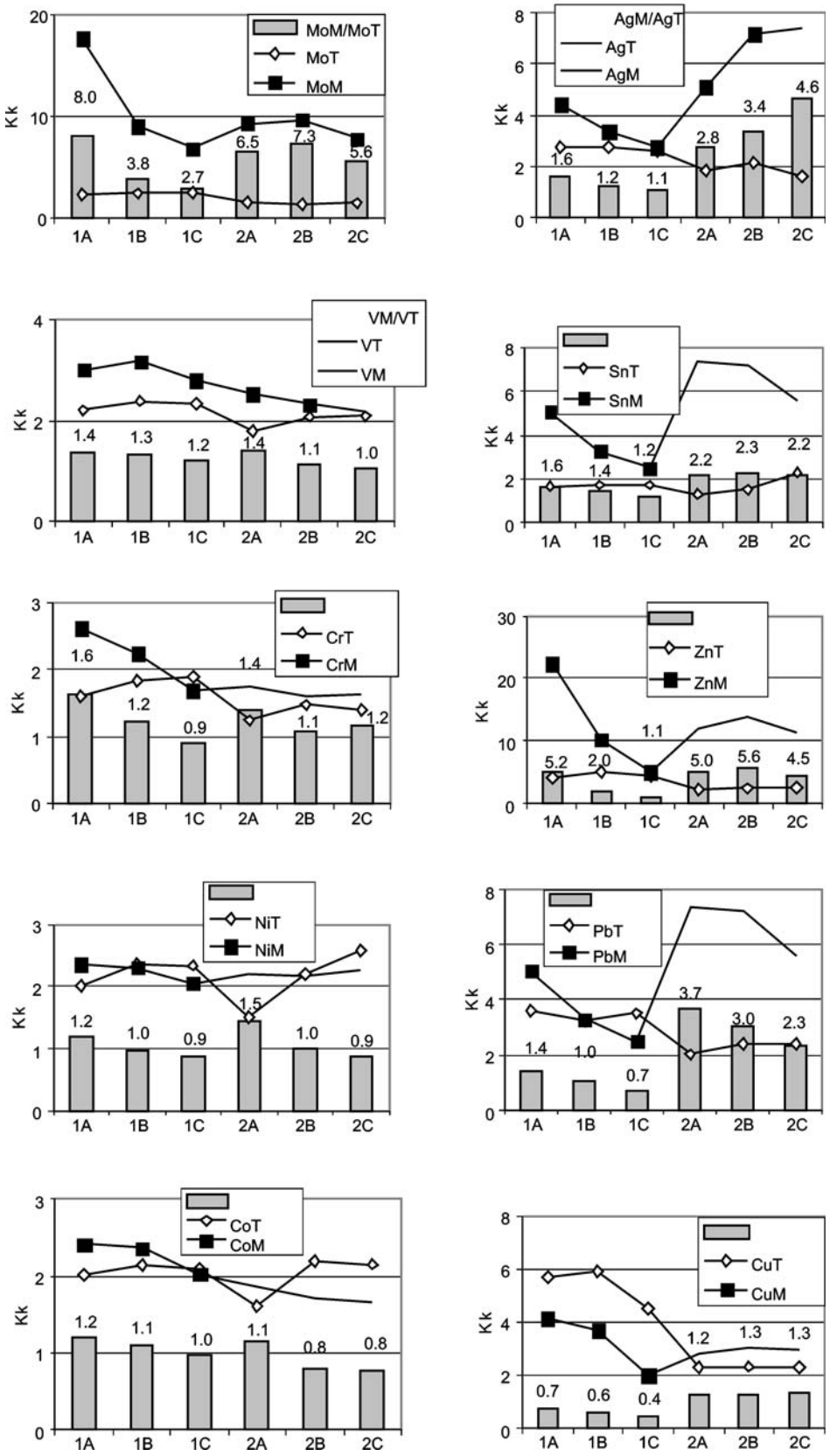

Fig. 6. Accumulation of elements (Kk) in different zones and layers of metal processing area (M) and transport (T) area and the ratio of accumulation in M area to T area

1A, 1B, 1C – upper, middle and lower layers of the nearer zone; 2A, 2B, 2C – upper, middle and lower layers of the further zone

