Pol. J. Environ. Stud. Vol. 20, No. 6 (2011), 1433-1440

*Original Research*

# Simulative Evaluation of Pb, Cd, Cu, and Zn Transfer to Humans: The Case of Recreational Parks in Poznań, Poland

**Jean Bernard Diatta*, Witold Grzebisz**

Department of Agricultural Chemistry and Environmental Biogeochemistry, Poznań University of Life Sciences, Wojska Polskiego 71F, 60-625, Poznań, Poland

*Received: 7 February 2011*
*Accepted: 27 May 2011*

**Abstract**

Soil samples (77) were collected in October 2009 at a depth of 0-10 cm from the following recreational parks within the city of Poznań Marcinkowski Recreational Park – MRP (18), Wodziczko Recreational Park – WRP (16), Solacki Recreational Park – SRP (26), and Park/Reserve Zurawiniec – PRZ (17). The following physical and chemical soil analyses were performed: particle size, organic carbon, pH, electrical conductivity, and cation exchange capacity. Furthermore, pseudo total amounts of Pb, Cd, Cu, and Zn were extracted by 6 moles HCl $dm^{-3}$. Bioavailable forms were assayed using the physiologically based extraction test (PBET). On the basis of metal concentrations, potential intakes by children and adults were calculated and risk assessment models elaborated.

Results showed that investigated city parks (MRP, WRP and SRP) exhibited a high capacity to potentially mitigate the mobility of contaminants (pH: 7.1-7.3, CEC 12.0-21.1 $cmol_{(+)} \cdot kg^{-1}$) as compared to PRZ ($pH_{CaCl_2}$=5.6) and both silt and clay (320 $kg^{-1}$), characterized by practically weak buffering properties. The concentrations of all metals exceeded background levels by factors varying, as follows: Cd 6-14; Pb 2-6; Cu 2-3; and Zn 1-4-fold. This enrichment was observed even in the case of the PRZ site, the least anthropogenically impacted. Potential metal intakes by children (particularly) and adults, in cases of accidental swallowing, exhibited the quantitative pattern: Zn > Pb > Cu > Cd, irrespective of investigated parks. Amounts of metal intakes were higher for children, with 94% as compared to 6%, for adults with the following contribution of parks: MRP (42%) > WRP (27%) > SRP (21%) > PRZ (10%). Risk assessment models generated coefficients of determination ($R^2$) varying from 0.57 to 0.81 with a sequence: Zn > Cd > Cu > Pb, which implies that 81, 67, 65, and 57% of respective potential metal intakes can be basically predicted by the knowledge of the level of bioavailable metals fractions.

**Keywords:** recreational parks, heavy metals, PBET, metal intake, assessment models

## Introduction

The concentration of contaminants in urban environments has been progressively pointed out during the last three decades. As a number of people living in towns and cities has increased, larger human populations are being exposed to the negative effects of the urban environment [1-6]. This is more acute in intensively urbanized agglomerations, where car-based transportation services as well as coal burning for heating purposes are practically not substitutable. In pollution research, soil is mainly considered as a medium of plant growth and agricultural production, but in

*e-mail: Jeandiatta63@yahoo.com

urban conditions, changes in the chemical nature of the soil can lead to adverse interactions regulating the toxicity of heavy metals to soil flora and fauna and also humans [7-11].

There has been a growing concern for the potential contribution of metal toxicity in humans. Some trace metals (such as Cu and Zn) at small amounts are harmless [12], but some (notably Pb and Cd) even at extremely low concentrations are toxic and are cofactors, initiators, or promoters in many diseases, including cardiovascular diseases and cancer [1, 13-17]. Young children are particularly vulnerable to heavy metal poisoning for two reasons. Firstly, young children are more likely to ingest significant quantities of soil than adults because of the behavior of mouthing non food objects and repetitive hand/finger sucking. Secondly, children have a much higher absorption rate of heavy metals from their ingestion system and higher hemoglobin sensitivity to heavy metals that adults [18, 19].

Particularly toxic elements tend to accumulate in parenchymous organs, primarily in the liver, kidneys or pancreas, and under prolonged exposure also in bones and brain tissue (Pb) and in hair bulbs (Cd), [5, 17, 20]. Lead and cadmium disturb many metabolic processes, blood pressure, among others, or the functions of the central nervous system [4, 5, 21, 22]. The influence of these metals on a child's organism is often described as deceitful, because the effects are usually long-term and may appear as disturbances in mental development, which affects the future state of health and life. A number of toxicological studies carried out in cities have demonstrated that the main way of incorporating contaminants, Pb and Cd among others, is *via* the digestive system. According to Dutkiewicz et al. [13], up to 50-70% of Pb and Cd ingested by a child's organism originate from dust deposited on ground, dirt on hands, and even dust at home [20, 23].

City dwellers, children, and adults have opportunities to spend leisure hours in city recreational parks. This is strictly related to their different ecological functions characterized by the presence of both the lawn cover and tree stands [24, 25]. These also are strictly under anthropogenic pressure (maintenance, path building, incorporation of compost-based materials for lawn renovation, plus dry and wet dust deposition), which potentially and permanently incorporates heavy metals in these ecosystems. One of the great concerns remains not only in the total amounts of metal burden in soils of these parks but practically in the degree/rate at which they may release and be further bioavailable [26]. The probability of metal ingestion increases with the frequency of attendance and contact with dust/soils within the recreational parks. Hence the need for an experimental and simulative-based assessment of possible metals transfer from soil to humans.

