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Assessment of Heavy Metal Pollution in Urban Soils of Havana City, Cuba

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Abstract Concentrations of Co, Ni, Cu, Zn, Pb and Fe in the top-soils (0–10 cm) from urbanized and un-urbanized areas of Havana city were measured by X-ray fluorescence analysis. The mean Co, Ni, Cu, Zn and Pb contents in the urban topsoil samples (13.9 ± 4.1, 66 ± 26, 101 ± 51, 240 ± 132 and 101 ± 161 mg kg^{-1}, respectively) were compared with mean concentrations for other cities around the world. The results revealed the highest concentrations of metals in topsoil samples from industrial sites. Lowest metal contents were determined in the un-urbanized areas. The comparison with Dutch soil quality guidelines showed a slight contamination with Co, Ni Cu and Zn in all studied sites and with Pb in industrial soils. On the other hand, the metal-to-iron normalisation using Earth crust contents as background showed that soils from urbanized areas in Havana city (industrial sites, parks and school grounds) are moderately enriched with zinc, moderately to severe enriched (city parks and school grounds) and severe enriched (industrial sites) with lead. The values of integrated pollution index (IPI) indicated that industrial soils are middle and high contaminated by heavy metals ($1.19 \leq \mathrm{IPI} \leq 7.54$), but enrichment index values (EI) shows that metal concentrations on the studied locations are not above the permissible levels for urban agriculture, except soils from power and metallurgical plants surroundings.

Keywords Urban soils · Metal pollution · X-ray fluorescence · Havana · Cuba

Assessment of metal contents in soils and the risks due to exposures are important in environmental management decisions and overall protection of human health (Biasioli et al. 2007; De Miguel et al. 2007; Mielke et al. 2010). Elemental concentrations in soils arise from both natural processes and anthropogenic pollution sources. Trace elements such as zinc, chromium, copper, cobalt, and iron are beneficial for both plants and humans, but toxic effects may manifest at concentrations higher than certain threshold for each element. Other trace elements such as lead, cadmium, mercury, etc. are known to have no beneficial biological functions in humans. In particular, childhood lead poisoning remains a serious environmental health problem, affecting the central nervous system and acting as co-factor in many other illnesses (Brewster and Perazella 2004; Navas-Acien et al. 2007). Lead in soil is the primary causative agent of concern in addressing the population of children at risk of lead poisoning. Children are often more susceptible to chemical exposures because of their often hand-to-mouth activity and greater gastrointestinal absorptions rates than adults.

By the end of 2008, Havana city had about 2.1 million urban inhabitants (20% of the total population of Cuba) and the 16% correspond to less than 14-year-old children (CNSO 2008). With the constant population growth and economic development, the percentage of population living in Havana is increasing dramatically and, consequently, the environmental quality of urban soils is becoming more and more important concerning the human health. On the other hand, Havana has the largest and most developed system of urban agriculture in Cuba (Altieri et al. 1999), however, very short amount of information is available about metal content in Havana urban soils. The objectives of this study were to investigate the concentrations of cobalt (Co), nickel (Ni), cooper (Cu), zinc (Zn) and lead (Pb) in the

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surface soils throughout Havana city and to evaluate the soil environment quality in terms of metal contamination.

Materials and Methods

Surface soils (0–10 cm) were collected at representative sites around Havana city during the same week. The sampling was designed to investigate trace metal concentrations in representative soils: urbanized area (44 industrial sites, 16 city parks and 12 school grown sites) and 8 un-urbanized areas from the suburbs. Composite samples, consisting of four soil cores, were collected at each site (approximately 5 × 5 m). This sampling strategy was adopted in order to reduce the possibility of random influences from urban waste. All the samples were collected with a spatula and kept in PVC packages. Back in the laboratory, all samples were dried at 50°C and large rock and organic debris were removed before sieving. The fraction smaller than 1 mm was ground to a fine powder (<125 μm) in an agate mortar. The pulverized samples were newly dried at 60°C until obtaining a constant weight.

