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HEAVY METAL LOADS IN THE SOIL OF DEBRECEN

SÁNDOR SZEGEDI

Department of Meteorology, University of Debrecen; H-4010 Debrecen P.O.B. 9; Hungary; E-mail: szegedis@puma.unideb.hu

Abstract

Results of examinations on the amount, and spatial distribution of heavy metal compounds in the soil of Debrecen, their geographic, pedologic and ecologic aspects are presented in this study. The effects of the differences in traffic conditions, build-up/land use and the density of vegetation on the heavy metal content of the soils have been examined in city of Debrecen and its closer environment. Cadmium-, cobalt-, nickel-, lead-, and copper-contents of the soil samples taken from 88 sites of the sample area have been studied after acidic extraction, using atomic absorption spectrometer with the flame technique. Close-to-background concentrations of heavy metals in unpolluted soils of the forested area of the Nagyerdő were determined. Spatial differences in the heavy metal content of the soils for the whole area of Debrecen have been studied. Influence of soil properties (humus, Calcium-Carbonate content, pH and grain-size distribution) on the binding and mobility of heavy metals in the soil has been examined. Vertical distribution and mobility of heavy metal compounds in acid sandy soils was determined. Heavy metal content of soil in the most sensitive areas, playgrounds, recreational areas, urban gardens and grazing fields along busy roads has been surveyed.

Keywords: Heavy metal compounds; urban soils; atom absorption spectrometry

1. Introduction

Human activities – especially during the last fifty years – have increased the amount of heavy metals in the environment significantly. Atmospheric concentrations of lead, for example, have increased by fifteen times compared to the level before the beginning of the civilisation. Most important reason for this is the use of leaded fuels. Heavy metal compounds emitted into the atmosphere bind to aerosol particles and move in the atmosphere. Particles larger than 10 µm in diameter can travel only about 100-200 metres, while those ones that are smaller than 10 µm in diameter can get as far as 1,000 kilometres and the finest particles under 0.1 µm in diameter can travel 10,000 kilometres in the atmosphere. They reach the surface of the soil through dry out (gravitational settlement) and wet out (precipitation), and from there they get into the soil.

Traffic density (vehicles per hour), distance from busy roads, build-up/land use type and plant cover of the surface determine the emission, transmission and fall out of heavy metals.

Soil properties (pH, clay mineral and humus content) are decisive for their behaviour in the soil. If pH, humus and clay mineral content are high, the majority of heavy metals can become biologically inactive, since the soil can bind them in forms that are not accessible for plants. Heavy metals which are available in the soil, or in the soil solution, can reach the ground water, or – with the transmission of plants – human nutrition chain. Acidic soils with low humus and clay mineral content are less active in binding of heavy metals.

Plant and animal systems need the majority of the heavy metals in a small amount, but concentrations significantly higher than natural levels are toxic for the living organisms. The urban environment is endangered by the heavy metal pollution in an increased degree: the majority of the emission sources are located there and their effects influence directly a significant part of the population.
The aim of this research was:

- To determine close-to-background of heavy metal loads in unpolluted soils of the forested area of the Nagyerdő.
- To study spatial differences in lead, cadmium (both resulting from traffic), cobalt, nickel and copper content of the soil for the whole area of Debrecen.
- To examine the factors which are responsible for the development of the spatial differences: the effects of the density of traffic, the build-up/land use type and plant cover of the surface.
- To study how soil properties (humus and Calcium-Carbonate content, pH and grain-size distribution) influence the binding and mobility of heavy metals in the soil.
- To examine vertical distribution and mobility of heavy metal compounds in acid sandy soils.
- To determine heavy metal content of soil in the most sensitive areas: playgrounds, recreational areas, urban gardens and grazing fields along busy roads.

2. Research area

The choice of Debrecen is advantageous from many aspects. The city lies on the edge of different soil types; therefore, the mobility of heavy metals can be examined in different soil types (sandy soils, chernozem, and meadow soils).

