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APPLICATION OF SOIL-PLANT TRANSFER COEFFICIENTS AND PLANT POLLUTION INDICES FOR EVALUATING HEAVY METAL CONTAMINATION WITHIN THE MARCINKOWSKI'S RECREATIONAL PARK (POZNAŃ)*

Summary. Soil and grass samples were collected in October 2009 within the Marcinkowski's Recreational Park (MRP) of the city Poznań. Thirty six soil samples were collected at two depths (i.e., 18 samples at 0-10 cm and 10-20 cm) and additional grass samples (18). Pseudo total amounts of Pb, Cd, Cu and Zn were extracted by 6 mol HCl per 1 dm^3; the same metals were also assayed in grass samples. These data were used for calculating soil-plant Transfer Coefficients (TC) and Plant Pollution Index (PPI). Results dealing with soil properties showed a downward homogeneity, a fact stressing on the strong impact of urbanization. High levels of silt and clay as well as organic carbon were decisive in shaping the size the buffering capacity, which in turn may have been fully controlled by the alkaline pH, *ca* 7.3. Amounts of Cd and Pb exceeded *ca* 9 and 6-fold, respectively the background values, whereas for Cu and Zn, *ca* 3-fold. The occurrence of such relatively high levels of Cd and Pb could be attributed to the impact of heavy traffic. Values of TC and PPI followed the sequences (based on means): for TC: Cd > Zn > Pb > Cu, and for PPI: Cd > Pb > Zn > Cu. Among all investigated metals, Zn contributed the most to the whole contamination of grass growing within the park. The influence of Pb and Cd was less pronounced.

Key words: Recreational City Parks, heavy metals, Transfer Coefficients (TC), Plant Pollution Index (PPI)

Introduction

The significance of heavy metals for the environment quality has been reported in several European Union Directives 2004/107/EC (arsenic, cadmium, mercury, nickel,

*The investigations were conducted within the project of the Poznań city: Proj. bad. M. P-ń um. RoM.V/3420, 2009.

for instance) and Directive 2008/50/EC; Directive 2004/35/EC; Directive 2008/1/EC (for bioindicators), where it was stressed on the serious threat for human health evoked by the presence of these metal in the food chain as well as in the environment. This is why the use of bioindicators for supporting technical monitoring, mainly chemical, of city environments is being strongly encouraged. For Polish conditions, the Directive 9 September 2002 (ROZPORZĄDZENIE... 2002) also regulates heavy metal contents, particularly for protected areas, recreational urban parks among others. Pollution of soil by potentially toxic metals is often assessed in terms of total concentrations. However, many forms of metal are strongly held in soil and generally become immobile, although several factors (pH, redox, soluble organic matter, etc.) may mobilize such forms (MADRID et AL. 2006). Depending on the metal, its speciation and toxicity mechanism, the most mobile (or soluble) forms are more likely to be harmful or taken up by plants than those held strongly in the soil matrix.

The bioavailability of essential micronutrients such as copper and zinc is influenced first by their natural (bio)affinity for plants, which are able to solubilize insoluble forms as necessary (GUPTA et AL. 1996, MCBRIDE 1989). The chemistry of heavy metals in urban soils is far from understood, and several aspects of their dynamics need further study, for example the degree of interaction of contaminants with soil constituents and further availability. In the case of cadmium and lead, toxic by nature, their uptake by plants has no physiological basis, hence the rate of phytoaccumulation is a matter of their chemical specificity and geochemical processes (KLOKE et AL. 1984, FREYTAG 1986, KABATA-PENDIAS and PENDIAS 1992, PUSCHENREITER et AL. 2005). Therefore interactions at the level *soil metals – plant uptake* commonly considered as Bioavailability Factors (BF) or transfer factors (TF) (KNOX and ADRIANO 2000, MÂŞU and DRAGOMIR 2008, DIATTA et AL. 2009) play one of the key role in biogeochemical monitoring studies. According to KNOX and ADRIANO (2000), the BF may be defined as the ratio of the metal content in the exchangeable phase ($[M]_{ex}$) to total metal content in the soil ($[M]_T$), BF = $[M]_{ex}/[M]_T$. This index indicates the fraction of the total content of a metal in the soil, that is considered readily available to plants. The TF is the ratio of the metal content in plant tissue ($[M]_P$) to the total content of metal in the soil ($[M]_T$), TF = $[M]_P/[M]_T$. It is normally considered as a measure of plant uptake by the roots and subsequent translocation to the aerial portion of the plant.

