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SELECTED HEAVY METALS AND THEIR BEHAVIOUR IN URBAN SOILS VERSUS SOIL QUALITY STANDARDS

Urban soils reveal great diversity in a potential bioavailability of heavy metals. In Zielona Góra urban area, the bioavailability of Cd, Cu, Ni, Pb and Zn ranged from 1.9 to 98.7%, from 0.8 to 93.3%, from 1.3 to 91.3%, from 0.7 to 99.9% and from 0.4 to 98.9%, respectively. At the same time, in the properties of the soils under analysis some complicated correlations were found. Despite high reaction of the soils (on average pH in water is 7.17 and 6.78 in 0.01 M $CaCl_2$) higher plants take up Cd, Pb and Zn in large amounts, namely wild privet takes up 1.62 mg $Cd\cdot kg^{-1}$ and 242.4 mg $Zn\cdot kg^{-1}$ at the maximum, and small-leaved lime 31.5 mg $Pb\cdot kg^{-1}$ at the maximum. In the procedure of determining the critical values characteristic of urban environment, an anthropogenic effect on the formation of urban soils, hence on different soil behaviour, mainly potentially high bioavailability of contaminants, has to be taken into account.

1. INTRODUCTION

Various methodological approaches were suggested to the soil condition description; however, in the majority of cases the critical values referred to the total content of heavy metals (KABATA-PENDIAS [16], EIKMANN, KLOKE [9], MARTINEZ et al. [18], MILANI et al.[20]). At the same time some attempts were made to explain soil sorption as the phenomenon fundamental to the bioavailability of soil contaminants (CASTILLO, ITURRONDOBEITIA [7]). Many authors suggest that urban areas can be used after their separation and internal division (EIKMANN, KLOKE [19], BACHMANN et al. [1], MARTINEZ et al. [18]). Based, to some extent, on the above activities, legal regulations concerning soil condition were enforced, for example, EBBodSchG (BACHMANN et al. [1]), the regulation of the Minister of Environment concerning soil quality standards and ground/earth quality standards (Journal of Law 02.165.1359). In standards, the total content of heavy metals versus basic soil qualities can be found.