The main purpose of the current study was to evaluate the amounts of Pb, Cd, Zn, and Cu, that may be potentially ingested in the case of incidental soil consumption in selected recreational parks of the city of Poznań. Additionally, the PBET (physiologically based extraction test) method [27, 28] was applied to outline the concentrations of metals in readily bioavailable forms.

Table 1. Sampling sites (parks) and the number of soil samples.

| Site | Abbreviation | 0-10 cm |
|---|---|---|
| Marcinkowski Recreational Park | MRP | 18 |
| Wodziczko Recreational Park | WRP | 16 |
| Solacki Recreational Park | SRP | 26 |
| Park/Reserve Zurawiniec | PRZ | 17 |

## Material and Methods

### Brief Outline of Recreational Parks (RP)

The four investigated recreational parks (RP) are located within the city-agglomeration of Poznań, Poland: Marcinkowski Recreational Park (MRP, 52º24'15"N, 16º55'4"E), Wodziczko Recreational Park (WRP; 52º25'11"N, 16º54'56"E), Solacki Recreational Park (SRP; 52º25'17"N, 16º54'15"E), and Park/Reserve Zurawiniec (PRZ; 52º27'27"N, 16º55'48"E). The MRP, (formerly Frederic Schiller) was created during the period 1905-06 and occupies currently an area of 9.4 hectares. It is located in the center of Poznań and surrounded by streets of heavy daily traffic. Trees and grasses form quite a similar area, which is yearly subjected to several maintenance activities. Solacki Recreational Park (SRP) is one of Poznań's most beautiful and highly attended leisure places. It was established in 1907-13 and its area spans to ca 14.63 hectares. The WRP occupies currently an area of 7.06 hectares. This park was set up in 1971-72 and lies close to the SRP. Park/Reserve Zurawiniec (PRZ) was the widest investigated area consisting of ca 55.0 hectares. This complex (Park/Forest) was created in 1959 and involves a reserve – Zurawiniec of 1.27 hectare. The site is located close to a housing estate (Batory).

### Soil Sampling and Chemical Analyses

Soil samples were collected in October 2009 at a depth 0-10 cm from all recreational parks as reported above. (Table 1 synthetically sums up these details). The collected soil samples were first air-dried, crushed to pass a 1.0 mm screen mesh and stored in plastic bags before chemical analyses. The particle size composition was determined according to the areometric method of Bouyoucos-Casagrande [29]. The pH was determined potentiometrically [30] in 0.010 mole $CaCl_2$ $L^{-1}$ and the electrical conductivity (EC1:5) at soil/water ratio of 1:5, according to Rhoades [31]. Next, organic carbon ($C_{org}$) was assessed by the Walkley-Black method as reported by Nelson and Sommers [32], whereas the cation exchange capacity, (CEC) by the ammonium acetate test, i.e. 1 mole $CH_3COONH_4$ $L^{-1}$ pH 7.0 [33]. Lead, Cd, Cu, and Zn contents were extracted using 6 moles HCl $L^{-1}$ and the recovered amounts designated as pseudo total [26, 34]. Briefly, 20 $cm^3$ of 6 moles HCl $dm^{-3}$ were added to 2 grams of soil samples and rotated at 30 rpm for 1 hour before filtering. The physiologically based extraction test (PBET) used in the study was adopted from Ruby et al. [27]. The extraction solution consisted of 30.0 g glycine $dm^{-3}$ (i.e. 0.40 mole $L^{-1}$) with the pH adjusted to 2.0 with HCl. One gram of air-dried soil was extracted with 40 mL of the simulative gastric solution. The mixture was placed into a water bath sample holder at 37ºC and rotated end over end at 30 rpm for 1 hour. Metals in extracts were determined by the FAAS (flame atomic absorption spectrometry) method. All analyses were performed in duplications. Relative standard deviation (RSD) were calculated from pooled data for applied methods. In the precision test, the average RSD % of analyzed soil samples for all metals varied within the range 0.97 to 7.55%.

### Calculation of Heavy Metals Potentially Swallowed

The intake of heavy metals by children and adults in cases of accidental swallowing was calculated as reported below [5, 13, 15, 16, 18]:

$$D = C \cdot \frac{LC}{BW} \cdot \frac{FE}{T}$$

...where:

$D$ – dose of metal absorbed ($\mu g \cdot kg^{-1}$ body weight$\cdot day^{-1}$)

$C$ – concentration (in 6 moles HCl $L^{-1}$) of a heavy metal in soil ($mg \cdot kg^{-1}$)

$LC$ – length of contact with a soil per unit of time (mg soil$\cdot day^{-1}$)

$FE$ – frequency of exposure (hours, days, years)

$BW$ – body weight (15 kg for children below 6 years; 70 kg for adults)

$T$ – mean period of time, usually considered as 6 (70 years) ·350 days a year

Data from scientific reports estimate that the daily consumption of soil by children varies from 39 to 270 $mg \cdot day^{-1}$ [10]. Amounts of 200 $mg \cdot day^{-1}$ for 1-6-year-old children as compared to those older than 6 intaking 100 $mg \cdot day^{-1}$ and, for adults, 60 $mg \cdot day^{-1}$ [14, 15, 18] were applied for calculating intakes. Statistical evaluations were performed by using the Statgraphics® software and graphs elaborated by Excel® sheet facilities.