In pollution research, soil is mainly considered as a medium of plant growth and agriculture production, but urban conditions, changes in the chemical nature of the soil can lead to adverse interactions on soil flora and fauna, toxicity and exposure of the population, particularly young children, to toxic substances. The sources and distribution of potentially toxic elements like Cd, Cr, Ni, Pb, Cu in the urban environments have been widely studied (KELLY et AL. 1996, GREGER 1999, MADRID et AL. 2002, ELIK 2003). Specific man made activities can significantly influence the deposition of these elements in towns, but traffic is also an important source, influencing the phytochemistry of the grass cover within recreational parks. Therefore a complete assessment of the contamination state should involve additional indices directly related to plant contamination by heavy metals – PPI (SANKA et AL. 1995, DIATTA et AL. 2003).

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The purpose of the current work was to assess the level of soil and grass contamination within the Marcinkowski Recreational Park. Specifically, this approach was undertaken by using soil-plant transfer coefficients as well as plant pollution indices.

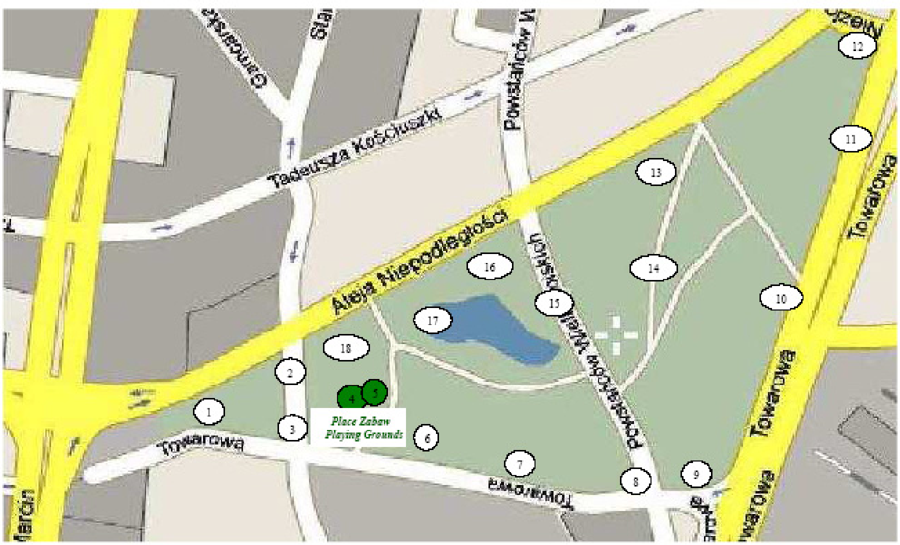
Materials and methods

Brief outline of the Marcinkowski Recreational Park (MRP)

The Marcinkowski Recreational Park (52.40°N, 16.92°E, Poznań), formerly Frederic Schiller, was established *ca* 1905-1906 and occupies currently an area of 9.4 ha. The park is located in the center of Poznan and surrounded by streets of heavy daily traffic. Trees and the grass occupy quite a similar area, which is yearly subjected to several maintenance activities.

Soil and grass sampling and chemical analyses

Thirty six soil samples were collected in October 2009 at two depths (i.e., 18 samples at 0-10 cm and 18 samples at 10-20 cm) and additional grass samples (18) from the Marcinkowski Recreational Park (Fig. 1). Prior to chemical analyses, soil samples were air-dried, crushed to pass a 1.0 mm screen and stored in plastic bags before chemical analyses. The particle size composition was determined according to the areometric



52,40°N 16,92°E (Poznań) [www.mapa.szukacz.pl]

Fig. 1. Characteristics of the investigated area (MRP). Soil and grass sampling sites are numbered in circles

Rys. 1. Charakterystyka terenu badawczego (MRP). Stanowiska pobrania próbek gleb i trawy ponumerowano w kółeczkach method of Bouyoucos-Casagrande (GEE and BAUDER 1986). The pH was determined potentiometrically by Polish standard (POLSKA NORMA 1997) in 0.010 mol $CaCl_2$ per 1 dm^3 and the electrical conductivity ($EC_{1:5}$) at soil/water ratio of 1:5, according to RHOADES (1996). Next, organic carbon (C_{org}) was assessed by the Walkley-Black method as reported by NELSON and SOMMERS (1986), whereas the Cation Exchange Capacity (CEC) by the ammonium acetate test, i.e., 1 mol CH_3COONH_4, pH 7.0 (THOMAS 1982). Copper, Zn, Pb and Cd contents were extracted by using 6 mol HCl per 1 dm^3 and the recovered amounts designated as pseudo total (GUPTA et AL. 1996). All analyses were performed in duplications.