Traffic is the only considerable source of emission in the sample area; others are minor pinhole sources.

Debrecen is an important transport junction (Fig. 1) in Northeast Hungary. 36.3% of the total traffic is transit by nature (Korompai, 1994). Traffic between the quarters/sections of the city and the traffic directed to the city centre is considerable. The average age of the motor cars is ten years, their greater proportion (almost two third of them) had used leaded petrol before April 1999. High lead concentrations in the soil can be explained by the fact that 0.16 g/l lead had been added to the petrol. Since the lead remains in the soil for centuries, the problem survives the use of the leaded petrol. The heavy metal content of the soil will be a potential source of danger in the future since it can be mobilised in soils that become acid as a result of the acid precipitation.

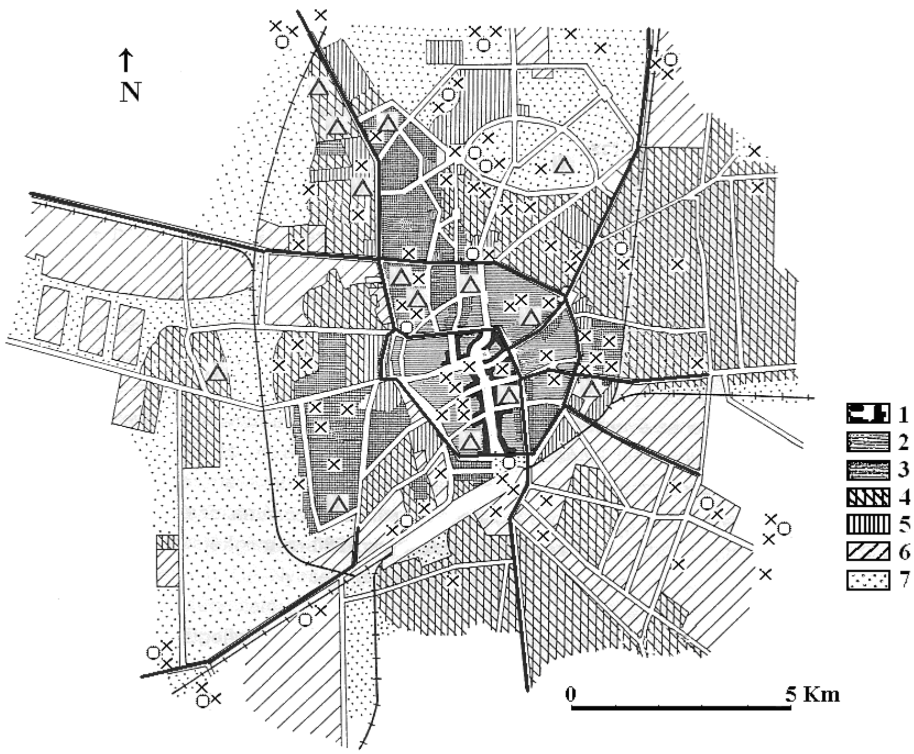

Fig. 1. Sample sites and the build-up/land use units of Debrecen (Based on Csorba, 1997 and Süli Zakar, 1994.)
Legend: 1-2: city centre; 3: housing estates; 4: detached and semi detached houses; 5: public institutions with green areas; 6: industrial areas; 7: urban green spaces, and cultivated areas; ×: locations of soil samples; ○: locations of plant samples: Δ: locations of soil samples from playgrounds.

3. Sampling and research method

Average soil samples have been taken from 88 sample sites from the area of Debrecen and from the surrounding agricultural and forest areas from the surface and from 15 centimetres of depth to follow the track of infiltration. The majority of samples have been taken along a Northwest-Southeast cross-section across the city (Fig 1.). At least one sample has been taken along busy roads that run at the border of each territorial unit (build-up/land use type). The rest of the samples have been taken from the inner parts of the area, from parks, free areas, gardens and playgrounds.