## Results and Discussion

### Soil Physical and Chemical Properties

The settlement of cities along with the similarities in their expansion are one of the basic factors influencing the characteristics of their soils. This originates from the fact that urban soils are continuously under anthropogenic pressure, hence their physical, as well as chemical properties are frequently disparate and do not follow a stringent natural trend [35, 36]. This concerns also city recreational parks subjected to a number of activities such as maintenance, incorporation of organic mass for the renovation of green cover (i.e. grasses), etc. Data listed in Table 1 show ranges characterized decidedly by significant scattering in one and mean values, as well as standard deviation (SD) showing quite similar values (the case of $C_{org}$ and pH) on the other hand. Among all investigated parks, the PRZ (Park/Reserve Zurawiniec) exhibited the lowest values for all parameters, which implied that the anthropogenic impact in this site was significantly limited.

Geochemical processes are generally regulated by a bulk of factors, of which pH, fine-textured soil particles (clay and silt), and organic carbon content play key roles [37]. These parameters shape strictly buffering properties, for instance cation exchange capacity (CEC). As may be observed from Table 1, the soil characteristics of MRP, WRP, and SRP sites typically revealed that their capacity to potentially mitigate the mobility and/or migration of contaminants is significantly developed (mean pH 7.1-7.3, mean CEC 12.0-21.1 $cmol_{(+)} \cdot kg^{-1}$). The relatively low level of both silt and clay (i.e. 320 $kg^{-1}$) in the case of the PRZ site and the slightly acidic pH, $pH_{CaCl_2}$=5.6, practically weakened the buffering properties of this ecosystem. The above-reported cases are of great environmental value, since further geochemical fates of contaminants (heavy metals, among others) are basically under their control [38, 39].

### Pb, Cd, Cu, and Zn Levels in Park Soils

Risk assessment and toxicological studies frequently proceed by several steps consisting of the identification of the contaminant (type), its level (concentration), and impact on the biota (toxicity effect). Heavy metals analyzed in the study may be divided into two operational groups: Pb and Cd, whose toxicity is a matter of their chemical feature contrary to Cu and Zn, exhibiting harmful effects along with the raise of their concentrations in the soil. Most practically, knowledge of the total (or pseudo total) (Table 3) concentration seems to set a targeted insight/forecast in further behaviour of contaminants. Health disorders related to heavy metals may require the application of consequently strict thresholds in order to reduce significantly or avoid easy contact with pollutants [2, 26]. For this purpose, reference background levels as those suggested by Czarnowska [40], i.e. Pb – 9.8, Cd – 0.18, Cu – 7.1, and Zn – 30 $mg \cdot kg^{-1}$, are fully convincing for the rough evaluation of the contamination state of soils of investigated parks.

The assessment based on mean values has revealed that the concentrations of all metals exceeded background levels by factors varying, irrespective of investigated parks, as follows: Pb 2-6; Cd 6-14; Cu 2-3; and Zn 1-4-fold. This enrichment was observed even in the case of the PRZ site, the least anthropogenically impacted. Cadmium and Pb are worth attention. Three reasons may be evoked for explicitly elucidating this state: car traffic, dust deposition, and maintenance works within parks. The high soil enrichment with Cd and Pb under city conditions could be attributed to the effect of the first two factors [3] and, last but not least,

Table 2. Selected physical and chemical characteristics of soils collected from Poznań recreational parks.

| Parameter | | MRP[1] (*n=18*) | | WRP[2] (*n=16*) | | SRP[3] (*n=26*) | | PRZ[4] (*n=17*) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Range | Mean±SD* | Range | Mean±SD | Range | Mean±SD | Range | Mean±SD |
| Silt+Clay | $g \cdot kg^{-1}$ | 220-760 | 538±136 | 280-500 | 350±73 | 112-924 | 597±176 | 164-560 | 320±106.1 |
| $C_{org}$ | | 15.8-43.0 | 28.8±8.7 | 20.7-35.8 | 27.6±6.4 | 19.6-52.4 | 29.3±8.2 | 12.5-32.4 | 22.6±6,2 |
| $pH_{CaCl_2}$ | | 6.9-7.6 | 7.3±0.2 | 7.1-7.5 | 7.2±0.1 | 6.4-7.3 | 7.1±0.2 | 4.1-6.9 | 5.6±1.1 |
| EC ($\mu S \cdot cm^{-1}$) | | 86.3-274 | 119.7±42.5 | 76.6-449 | 152.7±86.6 | 52.9-377 | 127.6±75.9 | 33.4-157.4 | 70.5±33.1 |
| CEC ($cmol_{(+)} \cdot kg^{-1}$) | | 11.3-21.8 | 15.8±2.6 | 7.6-17.1 | 12.0±2.9 | 9.9-33.8 | 21.1±6.9 | 4.2-23.9 | 8.7±4.9 |

[1]MRP – Marcinkowski Recreational Park, [2]WRP – Wodziczko Recreational Park, [3]SRP – Solacki Recreational Park, [4]PRZ – Park/Reserve Zurawiniec; *Standard deviation

Table 3. Heavy metal contents (pseudo total) in soils of investigated recreational parks.