The metal concentrations were estimated by X-ray Fluorescence Analysis (XRF) using the Certified Reference Materials (CRM) IAEA-SL-1 “Lake Sediment”, IAEA-Soil-5, IAEA-356 “Polluted Marine Sediment”, USGS-BCR-2 “Basalt Columbia River” and BCSS-1 “Marine sediment” from the Canadian National Research Council as standards. All samples and CRM were mixed with cellulose (analytical quality) in proportion 4:1 and pressed at 15 tons into the pellets of 25 mm diameter and 4–5 mm height. Pellets were measured using Canberra Si(Li) detector (150 eV energy resolution at 5.9 keV, Be window thickness = 12.0 μm) coupled to a MCA. A ^{238}Pu (1.1 GBq) excitation source with ring geometry was used. All spectra were processed with WinAxil code (Winaxil 2005). Detection Limits were determined according to Padilla et al. (2007) (in concentration units) as $L_D = 3\sigma/mt$, where m is the sensibility in counts seg^{-1} per concentration unit, σ is the standard deviation of the area of the background windows (peak window at 1.17 times the FWHM) and t is the measuring time (6 h).

The accuracy was evaluated using the SR criterion, proposed by McFarrell (Quevauviller and Marrier 1995):

$$SR = \frac{|C_X - C_W| + 2\sigma}{C_W} \cdot 100\%$$

where C_X experimental value, C_W certified value and σ is the standard deviation of C_X. On the basis of this criterion the similarity between the certified value and the analytical data obtained by proposed methods is divided into three categories: $SR \leq 25\% =$ excellent; $25 < SR \leq 50\% =$ acceptable, $SR > 50\% =$ unacceptable. The analysis of five replica of the CRM IAEA Soil-7 is presented in Table 1. All heavy metals (Fe, Co, Ni, Cu, Zn and Pb) determined by XRF are “excellent” (SR ≤ 25%) and the obtained results shows a very good correlation (R = 0.999) between certified and measured values.

Results and Discussion

The highest metal contents were recorded from industrial sites (Table 2) and the lowest from un-urbanized areas. Table 3 depicted the correlation coefficient matrix, listing the Pearson’s product moment correlation coefficient. A very significant correlation ($p < 0.01$) was found between Zn and Pb (r = 0.76), Cu and Pb (r = 0.63), and Cu and Zn (r = 0.60). The high correlations between soil metals may reflect that these heavy metals had similar pollution level and similar pollution sources. To assess the natural background concentrations of elements in soils and the possible elevation of elemental content in soils, we compared the results of this study with Earth crust element levels (Table 2) and with metal ranges reported for different cities in the literature (Table 4).

Cobalt varied from 7.7 to 21.9 mg kg^{-1} (mean: 13.9 mg kg^{-1}) and Ni from 33 to 134 mg kg^{-1} (mean: 66 mg kg^{-1}). Both metals have a relative good correlation (r = 0.51, $p < 0.05$) and their average contents in all studied sites (industrial, parks, school grounds and un-urbanized soils) are similar to the Earth crust values. Hence, its origin must be non anthropogenic.

However, the Cu, Zn and Pb mean concentrations (101, 240 and 101 mg kg^{-1}, respectively) in Havana surface soils were significantly higher than their corresponding concentrations in Earth crust. For Cu and Zn the higher mean concentrations are comparing to those reported in other cities of the world (see Table 4). It should be noticed that this group of chalcophilic elements is associated with anthropogenic aerosols in the atmosphere and have fairly low concentrations in soils. Consequently, deposition of aerial pollution-derived particles over the years could alter

Table 1 XRF analysis of CRM soil-7[a], SR values and detection limits

Metal	Certified value	Measured value	SR (%)	L_D (mg kg^{-1})
Fe (%)	2.57	2.43 ± 0.19	22	9
Co	8.9	9.2 ± 0.8	20	6
Ni	26	25.6 ± 0.9	17	7
Cu	11.0	10.3 ± 0.6	15	6
Zn	104	104 ± 5	9	5
Pb	60	56 ± 4	8	4

[a] Mean ± SD, n = 5, in mg kg^{-1}, except Fe

Table 2 Averages^{a} (ranges) of metal concentrations (mg kg^{-1} dry wt.) in Havana urban soils