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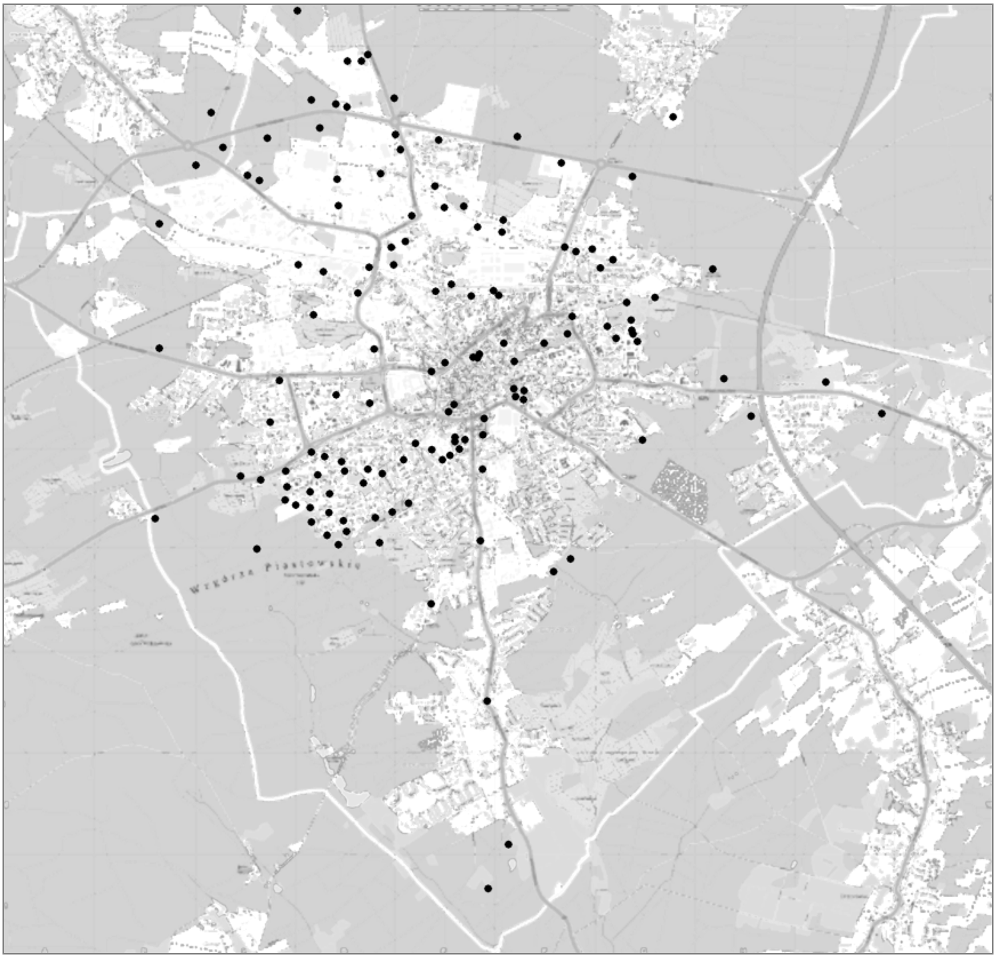
Contamination of anthropogenic soils is influenced not only by their sorption properties, reaction and redox potential, but also by the age of soil and its structure (BLUME, SUKOPP [3], HILLER, MEUSER [13], BURGHARDT [5], [6]). Many researchers revealed a relatively high pollution of soils along the roads and in industrial and post-industrial areas (BURGHARDT [5], MEUSER [19], BURGHARDT [6]). Meanwhile, these areas have been intensively rebuilt recently, and some are constructed from the start. This is connected with the fundamental changes of soils, as huge masses of soil are brought from other areas or brought to the surface from deeper layers. They are less polluted than those which covered the areas described above. Thus the "high risk" areas cannot in fact be highly contaminated, especially the surface soil (GREINERT [10]). If trees and bushes are rooted in such layers, there is a considerable risk of their contamination. There is no clean environment whose soils are not clean, beginning with the direct activities of a child "eating its playground or carrying it away" (REN et al. [25], MAQUSOOD, SIDDIQUI [21], RYAN et al. [26], HUNT et al. [15]) and ending with complicated paths of food chain: from soils through vegetables and fruit from gardens, herbs to animals being bred up to a human beings (PERYEA [23], TRAUNFELD, CLEMENT [29], CLARK et al. [8]). Sometimes contaminants are inhaled with soil particles (secondary dusting as a result of wind erosion).

Some of the problems presented above incline us to determine the total content of heavy metals in urban soils, and the other ones to consider their potential availability to plants and animals. The fact that these elements are absorbed by the roots of plants growing in urban green areas has two aspects: the condition of ornamental plants (GREINERT [10], [11]) and the growing of vegetables and fruit in urban gardens (TRAUNFELD and CLEMENT [29], SIPTER et al. [28]). Recently, as in the framework of waste management, attention is also focused upon the so-called green wastes produced as a result of plant growing. The latter problem can be easily solved by using compost made of urban plants as a fertilizer (RAMOS [24], GREINERT [11]). It should also be stressed that contaminants may penetrate the deer layers of soil profile, posing a real risk to groundwaters.

2. METHODS

The tests were carried out in the town of Zielona Góra, the west of Poland, with 120 thousand inhabitants. It can provide a good example of typical historical European town development – from being an agricultural settlement (with great proportion of orchards and vineyards), through an industrial town to being the town whose heavy industry declined and was replaced with public services. Simultaneously the town has been spread.

The soil samples were collected in the districts reflecting various levels of urbanization – 104 soil profiles, 534 samples (the figure). The samples were supplemented with 34 collective surface humus layer samples taken from the area of approximately 20 m^2. Eighty samples of plant leaves were also collected. The test plants were as follows: small-leaved lime (*Tilia cordata* L.), black locust (*Robinia pseudoacacia* L.), wild privet (*Ligustrum vulgare* L.) and grasses (*Graminae*). Their leaves were collected from 15 locations in the summer and autumn 2007. At each location the leaf samples of the weight of ca. 0.5 kg were taken, each from 5 trees, 10 shrubs as well as from about 20 m^2 of lawn. Every sample was averaged by the material mixing before and after grinding.