| Metal | MRP[1] (*n=18*) | | WRP[2] (*n=16*) | | SRP[3] (*n=26*) | | PRZ[4] (*n=17*) | |
|---|---|---|---|---|---|---|---|---|
| | Range | Mean±SD* | Range | Mean±SD | Range | Mean±SD | Range | Mean±SD |
| | $mg \cdot kg^{-1}$ | | | | | | | |
| Pb | 14.3-95.9 | 61.5±25.0 | 14.4-80.4 | 41.2±18.1 | 12.4-67.1 | 30.7±16.7 | 2.5-93.4 | 16.4±21.1 |
| Cd | 1.0-2.56 | 1.58±0.40 | 0.59-6.66 | 2.56±1.92 | 0.37-5.50 | 2.03±1.62 | 0.22-7.16 | 1.0±1.63 |
| Cu | 7.3-44.9 | 23.8±10.5 | 5.20-50.2 | 18.1±11.0 | 5.05-124.5 | 16.5±23.0 | 1.1-111.5 | 13.7±27.3 |
| Zn | 32.5-225.5 | 115.6±46.3 | 23.3-291.3 | 68.8±62.8 | 15.9-202.9 | 53.7±42.9 | 6.1-100.3 | 25.3±23.8 |

[1]MRP – Marcinkowski Recreational Park, [2]WRP – Wodziczko Recreational Park, [3]SRP – Solacki Recreational Park, [4]PRZ – Park/Reserve Zurawiniec; *Standard deviation

to a bulk of activities in order to renovate the shrubs and grass covers. The high content of organic carbon ($C_{org}$) in (Table 2) implies that organic masses have been incorporated into soils for creating favorable growth conditions for grasses. The traceability of the type of inputs was not undertaken and seemed not quite feasible. It was then hypothesized that in addition to Pb and Cd, Zn and Cu levels could also have originated from these organic masses (composts, mostly), but the threat related to direct health disorders are generally agreed to be less [10].

Heavy metals in urban soils occur at several anionic as well as cationic forms, hence their geochemistry is predominantly controlled by soil reaction, i.e. pH and intermediately by the levels of fine soil particles. Of four investigated parks, three were characterized by pH from neutral to alkaline, even. Under such conditions it may be assumed that Pb, Cd, Cu, and Zn should react with $OH^-$ or the $HCO_3^-$ and $CO_3^{2-}$ group, and further be chemically stabilized. According to Davranche et al. [41], Diatta et al. [42], and Sokołowska [43], the surface charge of carbonates is accommodated mainly by protonation/deprotonation reactions. Moreover, carbonates tend to control and set their charges. This view was earlier supported by Abd-Elfattah and Wada [44], who stated that in neutral to alkaline soil conditions, the amounts of hydrated metals at the first degree of hydrolysis increase, which simultaneously enhances metal adsorption/retention. The following reaction is generally suggested:

$$Me^{2+}(aq) + nH_2O \rightarrow Me(OH)n^{2-n} + nH^+$$

The soil solution $pH_{CaCl_2}$ ranged between pH 7.1 and 7.3. Therefore, it can be expected that Pb, Cd, Cu, and Zn ions may potentially undergo hydrolysis. On the other hand, the low solution pH (i.e. 5.6) recorded for the PRZ site implies that more metals are prevailing as cationic ions (i.e. $Me^{2+}_{(aq)}$, which in turn supports the postulate of Appel and Ma [45].

The above mentioned geochemical processes are at the core of the potential bioavailability of Pb, Cd, Cu, and Zn. Data reported in Table 4 reveal, that metal sequences (based on mean values) may be established for the investigated parks:

Pb: SRP > MRP > WRP > PRZ
Cd: SRP > WRP > MRP > PRZ
Cu: WRP > SRP > MRP > PRZ
Zn: MRP > WRP > SRP > PRZ

The analysis of these sequences decidedly shows that Pb and Cd bioavailability follows a quite close trend, which implies that mechanisms involved in their possible transfer to park attendees (children and adults) may be basically similar. The physiologically based extraction test (namely PBET) stimulates the leaching of a solid matrix in the human gastro intestinal tract for children 2-3 years old. This age group was chosen because it was believe to be at the greatest risk from accidental soil ingestion [28, 28]. The extraction efficiency of the PBET is strengthened by its pH, whose value was set at

Table 4. Bioavailable forms (PBET extraction) of heavy metals in soils of investigated recreational parks.

| Metal | MRP[1] (*n=18*) | | WRP[2] (*n=16*) | | SRP[3] (*n=26*) | | PRZ[4] (*n=17*) | |
|---|---|---|---|---|---|---|---|---|
| | Range | Mean±SD* | Range | Mean±SD | Range | Mean±SD | Range | Mean±SD |
| | mg·kg⁻¹ | | | | | | | |
| Pb | 1.3-11.5 | 5.40±2.52 | 2.0-9.0 | 4.84±1.98 | 1.9-16.8 | 5.70±3.8 | 0.20-9.0 | 2.35±2.42 |
| Cd | 0.32-1.90 | 1.14±0.19 | 0.90-2.20 | 1.48±0.38 | 0.16-2.50 | 1.59±0.63 | 0.09-1.20 | 0.69±0.37 |
| Cu | 1.0-6.0 | 2.82±1.49 | 1.70-14.7 | 4.03±3.09 | 0.70-25.0 | 3.77±4.61 | 1.0-11.8 | 2.60±2.58 |
| Zn | 4.1-97.2 | 34.6±20.1 | 3.30-99.9 | 19.6±23.7 | 2.40-52.6 | 11.2±9.97 | 1.9-25.0 | 7.74±6.34 |