Soil samples had been dried until air-dry state. Heavy metals had been extracted by wet digestion using cc. nitric acid. Measurements have been carried out by atomic adsorption spectrometry using the flame technique. Humus content has been determined by the method of Tyurin, $CaCO_3$ content by titration, using the Scheibler calcimeter. Particle size measurements have been carried out by the pipette method and wet sieving. The electrometric technique has been used to determine pH.

4. Results and discussion

4.1. Spatial pattern, vertical distribution of the heavy metal content of the soil

Table 1 shows the heavy metal load of the soil surface in the build-up/land use units of the city. It can be seen that results are scattered in a wide range in most types. In practice, it means only one or two outstanding values in each type. The soil samples in every build-up/land use type can be placed into two categories based on lead concentration. The first one includes samples taken in a distance of 20-50 meters from the roads in inner parts of each unit. Heavy metal loads characteristic for a given type have been counted on the base of these samples. Lead-contents are far below the limits at these sites. The second group includes samples taken in areas within 2-20 meters from the roads. Outstandingly high heavy metal loads occur in this category.

High lead loads can usually be found in 10 meters wide zones along roads with high traffic density or which used to have high traffic density. The effect of the busy roads can be detected only to a relatively short distance (about 50 meters). In free spaces, as a result of undisturbed air motion – with homogeneous pedologic parameters –, heavy metal content of soils decreases roughly exponentially with the increasing distance from busy roads.

In each case, the cadmium content was less than 1 ppm. That is, exceeding of the limits had not occurred anywhere. Additional conclusions cannot be drawn from the results. This fulfils the expectations because the cadmium may get into the soil only in small amount from the attrition of the tires of the cars and from the exhaust gas. The presence of other sources can be excluded in the sample area.

No connection can be shown between the metal content of the soil and the distance of the sample sites from the busy roads in the cases of cobalt, nickel that are not of traffic origin. The behaviour of copper similar to that of lead: highest values have been measured Cobalt and the nickel has not accumulated in the A horizon of the soil. Based on their vertical dispersion in the soil (their amount increase parallel with the depth), it can be stated that these metals mostly originate from a natural (bedrock) sources in the study area. At some sites, the increase of cobalt and copper content results from former oil-firing (thermal power station, KLTE caloric centre). Exceeding of the limits has been detected at those sites.

Cobalt and nickel has not accumulated in horizon A of the soil. On the basis of their vertical distribution in the soil (their amount increase parallel with the depth), it can be stated that these metals mostly originate from a natural (bedrock) sources in the study area. At some sites, the increase of cobalt and copper content results from former oil-firing (thermal power station, KLTE caloric centre). Exceeding of the limits has been detected at those sites.

Traffic density, build-up and land use features play decisive role in formation of the characteristic heavy metal loads in the soils of build-up/land use types. Traffic density and the distance from roads determine the airborne heavy metal input into a given area. The nature of the build-up and land use governs the mobility/fall out of heavy metals within the area. Three factors are important: the height and density of the buildings and the plant density of the area (Csorba, 1997). Buildings higher than 10 meters modify the close-to-the-surface air motion, and the mobility of aerosols that carry heavy metal compounds. Vegetation binds a significant amount of heavy metals from the air, therefore less heavy metal will fall onto the soil.

Within the type of the green areas the contiguous forest areas (Nagyerdő) were separated because those sample sites were used to determine the background heavy metal content of the soil. Parks of the city and green areas of public institutions were handled together. In free spaces, as a result of undisturbed air motion, – with homogeneous pedologic parameters – heavy metal content of the soil decreases roughly exponentially as moving away from busy roads due to the filtering effect of the vegetation. Lowest lead concentration was found in the Nagyerdő outside the city, at a distance of 200 meters from the road to Pallag. At each sample site in the Nagyerdő soil heavy metal loads were far below the limits.

The cultivated areas can be divided into two groups. Heavy metal loads in soils far from roads are originated mainly from fertilisers and pesticides not from traffic. This is supported by the fact that in these areas lead is not the most important heavy metal pollutant. The 2-10 meter wide, grass strips along busy roads used as grazing lands for cattle gets large amounts of lead. Highest loads – usually over the limit value – have been found at those sites what pose potential danger for human health.