Element	Industrial sites (n = 48)	City parks (n = 16)	School grounds (n = 12)	Un-urbanized areas (n = 8)	Earth crust^{b}	Dutch regulation^{c}	
						TV	IV
Co	14.5 ± 4.5 (8.0–21.9)	12.5 ± 5.5 (7.7–19.3)	12.9 ± 1.5 (11.4–14.4)	14.8 ± 2.4 (13.1–16.6)	25	9	240
Ni	69 ± 31 (33–134)	65 ± 24 (35–85)	62 ± 19 (45–83)	58 ± 13 (49–67)	74	35	210
Cu	105 ± 59 (45–239)	87 ± 57 (36–169)	116 ± 26 (96–145)	83 ± 25 (66–101)	55	36	190
Zn	292 ± 152 (128–656)	161 ± 59 (111–242)	196 ± 61 (129–249)	151 ± 6 (146–155)	70	140	720
Pb	140 ± 207 (32–791)	49 ± 18 (32–66)	59 ± 38 (18–91)	28 ± 5 (24–31)	13	85	530
Fe (%)	3.9 ± 1.9 (1.4–6.7)	3.2 ± 1.9 (1.7–5.6)	3.6 ± 1.0 (2.5–4.6)	4.7 ± 0.8 (4.1–5.3)	5.0	–	–

[a] Arithmetic mean ± standard deviation

[b] Mason and Moore (1982)

[c] Swartjes (1999)

Table 3 Pearson's correlation coefficients between metal elements (n = 84)

Metals	Co	Ni	Cu	Zn	Pb
Co	1				
Ni	0.51*	1			
Cu	0.33	0.17	1		
Zn	0.05	0.15	0.60**	1	
Pb	0.13	0.03	0.63**	0.76**	1

Levels of significance: * $p < 0.05$; ** $p < 0.01$

their concentrations in surface soil. Although conceptually attractive, atmospheric deposition of anthropogenic particles may not be the only reason for the observed concentration differences between local and average soils, because such differences could also be explained by natural sources, i.e. a unique mineralogy in different parts of the study area.

To test this possibility, the average concentrations of elements determined from urbanized parts of the city were compared with corresponding concentrations in suburbs (un-urbanized sites), where population is scarce and air pollution is low. If the observed differences are due to mineralogy, the high concentration values observed in Havana soil should be fairly uniform throughout the study area. Concentrations of Pb (in all urban stations) and Zn (in industrial soils) were higher by a factor within 1.6–5.1 in urban stations (Fig. 1), suggesting that the observed differences were not due to a local geologic condition. Concentrations of Co, Ni and Cu, on the other hand, were comparable in both un-urbanized and urban parts of the study area with a ratio close to 1.0.

Due to the lack of an official Cuban guideline for healthy concentrations of metals in urban soils, metal concentrations are compared with soil quality standards which have been derived to assess soil quality by the Dutch

Table 4 Mean (±SD) concentrations (mg kg^{-1}) in urban soils from different cities in the world

City	Co	Ni	Cu	Zn	Pb	Reference
Havana, Cuba	13.9 ± 4.1	66 ± 26	101 ± 51	240 ± 132	101 ± 161	Present study
Ljubljana, Slovenia	NA	26 ± 5	39 ± 19	148 ± 73	87 ± 58	De Miguel et al. (2007)
Sevilla, Spain	NA	28 ± 6	55 ± 51	105 ± 55	123 ± 153	De Miguel et al. (2007)
Torino, Italy	NA	185 ± 93	90 ± 65	182 ± 112	169 ± 224	Biasioli et al. (2007)
Belgrade, Serbia	NA	68 ± 29	28 ± 17	118 ± 120	56 ± 46	Crnkovic et al. (2006)
Guangzhou, China	NA	26 ± 18	63 ± 78	169 ± 145	109 ± 78	Lu et al. (2007)
Hong Kong, China	NA	NA	25 ± 12	168 ± 75	93 ± 37	Li et al. (2001)
Missouri, USA	9.7 ± 4.9	16 ± 5	18 ± 17	95 ± 117	49 ± 40	Ikem et al. (2008)
Naples, Italy	NA	NA	74 ± 56	251 ± 253	262 ± 337	Imperato et al. (2003)
Stockholm, Sweden	NA	13 ± 5	71 ± 201	171 ± 174	101 ± 208	Linde et al. (2001)
Ankara, Turkey	10 ± 3	78 ± 45	250 ± 680	200 ± 180	158 ± 617	Yay et al. (2008)
Shenyang, China	NA	NA	51 ± 20	138 ± 68	75 ± 99	Sun et al. (2010)
Thane, India	63 ± 24	171 ± 126	155 ± 81	689 ± 2025	42 ± 4	Bhagure and Mirgane (2010)
Hangzhou, China	NA	NA	52 ± 31	207 ± 52	88 ± 79	Lu and Bai (2010)