[1]MRP – Marcinkowski Recreational Park, [2]WRP – Wodziczko Recreational Park, [3]SRP – Solacki Recreational Park, [4]PRZ – Park/Reserve Zurawiniec; *Standard deviation

Table 5. Potential intake of metals ($\mu g \cdot kg^{-1}$ body weight $day^{-1}$) by children and adults in the case of incidental swallowing of soils of recreational parks.

| Metal | MRP[1] (*n=18*) | | WRP[2] (*n=16*) | | SRP[3] (*n=26*) | | PRZ[4] (*n=17*) | |
|---|---|---|---|---|---|---|---|---|
| | Range | Mean±SD* | Range | Mean±SD | Range | Mean±SD | Range | Mean±SD |
| | Children | | | | | | | |
| Pb | 0.191-1.28 | 0.820±0.33 | 0.191-1.07 | 0.550±0.24 | 0.165-0.895 | 0.410±0.22 | 0.033-0.329 | 0.161±0.10 |
| Cd | 0.03-0.034 | 0.021±0.005 | 0.008-0.089 | 0.034±0.026 | 0.005-0.073 | 0.027±0.022 | 0.003-0.0021 | 0.008±0.005 |
| Cu | 0.097-0.599 | 0.320±0.14 | 0.069-0.669 | 0.241±0.15 | 0.067-1.66 | 0.223±0.31 | 0.014-0.607 | 0.102±0.144 |
| Zn | 0.433-3.01 | 1.540±0.62 | 0.318-3.88 | 0.920±0.84 | 0.212-2.71 | 0.721±0.53 | 0.081-1.34 | 0.340±0.31 |
| | Adults | | | | | | | |
| Pb | 0.012-0.082 | 0.053±0.021 | 0.012-0.069 | 0.035±0.015 | 0.011-0.058 | 0.026±0.014 | 0.0021-0.021 | 0.010±0.06 |
| Cd | 0.0009-0.0022 | 0.0014±0.0003 | 0.001-0.006 | 0.002±0.002 | 0.0003-0.0047 | 0.0017±0.0014 | 0.0002-0.0014 | 0.0005±0.0003 |
| Cu | 0.006-0.038 | 0.020±0.009 | 0.004-0.043 | 0.016±0.009 | 0.004-0.107 | 0.014±0.020 | 0.0009-0.039 | 0.0065±0.0092 |
| Zn | 0.028-0.193 | 0.099±0.040 | 0.020-0.25 | 0.059±0.054 | 0.014-0.174 | 0.046±0.037 | 0.0052-0.086 | 0.022±0.020 |

[1]MRP – Marcinkowski Recreational Park, [2]WRP – Wodziczko Recreational Park, [3]SRP – Solacki Recreational Park, [4]PRZ – Park/Reserve Zurawiniec; *Standard deviation

2.0 and the physico-chemical feature of glycine, which acts as a metals ligand. This may partly explain the high levels of recovery of some metals such as Cd and Zn, generally reported to form weaker bonds with soil colloids than Cu and Pb. The share of PBET-based metals in their pseudo total contents follows the sequence: Cd > Zn > Cu > Pb, which in relative (%) mean values represent: 69 > 28 > 19 > 14. According to Sanderson [46], the electronegativity of these metals varies 1.69, 1.65, 1.90, 2.33, respectively, which implies that Cd and Zn may be of greatest threat in cases of incidental soil swallowing. This is due to the fact that they dissolve and release more easily [10, 22, 26, 47], hence their potentially enhanced bioassimilation.

## Simulative Pb, Cd, Cu, and Zn Intake from Soils

One of the most decisive steps in contamination as well as pollution investigations is the assessment of the impact of given chemicals, heavy metals among others, on the living biota [3, 5, 9, 19]. It seems therefore, that the determination of metal forms (total, soluble, bioavailable) is a supportive and well targeted decision allowing to gather preliminary information over their possible impact in given media. Data listed in Table 5 explicitly outline potential metals intake by children, particularly, and adults, in case of accidental swallowing. All investigated parks exhibited a similar quantitative pattern, i.e. Zn > Pb > Cu > Cd, irrespective of the age group. As can be observed, potential metal intakes depended primarily both on the levels of metals in the soils and individual body weight. This sequence is fully in line with that reported by Jasiewicz et al. [11] in the case of metals potential intake from sandboxes within the city of Kraków. Investigations carried out by Ljung et al. [10] over the bioaccessibility of selected contaminants in Swedish soils have reported the following percentage-based sequence: Ni = Cr = Pb << As < Cd. Based on their studies dealing with metals intake from <4 mm and <50 micron soil particle sizes, authors have stressed that the bioaccessible amount of metals in ingested soils are shaped by pH and clay content.

Children deserve the greatest concern due to their enhanced susceptibility over adults to effects induced by heavy metal toxicity. The calculated amounts of metal intakes were significantly higher for children with 94% as compared to 6%, for adults. The contribution of investigated parks followed the sequence: MRP > WRP > SRP > PRZ, respectively in relative (%) values: 42 > 27 > 21 > 10. In other words, young park attendees may face more risk of potential metal intakes when spending long hours in Marcinkowski Recreational Park and less in the case of the Park/Reserve Zurawiniec. Wodziczki and Solacki parks reflect a similar trend, and occupied the intermediate position.