There are two groups within the type of housing estates. The first one includes 6-10 storied concrete blocks, while the other includes 2-4 storied blocks of freehold flats (Csorba, 1997). The rows of tall concrete blocks perpendicular to the prevailing wind direction can block the spreading of pollutants. This can be seen in the difference between the samples taken in a distance of 50 meters from each other on the two sides of the row of houses in sparsely vegetated areas along the roads, in front of the houses and behind them. The rows of buildings parallel with the frequent wind directions may strengthen the wind because of the channel effect that can take the heavy metal bearing aerosols to a great distance from the road. These effects can be seen most clearly in the case of the tall houses of the estates. This effect does not (or rarely) appear in the case of the small blocks of freehold flats. In that group the higher density of vegetation decreases the amount of heavy metals that can reach the soil directly.

The picture is less obvious in the type of detached, semi-detached houses. Buildings influence air motions insignificantly, and vegetation density of the sites can be very varying. Significant differences are caused by the distances of the building-sites from the roads, and whether they are directly adjacent with the busy roads. The role of the vegetation seems to have secondary importance.

Significant differences have been observed in the area of the city centre between heavy metal loads of the streets, squares and the yards. The tall closed-front rows of houses in the city centre hinder the distribution of the heavy metal containing dust, so it stays above the streets. The surface is usually only scarcely vegetated, so the heavy metal compounds from the falling dust get directly into the soil, if it is not strongly condensed as a result of treading.

Table 1. Heavy metal content of the topsoil in the build-up/land use units of Debrecen (values are given in ppm).

build-up/land use units and number of samples	Pb		Cd		Co		Cu		Ni	
	range	average	range	average	range	average	range	average	range	average
Cultivated areas 10	7-136	28	<1	<1	2-14	4	2-19	10	12-49	24
Green spaces 8	5-42	22	<1	<1	2-6	2	6-24	13	11-61	24
Detached and semi detached houses 19	8-75	29	<1	<1	2-9	4	4-72	24	11-35	21
City center 15	7-167	63	<1	<1	2-10	5	11-44	25	14-49	22
Housing estates19	12-60	26	<1	<1	3-10	8	3-28	15	4-47	23
Industrial areas 12	18-208	63	<1	<1	2-37	8	10-59	20	8-36	20
Rural background 5	4-14	7	<1	<1	4-9	6	3-7	5	3-13	8

In industrial areas the development of high soil heavy metal loads can be attributed to two factors. On one hand, traffic density of these areas is very high. On the other hand, some industrial sources also contribute to the increase in the heavy metal concentration of the atmosphere and the soil. It is typical that in the southern industrial area, high loads were found even along a dirt-track with insignificant traffic.

Heavy metal content of soils in playgrounds and recreational areas was far below the tolerable levels at each location. High loads of copper in the soil of urban gardens and vineyards are due to pinhole sources and vast use of copper containing pesticides. Concentrations of lead in soils and plants higher than tolerable values occurred in the 2-10 meters neighbourhood of busy roads. This poses a serious problem because those areas are used as grazing fields.

4.2. The role of the most important soil properties in the binding of heavy metals

4.2.1.Humus content

Heavy metal content of surface samples – as it was expected – was higher than that of ones from a depth of 15 centimetres. If the soil is not disturbed, most of lead and copper deposited on the surface binds in the upper few centimetres. This can be explained by the higher humus content of the topsoil. The cobalt and the nickel bind to the humus molecules more weakly, and their accumulation in the soil happens independently from the humus content. The positive metal ions may bind to many free negative places of the humus molecules (Duffs, 1980). The higher is the humus content, the higher heavy metal loads will occur if the same amount of metal deposits on the soils.