Dried grass (aboveground parts) samples (0.20 g) were digested in concentrated nitric acid by using MARS 5 CEM Corporation equipment. The recovered digests were filtered and Cu, Zn, Pb and Cd were determined by the FAAS method (Flame Atomic Absorption Spectrophotometry, Varian Spectra 55B). All chemical tests were run in duplication and statistical evaluations were performed by using the Statgraphics® software and Excel® sheet facilities.

Indices (TC and PPI) calculation

Heavy metals determined in soils and grass samples have been used in calculating the soil-plant transfer coefficients (TC = Metal in grass/Metal in soil) as well as the Plant Pollution Index:

$$PPI = \frac{1}{n} \cdot \sum_{i=1}^{n} \cdot 100 \cdot \frac{VP_i}{LP}$$

where: n – number of heavy metals, VP and LP – content of a given metal in the grass and the threshold values, respectively. The latter ones were applied as reported by KABATA-PENDIAS and DUDKA (1991): Cu – 50; Zn – 100; Pb – 10; Cd – 0.5 ($mg \cdot kg^{-1}$).

Results and discussion

Soil properties

Urban soils are generally reported to be largely under anthropogenic pressure, hence their physical as well as chemical properties are frequently disparate and do not follow a stringent trend (CZARNOWSKA 1997, DĄBKOWSKA-NASKRĘT and RÓŻAŃSKI 2002). This concerns also city recreational parks, subjected to a number of activities such as maintenance, incorporation of organic mass, renovation of green cover (i.e. grass), etc. Data reported in Table 1, outline ranges characterised decidedly by significant scattering (except for pH), and support this observation. Furthermore, investigated parameters were also related to the sampling depths, i.e. 0-10 and 10-20 cm, with slightly higher values (case of clay + silt and electrical conductivity) observed for the upper one.

The analysis of soil properties on the basis of mean values showed a "striking" downward homogeneity (except for C_{org}) of soils within the park, a fact stressing on the strong impact of urbanization. The significantly high levels of silt and clay as well as C_{org}

Table 1. Selected physical and chemical properties of soils within the Marcinkowski Recreational Park (n = 18)
Tabela 1. Wybrane właściwości fizyczne i chemiczne gleb w obrębie Rekreacyjnego Parku Marcinkowskiego (n = 18)

Parameter Parametr	0-10 cm		10-20 cm	
	range zakres	mean ±SD* średnia ±SD*	range zakres	mean ±SD* średnia ±SD*
Silt + Clay (g kg^{-1}) Pył + ił	220-760	538 ±136	220-920	530 ±182
C_{org} (g kg^{-1})	15.8-43.0	28.8 ±8.7	13.1-36.5	19.3 ±5.7
pH_{CaCl2}	6.9-7.6	7.3 ±0.2	7.1-7.4	7.3 ±0.1
EC ($\mu S \cdot cm^{-1}$)	86.3-274.0	119.7 ±42.5	75.0-139.3	103.7 ±18.0
CEC ($cmol_{(+)} \cdot kg^{-1}$)	11.3-21.8	15.8 ±2.6	10.1-20.5	15.8 ±2.7

*SD – Standard Deviation.
*SD – Odchylenie standardowe.

strongly influenced the size of the buffering capacity (CEC), which in turn may have been fully controlled by the alkaline pH, *ca* 7.3. Such soil characteristics play an important role in the reduction of heavy metals mobility and next their uptake by the flora and fauna (KNOX and ADRIANO 2000, MÂŞU and DRAGOMIR 2008).

Heavy metals in soil within the MRP – contamination state

Sources of heavy metals in urban ecosystems are numerous, and these include among others car traffic, household chimney fallouts (KELLY et AL. 1996), incorporation of municipal composts before laying lawns. The multidimensional origin of metals and their long persistence in these soils is a matter of great concern. Data listed in Table 2 showed that metal contents in soils varied widely as reflected by appropriate scattering in ranges, mostly observed in the case of soils. The Marcinkowski Recreational Park (MRP), by its location and technical infrastructure, still attracts many visitors (children as well as adults). The danger related to heavy metals induced health disorders requires the application of consequently strict thresholds in order to reduce significantly or avoid an easy contact with pollutants (KLOKE et AL. 1984, SÁŇKA et AL. 1995, GUPTA et AL. 1996). Therefore it seems more reasonable to refer to heavy metals background levels as those suggested by CZARNOWSKA (1996): Pb – 9.8, Cd – 0.18, Cu – 7.1, Zn – 30 $mg \cdot kg^{-1}$ for rough evaluating the contamination state of soils within the investigated park.