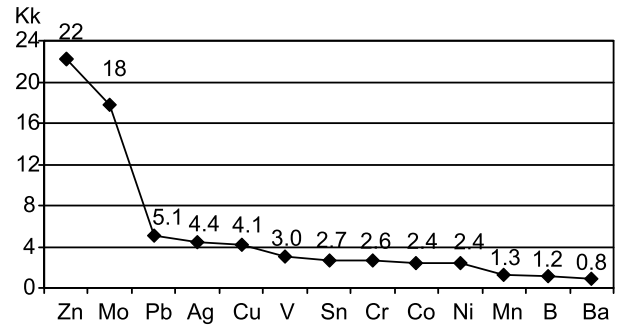

Fig. 7. Accumulation of elements in upper layer of the nearer zone of metal processing area

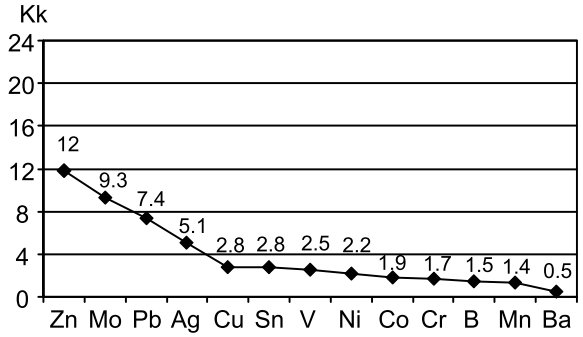

Fig. 8. Accumulation of elements in upper layer of the further zone of metal processing area

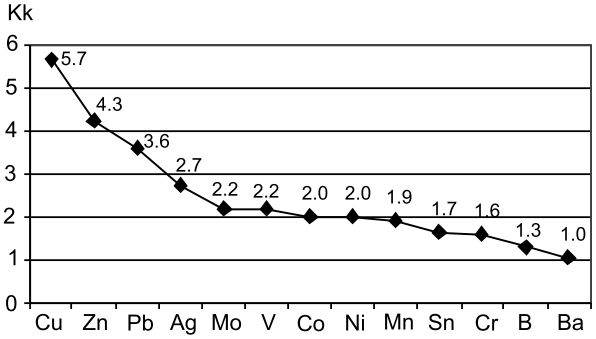

Fig. 9. Accumulation of elements in upper layer of the nearer zone of transport area

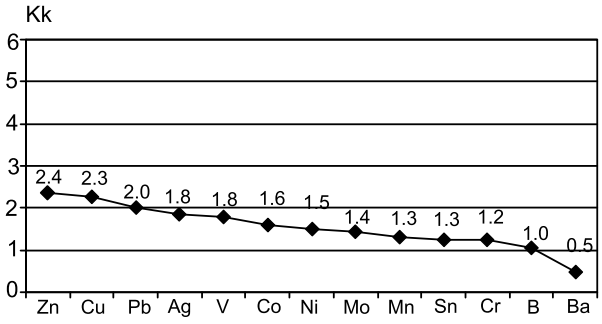

Fig. 10. Accumulation of elements in upper layer of the further zone of transport area

(5.1) > Ag (4.4) > Cu (4.1) >V (3.0) > Sn (2.7) > Cr (2.6) > Co, Ni(2.4). In the A layer of the M2 zone the order is almost the same Zn > Mo > Pb > Ag > Cu > Sn > V > Ni (Fig.8) demonstrating a stability of the association of plant of drills. Meanwhile in the A layer of the T1 zone, the sequence is quite different with much lower accumulation of Mo and Zn (Fig. 9): Cu (5.7) > Zn (4.3) > Pb (3.6) > Ag (2.7) > Mo, V (2.2) > Co, Ni (2.0). In the A layer of the T2 zone the order changes to Zn > Cu > Pb (Fig. 10) demonstrating that Zn is the main pollutant. This might be related to the corrosion of roofs, windowsills, rainwater pipes *etc*.

CONCLUSIONS

The pollution by the plant of drills compared to the complex traffic pollution extends to great distance. Therefore, it causes the high and dangerous soil contamination. The traffic pollution is characterised by a shorter influence zone and similar element contents in different upper layers of the soil (until 25 cm depth). The input of the non-ferrous metals to total contamination in both areas is greater than that of the ferrous metals, but the ferrous metals (especially Mo) are more significant in the pollution of the metal processing plant. Cu is a specific element of trolleybus traffic pollution. Distribution of pollutants in upper depth layers of soil depends on the organic matter content, which is a good sorbent of heavy metals.

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