### Bioavailability *versus* Potential Intake: Risk Assessment Approach

The evaluation of metals intake by humans (children as well as adults) is a complex process involving the consideration of several environmental factors, some of which have been previously detailed. The need for quick and significantly reliable methods or assessment procedures hastens the use of simplified methodologies. Data obtained in the current work and their insight analysis allowed evaluating the risk of metals transfer to the living biota only on the basis of the levels of bioavailable metal fractions. Relationships illustrated in Fig. 1 stress the value of these simple models, since elaborated coefficients of determination ($R^2$) varied from 0.57 to 0.81, irrespective of investigated parks. The $R^2$-based sequence reflecting the degree of model applicability under such heterogenic conditions is as follows: Zn > Cd > Cu > Pb, which practically means that 81, 67, 65, and 57% of respective potential metal intakes can be basically predicted by knowledge of the level of bioavailable metals fractions. The relatively low time consumed by the whole extraction procedure along with the relevant chemical characteristics of the PBET are convincing factors to be considered in risk assessment investigations related to heavy metal contamination or pollution. This approach is particularly applicable and recommendable for city recreational parks or other sties, where humans (children as well as adults) spend hours in full contact with soil particles.

## Conclusions

1. Investigated city parks (MRP, WRP, and SRP) revealed that their capacity to potentially mitigate the mobility of contaminants is significantly developed (pH: 7.1-7.3, CEC 12.0-21.1 $cmol_{(+)} \cdot kg^{-1}$). The low level of both silt and clay (i.e. 320 $kg^{-1}$) in the case of PRZ and its slightly acidic soil ($pH_{CaCl_2}$=5.6), practically weakened the buffering properties of this ecosystem.
2. The assessment based on mean values has revealed that the concentrations of all metals exceeded background levels by factors varying as follows: Cd 6-14; Pb 2-6; Cu 2-3; and Zn 1-4-fold. This enrichment was observed even in the case of the PRZ site, the least anthropogenically impacted.
3. Potential metal intake by children particularly, and adults in cases of accidental swallowing exhibited the quantitative pattern: Zn > Pb > Cu > Cd, irrespective of investigated parks. The calculated amounts of metal intake were significantly higher for children with 94%,

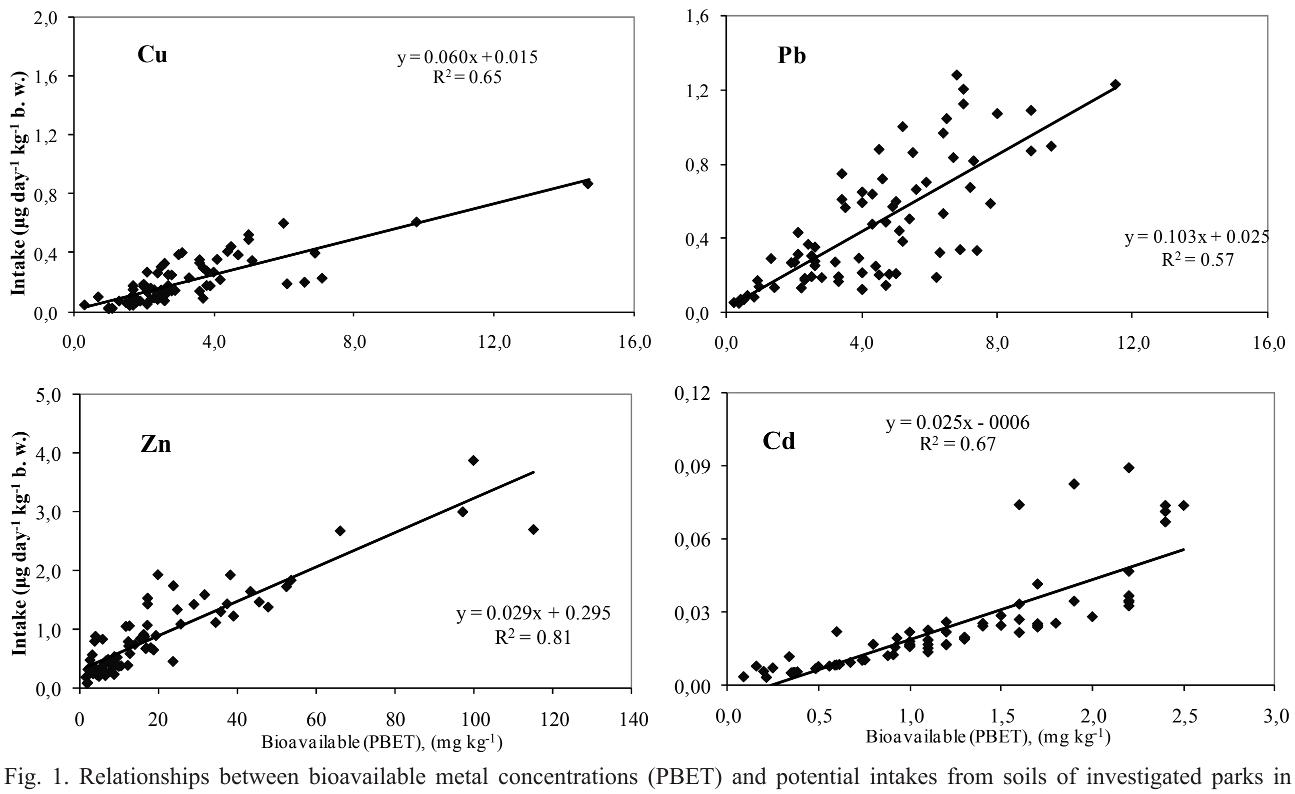


Fig. 1. Relationships between bioavailable metal concentrations (PBET) and potential intakes from soils of investigated parks in Poznań.

as compared to 6% for adults. The contribution of investigated parks followed the sequence: MRP > WRP > SRP > PRZ, respectively, in relative (%) values: 42 > 27 > 21 > 10.