Mean values reported in Table 2 explicitly revealed, that Cd and Pb contents exceeded *ca* 9- and 6-fold, respectively the background values, whereas for Cu and Zn, *ca* 3-fold. The occurrence of such relatively high levels of Cd and Pb could be attributed to the impact of heavy traffic, basically. The content of zinc deserves also attention due to the fact, that this metal may not be directly related to the effect of traffic. The high

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Table 2. Heavy metals contents in soils and grass samples within the Marcinkowski Recreational Park; n = 18 ($mg \cdot kg^{-1}$)
Tabela 2. Zawartość metali ciężkich w glebach i trawie w obrębie Rekreacyjnego Parku Marcinkowskiego; n = 18 ($mg \cdot kg^{-1}$)

Metal	Soils[a] – Gleby[a]		Grass samples – Próbki traw	
	range zakres	mean ±SD[*] średnia ±SD[*]	range zakres	mean ±SD[*] średnia ±SD[*]
Pb	17.9-98.7	56.4 ±23.2	2.2-8.3	5.1 ±1.8
Cd	1.0-2.7	1.6 ±0.4	0.3-1.0	0.6 ±0.2
Cu	8.5-45.8	23.3 ±11.6	0.6-4.8	2.1 ±1.4
Zn	38.2-230.5	102.8 ±42.3	7.0-50.7	23.5 ±14.3

[a]Mean values for both depths.
[*]SD – Standard Deviation.
[a]Wartości uśrednione dla obu głębokości.
[*]SD – Odchylenie standardowe.

content of organic carbon (C_{org}) in the 0-10 cm (Table 1) implies, that organic materials have been incorporated during maintenance activities in order to create favourable growth conditions for the grass. The traceability of the type of inputs was not undertaken and seemed quite not feasible. Authors have assumed, that Zn levels, and Cu to some extent, could have originated from these biomasses (composts, mostly). The threat related to direct health disorders are generally agreed to be less as compared to Cd and Pb, toxic by nature (KABATA-PENDIAS 1992, PUSCHENREITER et AL. 2005).

Relevance of Transfer Coefficients and Plant Pollution Indices

The uptake of heavy metals from the soil and their further translocation into aboveground plant parts is a process related basically to factors such as amount and specificity of a given metal, plant species, and geochemical reactions. The physiological performance of plants belonging to grasses (cereals, for instance), lays in the fact, that heavy metals are mostly retained in roots and less is transferred o the aboveground parts (DIATTA et AL. 2009). This is shown by mean metal content in grass samples (Table 2), where their concentrations are lower than those in soils by factors of *ca* 11 for Pb, 11 for Cu, 4 for Zn, and 3 for Cd. The strict analysis of this sequence revealed, that Pb and Cu, generally reported as metals less mobile in soils were similarly taken up, but less as compared to Zn and Cd, whose mobility in soils is greater (KNOX and ADRIANO 2000, MADRID et AL. 2006, MÂŞU and DRAGOMIR 2008). Therefore it may be formulated, that the concentration of Pb in the grass may not created any threat for park visitors and further for composting (after lawn cutting), reversely for Cd.

Values of TC and PPI as listed in Table 3 allow establishing the following sequences (based on means):

for TC: Cd > Zn > Pb > Cu
for PPI: Cd > Pb > Zn > Cu

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Table 3. Transfer coefficients (TC) and Plant Pollution Indices (PPI) for the Marcinkowski Recreational Park; n = 18
Tabela 3. Współczynniki transferu (TC) oraz wskaźnik skażenia trawy dla Rekreacyjnego Parku Marcinkowskiego; n = 18

Metal	Transfer Coefficient (TC) Współczynnik transferu (TC)		Plant Pollution Index (PPI) Wskaźnik skażenia rośliny (PPI)	
	range zakres	mean ±SD* średnia ±SD*	range zakres	mean ±SD* średnia ±SD*
Pb	0.026-0.315	0.116 ±0.078	22.1-83.4	51.0 ±17.9
Cd	0.146-0.611	0.366 ±0.145	52.0-195.0	110.0 ±38.8
Cu	0.018-0.270	0.103 ±0.068	1.1-9.6	4.1 ±2.7
Zn	0.053-0.521	0.245 ±0.143	7.0-50.7	23.5 ±14.3

*SD – Standard Deviation.
*SD – Odchylenie standardowe.