Location of soil sampling points

The quasi-total content of Cd, Cu, Ni and Zn (in aqua regia) and the content of heavy metals (in 0.1M HCl) potentially available to plants were determined by means of atomic absorption AAS FL (Varian). The soil extracts in aqua regia (3HCl: HNO_3) were made by ashing 10 g of airy dry soil in a furnace at a temperature of 550 °C (12 hours), and then at a sand bath by heat digesting ash in aqua regia (20 cm^3) until the volume was reduced by 1/3. The decrement was supplemented with a concentrated hydrochloric acid. The procedure of acid boiling and supplementing was repeated twice. Finally, after cooling, the content of the sample was taken to a measuring flask and filled up to 100 cm^3 with deionized water. Extracts in 0.1 M HCl, the fraction potentially available to plants (BAKER and AMACHER [2]), were prepared by cool digesting airy dry soil in 100 cm^3 of the solution and by shaking for one hour. The reaction was determined potentiometrically in distilled water and 0.01 M $CaCl_2$, mechanical composition – with the modified Casagrande method according to Prószyński, carbon content – with NDIR detection method and sorption properties – with the Kappen method. Statistic analysis was carried out using the software Statistica for Windows 8.0. The basic statistic data were defined together with correlations between soil condition indices at $\alpha = 0.01$ and 0.05.

3. RESULTS AND DISCUSSION

The functionality of anthropogenic urban soils depends, to a great extent, on their sorption properties. The possibilities of maintaining plants, ensuring the protection of drinking water taken from abyssal intakes, as well as minimizing contamination hazards are strongly related to sorption properties of soils. Within the area of urban gardens this aspect is additionally related to the production of "clean" food. Sorption depends, to a great extent, on the content of both organic matter and mineral colloidal fraction. Skeleton part impurities, such as building debris, reduce the soil capacity to sorb cations which is proved by HILLER and MEUSER [13] who tested the soils in the Ruhr Basin. Kahle and Coburger (1996) focused their attention on the effect of soil sorption capacity on soil use, which is connected with fertilizing effect or its lack as well as with the depth of mechanical transformation of natural soil formations. The results of the tests carried out testify to diverse but generally low sorption capacity (table 1). Short duration of a newly formed soil cover has an influence on the disturbances of internal relations in soil and on the instability in the sorption phenomena. This is shown by a low coefficient of the correlation between the majority of the qualities of soils under analysis and the presence of potentially movable forms of Cd, Ni and Zn in urban soils. Movable forms of Pb and Cu were highly correlated with the saturation of sorption complex with cations of alkaline character ($r = –0.45$ and $r = –0.40$, respectively).

Table 1

Selected properties of soils in the Zielona Góra urban area

	N	Average	Min.	Max.	Std. Dev.
Content of parts: Ø > 20 mm (%)	534	1.83	0.00	38.05	4.76
Content of parts: Ø 20–10 mm (%)	534	2.36	0.00	24.18	3.34
Content of parts: Ø 10–1 mm (%)	534	19.78	0.00	67.03	12.10