NA not available

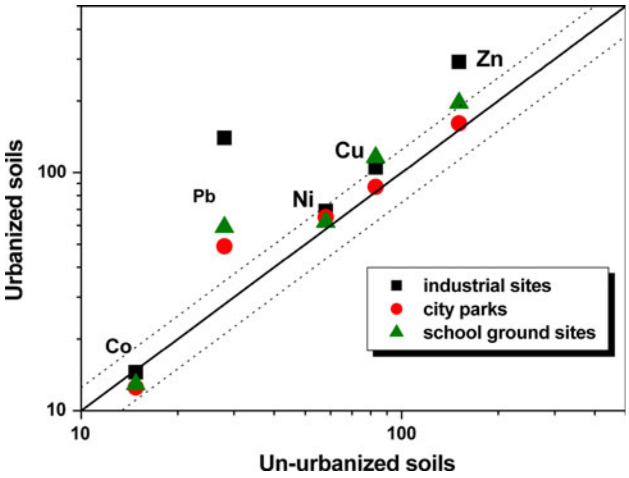

Fig. 1 Comparison of average concentrations (in mg kg^{-1}) of measured elements in urbanized and un-urbanized Havana soils (*straight line* represent y = x function, and *dashed lines* the 95% confidence levels)

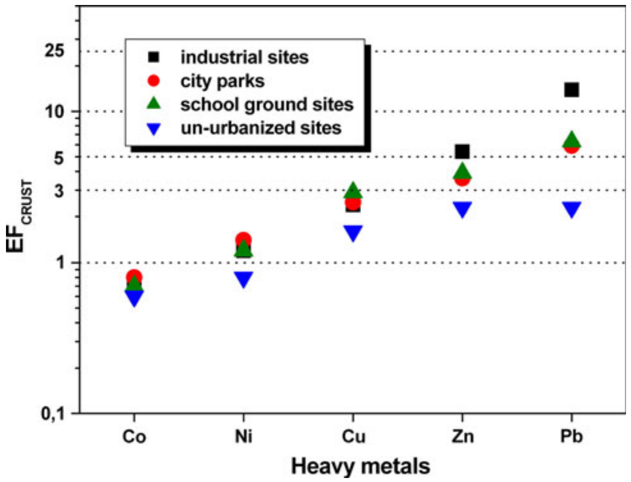

Fig. 2 Crustal enrichment factors (EF_{CRUST}) in Havana soils (*dashed lines* show the Birch's classification ranges)

Authorities: Target Value (TV) and Intervention Value (IV) (see Table 2). These standards allow soil and groundwater to be classified as *clean*, *slightly contaminated* or *seriously contaminated*. The TV is based on potential risks to ecosystems, while the IV is based on potential risks to humans and ecosystems (Swartjes 1999). According to Dutch classification, the Havana City urban soils can be considered as "slightly contaminated" with Co, Ni, Cu and Zn (independently of its use) and with Pb in industrial soils.

Soil modifications or changes may be derived through crustal enrichment factors (EF_{CRUST}) using this equation: $EF_{CRUST} = (C_x/C_{Fe})_{sample}/(C_x/C_{Fe})_{reference\ soil}$, where $(C_x/C_{Fe})_{sample}$ is the ratio of the concentration of a test element to the concentration of iron in the sample and $(C_x/C_{Fe})_{reference\ soil}$ is the same ratio but with a reference soil (Yay et al. 2008). Elemental concentrations of the earth crust (Table 2) and iron as a reference element were used in calculation of EF_{CRUST}. Iron was adopted as reference because it is one of the largest components of soil and the modification of iron by other anthropogenic sources is difficult.

Modification of soil composition is assumed to be significant when the EF_{CRUST} value of an element is bigger than 3. Smaller enrichments can exist due to differences between the compositions of the local soil and the reference soil used in these calculations. For Co, Ni and Cu (as well as Zn and Pb in un-urbanized sites), the average EF_{CRUST}'s are less than 3.0 (Fig. 2), which indicates that the soil's composition is not significantly altered by anthropogenic sources in most of the study area. However, taking into account the Birch's classification (Birch 2003) for metal enrichment, soils from urbanized areas in Havana city (industrial sites, parks and school grounds) are "moderately enriched" by zinc ($3 < EF_{CRUST} < 5$), "moderately to severe enriched" (city parks and school grounds) and "severe enriched" (industrial) by lead ($5 < EF_{CRUST} < 10$ and $10 < EF_{CRUST} < 25$, respectively). Lead and zinc have been identified as typical "urban" metals (Biasioli et al. 2007; De Miguel et al. 2007) whose most usual sources are traffic (i.e. vehicular emissions (Mielke et al. 2010)) and other industrial sources such as metallurgical industries and thermo-electric centers (Biasioli et al. 2007).