4. Risk assessment models based on simple relationships generated coefficients of determination ($R^2$) varying from 0.57 to 0.81. The $R^2$-based sequence Zn > Cd > Cu > Pb implies that 81, 67, 65, and 57% of respective potential metal intakes can be predicted by the knowledge of the level of bioavailable metal fractions.

## Acknowledgements

Authors acknowledge the funding support of investigations within the project of the city of Poznań: Proj.bad.M.P-ń um.RoM.V/3420, 2009.

## References

1. NRIAGU J.O. A silent epidemic of environmental metal poisoning? Environ. Pollut. **50**, 139, **1988**.
2. SÁŇKA M., STRNAD M., VONDRA J., PATERSON E. Sources and plant contamination in an urban environment and possible assessment methods. Intern. J. Environ. Anal. Chem. **59**, 327, **1995**.
3. ELIK A. Heavy metal accumulation in street dust samples in Sivas. Commun. Soil Sci. Plant Anal. **34**, (1-2), 145, **2003**.
4. POKPO J., OLSZEWSKI S., HUKAŁOWICZ K., MARKIEWICZ K., BORAWSKA M.H., SZEPAROWICZ P. Lead, cadmium, copper and zinc concentrations in blood and hair of mothers of children with locomotor system malformations. Pol. J. Environ. Stud. **12**, (3), 375, **2003**.
5. KONDEJ D. Heavy metals. Advantages and threats for human heath and environment. Bezpieczeństwo Pracy, **2**, 25, **2007** [In Polish].
6. CHAO W., XIAO-CHEN L., LI-MIN Z., PEI-FANG W., ZHI-YONG G. Pb, Cu, Zn and Ni concentrations in vegetables in relation to their extractable fractions in soils in suburban areas of Nanjing, China. Pol. J. Environ. Stud. **16**, (2), 199, **2007**.
7. LINTON R.W., NATUCSH D.F.S., SOLOMON R.L., EVANS C.A. Physico-chemical characterization of Pb in urban dusts. Environ. Sci. Technol. **14**, 158, **1980**.
8. MARKIEWICZ-PATKOWSKA J., HURSTHOUSE A., PRZYBYLA-KIJ H. The interactions of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with typical mixed brownfield deposit. Environ. Intern. **31**, 523, **2005**.
9. VIETMEIER D., VIERECK-GOTTE L., BIESADA M., EWERS U., GZYL J., TERAKOWSKI M. Practical manual for sampling, analysis and assessment of soil contamination. German Federal Environmental Agency Report II 3.3-91005-14/3, **1997**.
10. LJUNG K., OOMEN A., DUITS M., SELINUS O., BERGLUND M. Bioaccessibility of metals in urban playground soils. J. Environ. Sci. Health Part A Tox. Hazard. Subst. Environ. Eng. **42**, (9), 1241, **2007**.
11. JASIEWICZ C., BARAN A., ANTONKIEWICZ J. Assessment of chemical composition and sanitary state of Sand in selected sandboxes in Krakow. J. Elementol. **14**, (1), 79, **2009**.
12. NATIONAL ACADEMY OF SCIENCES. Medical and Biological Effects of Environmental Pollutants: Copper. National Research Council, Washington, DC, **1977**.
13. DUTKIEWICZ T., KULKA E., SOKOŁOWSKA D. Evaluation of lead and cadmium intake pathways at children from industrial areas. Bromat. Chemic. Toksykol. **XV**, (1-2), 41, **1982** [In Polish].
14. US EPA. Guidelines for carcinogen Risk Assessment Register (51 FR 33992-34003) Washington, D.C., **1986**.
15. BIESIADA M (Ed.). Health risk evaluation of inhabitants of Wiślinki as relatred to the impact of phosphate-gypsum slag heap. Inst. Med. Pr. i Zdrow. Środow., Sosnowiec, pp. 72, **2006** [In Polish].
16. KULKA E. Assessment of pre-schoolers exposure to lead and cadmium. Long-term programme – Environment and Health. Instytut Ekologii Terenów Uprzemysłowionych, **6**, 6, **2004** [In Polish].
17. MYŚLIWIEC M., BALCERSKA A., ZORENA K., JĘDRZEJCZYK A., MALINOWSKA E., MYŚLIWSKA J. Increasing incidence of diabetes mellitus type 1 in children – the role of environmental factor. Pol. J. Environ. Stud. **16**, (1), 109, **2007**.
18. US EPA. Guidelines for Human Health Risk Assessment of Chemical Mixtures. Federal Register (51 FR 34014-34025) Washington, D.C., **1986**.
19. JAKUBOWSKI M. Quantitative evaluation of chemicals intake. In: Basic methods of heath risk assessment. Eds. Barański B. and Szymczak W., IMP im. Nofera J., Łódź, **1995** [In Polish].
20. CENTER FOR DISEASE CONTROL: Preventing Lead Poisoning in Children. Atlanta, CDC, **1991**.
21. PENTSCHEW A. Morphology and morphogenesis of lead encephalopathy. Acta Neuropathologica **5**, 133, **1965**.
22. WHO. Health risks of heavy metals from long-range transboundary air pollution. WHO regional Office for Europe, Scherfigsvej 8, DK-2100 Copenhagen, Denmark. pp. 144, **2007**.
23. MOREL F. Detection of child saturnism by the family doctor. Rev. Prat. Med. Gen. **15**, (531), 577, **2001**.
24. SZUMACHER I. Ecological functions of urban parks. Prace i Studia Geograficzne **36**, 107, **2005** [In Polish].
25. URBAŃSKI P., SZPAKOWSKA B., RASZEJA E. Recreational values of green areas of Poznan. Nauka Przyr. Technol. **2**, (4)#27, 1, **2008** [In Polish].
26. GUPTA S.K., VOLLMER M.K., KREBS R. The importance of mobile, mobilisable and pseudo total heavy metal fractions in soil of three-level risk assessment and risk management. Sci. total. Environ. **178**, 11, **1996**.
27. RUBY M.V., DAVIS A., SCHOOF R., EBERLE S., SELLSTONE C.M. Estimation of lead and arsenic bioavailability using a physiologically based extraction test. Environ. Sci. Technol. **30**, 422, **1996.**
28. RUBY M.V., SCHOOF R., BRATTIN W., GOLDADE M., POST G., HANOIS M., MOSBY D.E., CASTEEL S.W., BERTI W., CARPENTER M., EDWARDS D., CRAGIN D., CHAPPELL W. Advances in evaluation the oral bioavailability of inorganics in soil for use in human health risk assessment. Environ. Sci. Technol. **33**, 3697, **1999**.
29. GEE G.W., BAUDER J.W. Particle size analysis. In: Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods. Klute A. (Ed.) 2nd ed. pp. 383-411. Agron. Monogr. 9 ASA and SSSA, Madison, WI, **1986**.
30. POLISH STANDARD. Polish Standardisation Committee, ref. PrPN-ISO 10390 (E), Soil quality and pH determination. First edition, **1994**.