	N	Average	Min.	Max.	Std. Dev.
Content of parts: Ø < 1 mm (%)	534	76.03	21.00	100.00	15.41
Content of parts: Ø < 0.02 mm (%)	535	4.87	0.00	55.00	6.09
Content of parts: Ø < 0.002 mm (%)	535	0.98	0.00	18.00	2.33
TOC (%)	531	4.02	0.00	60.26	6.30
pH-H_2O	525	7.17	4.12	9.15	0.82
pH-$CaCl_2$	525	6.78	3.52	8.26	0.80
EC ($\mu S \cdot cm^{-1}$)	512	226.35	0.00	2500.00	229.12
Hh ($cmol \cdot kg^{-1}$)	532	0.84	0.00	18.28	1.48
S ($cmol \cdot kg^{-1}$)	529	10.66	0.00	24.70	7.09
CEC ($cmol \cdot kg^{-1}$)	529	11.51	0.95	40.40	7.24
V (%)	505	89.22	0.00	99.91	15.75
K in water extract ($mg \cdot kg^{-1}$)	527	391.75	31.20	2816.85	383.97
K in 0.1 M HCl ($mg \cdot kg^{-1}$)	527	1955.63	102.05	9796.80	1537.19
K in aqua regia ($mg \cdot kg^{-1}$)	534	7853.10	740.60	23568.60	4075.82
Ca in water extract ($mg \cdot kg^{-1}$)	532	1465.25	50.00	17120.25	1198.56
Ca in 0.1 M HCl ($mg \cdot kg^{-1}$)	526	15443.93	833.35	96000.00	18121.30
Ca in aqua regia ($mg \cdot kg^{-1}$)	523	27806.79	952.40	244000.00	34443.14
Mg in aqua regia ($mg \cdot kg^{-1}$)	535	500.22	14.80	1350.42	314.13
Na in water extract ($mg \cdot kg^{-1}$)	532	263.04	17.48	908.70	181.78
Na in 0.1 M HCl ($mg \cdot kg^{-1}$)	529	1908.62	65.80	18088.00	1699.18
Na in aqua regia ($mg \cdot kg^{-1}$)	533	3721.27	332.40	24217.60	2810.68
Fe in 0.1 M HCl ($mg \cdot kg^{-1}$)	531	535.32	5.50	2685.00	411.17
Fe in aqua regia ($mg \cdot kg^{-1}$)	532	6400.86	1270.00	13543.15	3070.39
Mn in 0.1 M HCl ($mg \cdot kg^{-1}$)	525	129.16	0.00	685.33	102.39
Mn in aqua regia ($mg \cdot kg^{-1}$)	533	229.10	13.60	2311.90	198.72
Cd in 0.1 M HCl ($mg \cdot kg^{-1}$)	525	0.12	0.00	0.78	0.11
Cd in aqua regia ($mg \cdot kg^{-1}$)	535	0.45	0.10	2.92	0.28
Cd 0.1 M HCl/aqua regia (%)	525	27.65	0.00	98.70	23.89
Cu in 0.1 M HCl ($mg \cdot kg^{-1}$)	526	7.20	0.26	94.39	8.81
Cu in aqua regia ($mg \cdot kg^{-1}$)	535	24.84	2.58	474.86	38.35
Cu 0.1 M HCl/aqua regia (%)	526	39.20	0.67	205.35	24.15
Ni in 0.1 M HCl ($mg \cdot kg^{-1}$)	526	1.73	0.00	17.03	1.38
Ni in aqua regia ($mg \cdot kg^{-1}$)	535	11.09	1.00	54.97	7.45
Ni 0.1 M HCl/aqua regia (%)	526	20.26	0.00	91.36	16.16
Pb in 0.1 M HCl ($mg \cdot kg^{-1}$)	526	11.16	0.00	98.02	10.63
Pb in aqua regia ($mg \cdot kg^{-1}$)	530	39.49	0.00	2406.71	132.14
Pb 0.1 M HCl/aqua regia (%)	514	51.55	0.76	99.96	28.80
Zn in 0.1 M HCl ($mg \cdot kg^{-1}$)	525	18.30	0.00	71.50	17.22
Zn in aqua regia ($mg \cdot kg^{-1}$)	535	80.80	5.40	510.55	79.76
Zn 0.1 M HCl/aqua regia (%)	526	27.39	0.00	98.87	19.99

One of the commonly perceived differences between urban soils and the non-urban soils is their reaction. The measurements of pH of the soil from the town of Zielona Góra show that the reaction of O horizon differs from those of deeper horizons. 21.9% of the O horizon showed neutral reaction, whereas 9.4% were alkaline. Deeper horizons proved to be neutral (24%) and alkaline (50.7%). It is a typical practice in surface urban soil reclamation to use bark and humus substrates during formation of green areas. Absorption of heavy metals by plants and their mobility in soil were investigated by, among others, HERMS and BRÜMMER [14]. On the other hand, slightly acid reaction is favourable for most of plants used for the formation of green areas. Also, purification of waters penetrating into the soil profile is most effective under these conditions.