In order to assess the soil contamination degrees and to estimate the possible impact to the human health, the Integrated Pollution Index (IPI) (Chen et al. 2005; Sun et al. 2010) and the Enrichment Index (EI) (Lee et al. 1998) were calculated for each urbanized soil use (Table 5).

IPI is defined as the mean values for all the Pollution Indexes (PI) of all considered metals:

$$IPI = \frac{1}{n}\sum_{i=1}^{n} PI_i$$

where, n is the number of metals considered in the study and PI is defined as the ratio of the heavy metal concentration to the geometric means of background concentration of the corresponding metal:

$$PI = C_i/S_i$$

where PI is the evaluation score corresponding to each sample, C_i is the measured concentration of the examined metals in the soils, and S_i is the geochemical background concentration of the metals (Chen et al. 2005). The background values (in mg kg^{-1}) utilized were the average concentrations determined in the eight studied un-urbanized areas, i.e., 14.8 for Co, 58 for Ni, 83 for Cu, 151 for Zn, and 28 for Pb, respectively, and soils were then classified as *low contaminated* ($IPI \le 1.0$), *middle contaminated* ($1.0 < IPI \le 2.0$) or *high contaminated* ($IPI > 2.0$).

Table 5 Integrated pollution index (IPI) and enrichment index (EI) of Havana urban soils

Soil use	IPI			EI		
	Min	Max	Mean	Min	Max	Mean
Industrial sites	1.19	7.54	2.07	0.58	2.74	0.93
City parks	0.71	1.58	1.16	0.35	0.88	0.60
School grounds	0.90	1.68	1.35	0.51	0.84	0.70

The EI was calculated by averaging the ratios of element concentrations to a permissible level. The permissible level was obtained from the threshold of the element concentration in soils above which crops produced were considered unsafe for human health (Lee et al. 1998; Kabata-Pendias and Pendias 2001). Taking into account that element enrichments can be from anthropogenic inputs or natural geological sources (Lee et al. 1998), all determined metals were selected to calculate the EI by using the following equation:

$$\mathrm{EI} = \frac{1}{5}\left(\frac{\mathrm{Co}}{50} + \frac{\mathrm{Ni}}{75} + \frac{\mathrm{Cu}}{100} + \frac{\mathrm{Zn}}{300} + \frac{\mathrm{Pb}}{100}\right).$$

An enrichment index of more than 1.0 indicates that, on average, element concentrations are above the permissible levels.

The IPI value of industrial sites soils varied from 1.19 to 7.54 with an average of 2.07 (Table 5). Samples corresponding to power and metallurgical plants were with IPI > 2.0 and the rest with IPI between 1.0 and 2.0. The IPI values of city parks and school grounds soils varied from 0.71 to 1.58 and 0.90 to 1.68, respectively. In both cases, 50% of the samples were with IPI between 1.0 and 2.0, corresponding, in all cases, to high traffic zones.

As was mentioned, Havana has the largest and most developed system of urban agriculture in Cuba. More than 5000 popular gardens have been developed throughout the 43 urban districts that conform Havana's 15 municipalities (Altieri et al. 1999). Garden sites are usually vacant or abandoned plots and are located in the same neighborhood if not next door to the gardener's house-holds. Most popular gardens provide food for the family, give a significant proportion to childcare centers, schools, hospitals, and needy community members, and sell some remaining goods for profit. EI values less than 1.0 in the major part of studied locations (Table 5) indicate that crops produced in these areas will be safe for human consumption although individual metals could hold the threat of metal toxicity to the plants (Kabata-Pendias and Pendias 2001). The exceptions are the soils located near the power and metallurgical plants surroundings, for which EI varied from 1.1 to 2.74. Hence, the metal concentrations on these locations are above the permissible levels for agriculture.

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