Compared to rural sites it is quite frequent in urban soils that higher heavy metal contents occur not in the surface layer but at a depth of 15 centimetres. Usually, the humus content is higer at 15 centimetres in these samples what indicates that the soil was disturbed. Further more, the connection between the heavy metal concentration and the humus content of the soil is not obvious always, because the amount of heavy metal that deposits on the soils can be different as well.

4.2.2. Clay fraction

The surface of the clay minerals carries free negative charges and binds the heavy metal ions exchangeable (Frank – Tölgyessy, 1993). The smaller is the diameter of the particle, the larger is its specific surface and the more heavy metal cations can it bind. Therefore, the role of clay minerals is important in the binding process of the metals in the soil. In the present study, the clay fraction of the soil was determined, which consists of each soil grains smaller than 0.002 mm in diameter. Most of them are not clay minerals. These particles have not the same binding characteristics as those of clay minerals. For this reason, it is not surprising that only in the case of nickel and cobalt appears to be connection between the clay and the heavy metal content.

4.2.3. pH

Hydrogen ions can displace metal ions from the free negative places of the humus molecules and clay minerals (McEldowney et al. 1993). Therefore, pH plays an important role in the mobility of metals in soils (Szabó Sz. 2004; Szabó Sz. – Szabó Gy. 2006). The more acidic is the soil, the less likely is to bind heavy metals steadily and the higher proportion remains in forms available for plants in the soil solution or the more infiltrates into deeper levels of the soil profile. The number of the samples taken from acidic sand-soil is not enough to make a statistical processing. In the majority of the samples the chemical reaction of the soil was between pH 6.9 and 8.0. In this interval the cadmium, and the cobalt is slightly mobile while the lead, copper and the nickel is poorly mobile. Lead and copper which are less sensitive to the pH, show a tendency to accumulate in the topsoil and their amount decreases with the growing depth, while more mobile cadmium, cobalt and nickel moves downwards in the soil profile. Parallel with the growth of the depth the cadmium-, cobalt-, and nickel-content increases.

4.2.4. Calcium-carbonate content

There are not any direct relationships between the $CaCO_3$ content and the heavy metal content of the soil. However, $CaCO_3$ influences the binding of the heavy metals in the soil through formation of carbonates and indirectly, through modification of the pH.

Connections between soil characteristics and heavy metal contents are less obvious in urban soils than in samples taken in rural locations. This is partly explained by the fact that original soil types are modified in the city. Original soil horizons are disturbed, and in extreme cases there are not any soil horizons, but soil layers put on top of one another. The originally significantly different pH of soil types becomes uniformed. Lime, which gets into the soils with the building debris, increases the $CaCO_3$ content and the pH of the soils, what favours the immobilisation of the heavy metals. The structure of urban soils deteriorates, the soil becomes condensed and the water permeability can deteriorate significantly as well. This hinders the movement of the heavy metal compounds downwards in the profile.

5. Conclusions

On the base of the results, it has been found that effect of busy roads on the heavy metal content of the soils in their neighbourhood can significantly vary according to the type of build-up and land use in their environment. Certain characteristic soil heavy metal loads can be established for each build-up/land use type.

Highest loads – as it was expected – have been found in the case of the lead. This often means the exceeding of the limits in the neighbourhood of busy roads. The exceeding of the limits has also been detected in the case of the nickel nearby the oil-firing – or former oil-firing – thermal power stations and caloric centres.

The calcium-carbonate- and the humus-content, the pH-value and the clay-content of the soil properties were studied from the point of view their role in binding heavy metals.

The $CaCO_3$ content influences the binding of heavy metals through forming of carbonates and indirectly, through the modification of the pH.

In contrast with the data studied in the literature, no obvious relationship was found with the clay mineral content of the soil, either.

The mobility of the heavy metals in the soil is strongly influenced by the chemical reaction of the soil. It can be seen in the case of the samples taken from acidic sandy soils that the less mobile lead and copper tend to accumulate in the topsoil, while the more mobile cadmium, cobalt and nickel moves downwards in the soil profile.

Strongest connections have been found between the heavy metal- and humus-content of the soil.

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