In urban space, heavy metals are emitted from numerous industrial and municipal sources. Also transport emissions and street flows (MACIEJEWSKA and KWIATKOWSKA [17]), percolation and erosive rain-wash of elements from waste dumps and their undersurface deposits (BLUME and SUKOPP [3], BURGHARDT [6], HILLER and MEUSER [13], MEUSER [9]), erosion of urban infrastructure elements (PALM and OSTLUND [22]), fertilizing materials, including composts based on sludge (RAMOS [24], SÆBØA and FERRINI [27], HEA et al. [30]), some plant protectants (GREINERT [12]) and many others contribute to the pollution of urban soils. The research presented proves that there is a significant correlation between the proportion of post-construction and mixed impurities (including municipal wastes) and the content of Cd, Cu, Ni, Pb and Zn in urban soils.

The presence of heavy metals in soils does not depend only on the number and character of their sources but also on the time of their emissions. Rapid development and rebuilding of cities over the past 30 years have resulted in the exchange of materials deposited on the surface of the majority of their storing areas. Additionally, during construction works, soils were mixed at a considerable depth, which caused dilution of heavy metals in soil matter. Thus, the majority of urban areas show a low pollution with heavy metals – in terms of standards they are clean and there are no limitations concerning their use. However, these standards refer to soil as “an accumulator”, and not “a transmitter” of contaminants. The results presented in table 2 show that the leaves of higher plants growing in

Table 2

Content of Cd, Pb, and Zn in the leaves of plants in urban green areas

Species	Sampling period	Content – min., max., average ($mg \cdot kg^{-1}$)		
		Cd	Pb	Zn
Tilia cordata L.	summer	n.w.–0.28 (0.17)	6.86–16.46 (9.76)	30.98–52.84 (41.94)
	autumn	0,18–0.88 (0.50)	14.42–31.50 (23.04)	31.26–91.86 (59.02)
Robinia pseudoacacia L.	summer	n.w.–0.60 (0.27)	3.82–8.46 (5.61)	42.84–107.98 (59.79)
	autumn	0.22–0.64 (0.40)	7.98–31.30 (17.21)	40.82–158.30 (75.40)
Ligustrum vulgare L.	summer	n.w.–1.62 (0.44)	3.44–14.86 (6.62)	41.06–85.20 (65.20)
	autumn	0.18–1.12 (0.53)	12.74–20.16 (15.15)	46.12–242.40 (117.41)
Graminae	summer	n.w.–0.38 (0.25)	1.76–12.34 (6.72)	44.76–108.44 (77.11)
	autumn	0.18–0.52 (0.32)	13.88–27.08 (18.67)	65.34–174.30 (105.89)

n.w. – below the detectability threshold of the method applied.

cities, despite their apparent cleanness, contain increased quantities of heavy metals. Only a small portion of them gets into the plant directly through leaf tissues, so it must be taken for granted that most of them are absorbed from soil.

The results obtained testify to a high solubility of the heavy metals in urban soil environment as well as the possibility of being absorbed easily and accumulated successively by plants. It should be assumed that with a strong "skeletoning" (debris accumulating) of urban soils, the migration of those impurities into the depth of soil profile is relatively simple – up to the level of groundwaters. The need to consider this fact when determining soil condition was indicated by MILANI et al. [20], who established soil criteria in terms of groundwater protection. It is an essential step because heavy metals are able to migrate within the soil profile at considerably lower acceptable concentration in groundwaters than in soils.

4. CONCLUSIONS

1. Urban soils show a great complexity of behaviour towards heavy metals, including sorption and desorption.

2. Municipal soils have fundamentally neutral or alkaline reaction, which affects chemical sorption of heavy metals. A time-dependent ion-exchange sorption is not explicit.

3. The uptake of heavy metals by higher plants depends not only on the properties of soils and their purity, but also on the features of the plant species, such as: growth form (high absorption by the wild privet shrubs), rooting strength and sucking strength (higher metal content in the black locust compared with that in the small-leaved lime), physiology of heavy metal uptake (high soil–plant transfer potential of Cd and Zn).

4. In urban areas, the permissible concentrations of heavy metals should be reduced due to their high potential mobility, independent of the soil properties.

5. An effective solution for dealing with heavy metals is to provide indications of soil condition in terms of living organisms and groundwaters.

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