Three aspects may be outlined from these sequences, i.e., i) geochemical, ii) physiological and iii) environmental. The reactions of metals with soil colloids depends strongly on pH, mineral colloid and organic matter content. Investigated soils were characterised by neutral to alkaline soil reaction, and significantly high levels of both clay and silt. These parameters are the first geochemical barriers efficiently reducing heavy metals mobility and their further uptake by plants, grass, among others. From reports of McBride (1989), Kabata-Pendias and Pendias (1992) and Markiewicz-Patkowska et al. (2005), it appeared clearly, that Cd and Zn, under neutral and alkaline soil conditions react with large amounts of OH^- groups and consequently become metallic anions easily taken up by plants. This may have been the case observed in the current study with TC values being significantly higher for Cd (0.366) and Zn (0.245) as compared to Pb (0.116) and Cu (0.103). The latter ones exhibit higher electronegativity values (2.33, 1.90, 1.69 and 1.65, respectively for Pb, Cu, Cd and Zn; Sanderson 1983), hence their enhanced affinity with soil colloids.

The PPI approach has been involved in the current study in order to stress on metals distinctly shaping the contamination state of grass growing within the park. As it was reported just above (Table 3, PPI sequence), the relative importance of individual indices showed, that Cd (PPI = 110) mainly, should be considered as the most serious contaminant of grass, followed by Pb, whose value was 51. It should be mentioned, that the highest the PPI value, the relatively strongest the contamination level, i.e., metal contents in the grass are becoming significantly higher than their respective threshold values. The obtained results are fully in line with the view, that Pb and Cd may be expected as originating mostly from car traffic. Most probably this contamination proceeded *via* uptake from soil and dust deposition, too. The last factor may be verified by the fact, that collected samples of grass were not rinsed out in order to reflect normal conditions at site (i.e., MRP).

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Contribution of heavy metals in the whole contamination of the grass

Contamination as well as pollution aspects are complex in terms of the number and kind of contaminants considered to reflect this state. Most often, several contaminants occur at a given site simultaneously, with the particularity, that one of them is dominating quantitatively and generally agreed to impact the most the system. The consideration of individual PPI, as reported above, may implies that investigated heavy metals were not in position to interact among each other. Linear relationships illustrated in Fig. 2, clearly outline the character and strength of the implication of individual heavy metals in the whole contamination state of the grass.

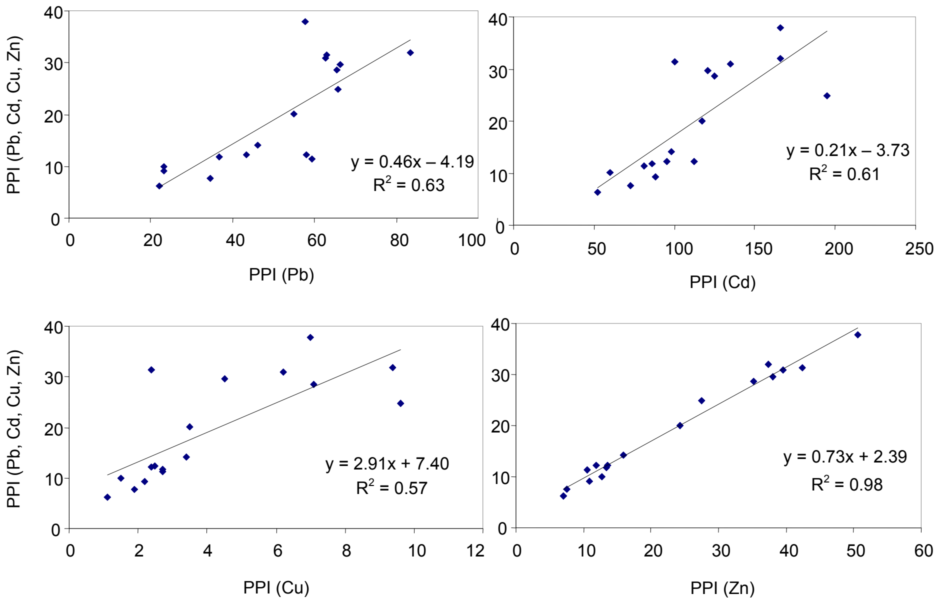

Fig. 2. Contribution of particular heavy metals in the whole contamination state of the grass within investigated park