31. RHOADES J.D. Salinity: Electrical conductivity and total dissolved solids. P. 417-435. In: Sparks D.L. et al. (Ed). Methods of soil analysis. Part 3. SSSA Book Ser. 5. SSSA, Madison, WI. **1996**.
32. NELSON D.W., SOMMERS L.E. Total carbon, organic carbon and organic matter. In SPARKS D.L. (Ed.) Methods of Soil Analysis, pp. 961-1010. Part 3. Chemical Methods. SSA Book Ser. 5. SSSA, Madison, WI, **1996**.
33. THOMAS G.W. Exchangeable cations. (pp. 159-165). Methods of Soil Analysis, Part 2. Second Edition, Page A. L., Miller R. H. and Keeney D.R. Madison, Wisconsin, USA. **1982**.
34. MADRID L., DIAZ-BARRIENTOS E., REINOSO R., MADRID F. Metals in urban soils of Sevilla: seasonal changes and relations with other soil components and plant contents. Eur. J. Soil Sci. **55**, 209, **2004**.
35. BIRKE M., RAUCH U. Urban geochemistry: investigation in the Berlin metropolitan area. Environ. Geochem. Health, **22**, 233, **2000**.
36. De KIMPE C.R., MOREL J.L. Urban soil management: a growing concern. Soil Sci. **165**, 31, **2000**.
37. McBRIDE M.B. Reaction controlling heavy metal solubility in soils. Adv. Soil Sci., **10**, 2, **1989**.
38. KABATA-PENDIAS A., PENDIAS H. Trace Elements in Soils and Plants, (2nd edition). CRC Press, pp. 365, **1992**.
39. PATERSON E., SÁŇKA M., CLARK L. Urban soils as pollution sinks – a case study from Aberdeen, Scotland. Applied Geochem., **11**, 129, **1996**.
40. CZARNOWSKA K. Total heavy metals content in rocks as geochemical background of soils. Rocz. Glebozn. T. **XLVII** Supl. 43, **1996** [In Polish].
41. DAVRANCHE M., BEAUFRETON S., BOLLINGER J.C. Influence of carbonates on the surface charge of a natural solid. Jour. Coll. Interf. Sci. **249**, 113, **2003**.
42. DIATTA J.B., KOCIAŁKOWSKI W.Z., GRZEBISZ W. Lead and zinc partition coefficients of selected soils evaluated by Langmuir, Freundlich, and Linear isotherms. Commun. Soil Sci. Plant Anal., **34**, (17&18), 2939, **2003**.
43. SOKOŁOWSKA Z. The role of surface heterogeneity on adsorption processes occurring in soils. Problemy Agrofizyki, **58**, 1-170, **1989** [In Polish].
44. ABD-ELFATTAH A., WADA K. Adsorption of lead, copper, zinc, cobalt and cadmium by soils that differ in cation exchange materials. Jour. Soil Sci., **32**, 271, **1981**.
45. APPEL C., MA L. Concentration, pH and surface charge effects on cadmium and lead sorption in three tropical soils. Jour. Environ. Qual. **31**, 581, **2002**.
46. SANDERSON R. T. Electronegativity and bond energy. J. Am. Chem. Soc. **105**, (8), 2259, **1983**.
47. DIATTA J.B., GRZEBISZ W., WIATROWSKA K. Competitivity, selectivity, and heavy metals-induced alkaline cation displacement in soils. Soil Sci. Plant Nutr. **50**, (6), 899, **2004**.