Rys. 2. Udział poszczególnych metali ciężkich w ogólnym stanie zanieczyszczenia trawy w badanym parku

The coefficients of determination (R^2) based sequence (Zn > Pb ≈ Cd > Cu) decidedly showed, that Zn shaped the most the whole contamination of the grass cover, despite the fact that its toxicity is basically quantitative and not qualitative. Interestingly are also the relationships exhibited by Pb (R^2 = 0.63) and Cd (R^2 = 0.61). These heavy metals are toxic by nature, therefore it may be assumed their "chemical" interactions to proceed similarly. The relatively high R^2 values of Pb and Cd deserve due attention in terms of a potential grass-induced contamination to MRP attendees, mainly at spring – summer periods. This topic is slightly out of the frame of the paper.

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Conclusions

1. Soil properties showed a downward homogeneity (except for C_{org}) a fact stressing on the strong impact of urbanization. High levels of silt and clay as well as C_{org} influenced buffering capacity, which in turn may have been fully controlled by the alkaline pH, *ca* 7.3.

2. Amounts of Cd and Pb exceeded *ca* 9- and 6-fold, respectively the background values, whereas for Cu and Zn, *ca* 3-fold. The occurrence of such high levels of Cd and Pb could be attributed to the impact of heavy traffic.

3. Values of Transfer Coefficients (TC) and Plant Pollution Indices (PPI) followed the sequences (based on means): for TC: Cd > Zn > Pb > Cu, and for PPI: Cd > Pb > Zn > Cu.

4. Among all investigated metals, Zn contributed the most to the whole contamination of the grass growing within the park. The influence of Pb and Cd was intermediate.

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ZASTOSOWANIE WSPÓŁCZYNNIKÓW TRANSFERU GLEBA-ROŚLINA I WSKAŹNIKÓW SKAŻENIA ROŚLIN DO OCENY STANU ZANIECZYSZCZENIA METALAMI CIĘŻKIMI REKREACYJNEGO PARKU MARCINKOWSKIEGO (POZNAŃ)

Streszczenie. Badania przeprowadzono w parku rekreacyjnym im. Karola Marcinkowskiego (około 9,4 ha powierzchni; 52,40°N, 16,92°E) w Poznaniu. Próbki gleb (w sumie 36 – 18 z warstwy 0-10 cm i 10-20 cm) i trawy (18) pobrano w październiku 2009 r. Określono takie właściwości, jak skład granulometryczny, zawartość węgla organicznego, pH, przewodność elektrolityczną oraz kationową pojemność wymienną. Pseudocałkowitą zawartość Pb, Cd, Cu i Zn oznaczono przy użyciu 6 mol HCl na 1 dm^3, te same metale badano także w próbkach trawy po uprzednim zmineralizowaniu tego materiału. Dane służyły do obliczenia współczynników transferu (TC) gleba – roślina oraz wskaźników skażenia roślin (PPI). Wyniki dotyczące właściwości gleby ujawniły pionową homogeniczność, która potwierdza silny wpływ urbanizacji. Wysoka zawartość iłu i pyłu oraz węgla organicznego były decydującymi czynnikami kształtującymi właściwości buforowe, a te z kolei silnie kontrolował wskaźnik pH (około 7,3). Ilości Cd i Pb odpowiednio przekroczyły 9- i 6-krotnie wartości tła geochemicznego, natomiast dla Cu i Zn – jedynie 3-krotnie. Występowanie tak względnie wysokich poziomów Cd i Pb mogło być spowodowane wzmożonym ruchem samochodowym w tej strefie miasta. Obliczone współczynniki transferu (TC) oraz wskaźniki skażenia roślin (PPI) były zmienne i ich wartości uszeregowano następująco – dla TC: Cd > Zn > Pb > Cu, natomiast dla PPI: Cd > Pb > Zn > Cu. Spośród wszystkich badanych metali Zn wykazał się największym udziałem w ogólnym zanieczyszczeniu trawy parku Marcinkowskiego. Wpływ Pb i Cd był pośredni.

Słowa kluczowe: Rekreacyjny Park Miejski, metale ciężkie, współczynniki transferu (TC), wskaźnik skażenia rośliny (PPI)

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