Assessment of heavy metal content in urban agricultural soils from the surrounding of steel-smelter plant using X-ray fluorescence

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Abstract
Concentrations of Cr, Co, Ni, Cu, Zn and Pb in the topsoils (0–10 cm) from ten farms located in the vicinity of a steel-smelter plant at Cotorro (Havana, Cuba) were measured by X-ray fluorescence analysis. The concentration ranges of Cr, Co, Ni, Cu, Zn and Pb were 54-186, 15-39, 19-137, 50-945, 91-7739 and 21-731 mg.kg^{-1} dry weight respectively. The metal mean contents in the farm topsoil samples were compared with metal contents reported for soils from the vicinity of other smelters worldwide. The Metal-to-Iron normalisation and estimation of the integral pollution indexes allowed observing that most metal polluted soils are from those farms, and that their location coincide with the prevalent wind direction in the studied area. The enrichment index values show that metal concentrations in soils from these farms are above the permissible levels for urban agriculture.

Key words: *heavy metals; Cuba; X-ray fluorescence analysis; land pollution; smelters; urban areas; agriculture; soils*

Estudio del contenido de metales pesados en suelos urbanos agrícolas adyacentes a una planta de acero mediante fluorescencia de rayos X

Resumen
Se determinan por fluorescencia de rayos X las concentraciones de Cr, Co, Ni, Cu, Zn y Pb en los suelos superficiales (0–10 cm) de 10 granjas agrícolas, localizadas en la vecindad de la planta de acero del Cotorro (La Habana, Cuba). Los intervalos de concentraciones de Cr, Co, Ni, Cu, Zn y Pb fueron de 54-186, 15-39, 19-137, 50-945, 91-7739 y 21-731 mg.kg^{-1} de peso seco respectivamente. Los contenidos medios de metales pesados en los suelos superficiales de las granjas se comparan con los niveles de metales pesados reportados en la literatura para suelos adyacentes a plantas de acero. La normalización de los metales al hierro y la estimación del los índices de polución integral, permitió determinar que los suelos contaminados por metales pesados son aquellos, cuya ubicación coincide con la dirección predominante de los vientos en la zona estudiada. Los valores del índice de enriquecimiento mostraron que las concentraciones de metales pesados en los suelos de esas granjas, superan los niveles permisibles para la agricultura urbana.

Palabras clave: *metales pesados; Cuba; análisis por fluorescencia de rayos X; polución del suelo; fundidores; áreas urbanas; agricultura; suelos*

Introduction

Urban soils are recognized as being different from agricultural and natural soils given their peculiar characteristics such as the low organic matter content and typically higher amounts of contaminants than those from rural origin, due to the higher density of anthropogenic activity in urbanized areas [1]. Smelters and metallurgical plants are included in the list of the main anthropogenic sources of heavy metals in soils, particularly in those located in their vicinity [2-4]. The implications associated with metal contamination are of great concern, particularly in agricultural production systems. As it is well known, urban horticulture is booming across all socioeconomic groups and around the world. Metal contamination in such products can exceed the precautionary values, and a dietary exposure to trace metals can result in significant human health risks [5-11].

The main steel-smelter plant in Cuba (Antillana de Acero) started its operation in 1958. It is located near Cotorro town (with 75 848 inhabitants [12]) in the south-eastern periphery of Havana city. Urban agriculture in Cuba has become a significant source of fresh products for the urban and suburban populations, and has extended throughout the island [13]. Cotorro municipality is not an exception. Different private and cooperative farms are established in local lands, including those located in the vicinity of the steel-smelter plant. Recent studies have demonstrated how inadequate some Cuban urban lands are for crops production, due to their relatively high heavy metal content. For example, soils surrounding power plants and refineries in Havana city [14], from residential areas in the city nearby a Ni+Co mining area [15] and lands in the vicinity of present and former Havana solid waste incinerators [16-17]. However, the heavy metal content in cultivated soils from Cotorro has not been studied yet. Therefore, the main objective of this study was to investigate the content of heavy metals in cultivated soils surrounding the steel-smelter plant of Cotorro, in order to assess the soil quality for agricultural purposes.

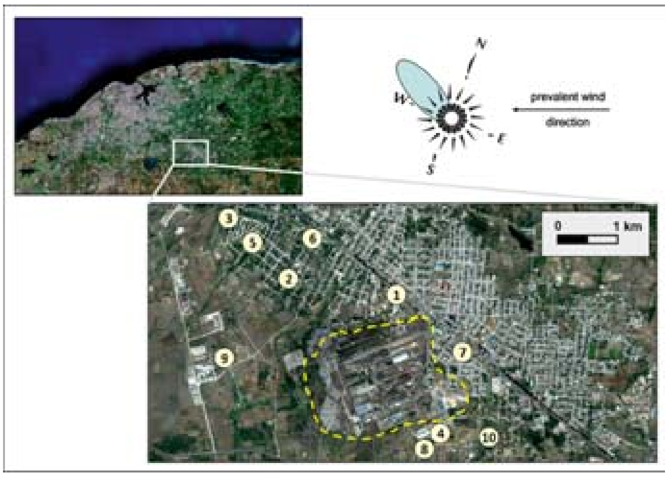

Figure 1. Location of the studied farms in Cotorro. (Dashed line–Smelter plant).

Materials and Methods

Soil samples (0-10 cm) were collected in 10 urban farms located in the vicinity of "Antillana de Acero" smelter during the same journey (figure 1), including farm 6, an area where a small Pb-smelter was formerly located . The main productions of selected farms are: vegetables (1, 3-6, 8 and 9) and fruit (mango, avocado, mammee, among others) and timber trees (2, 7 and 10). Composite samples, consisting of five soil cores, were collected at each site (approximately 100 × 100 m^2). 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, metallic and plastic pieces and organic debris were removed before sieving. The fraction smaller than 2 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 Cr, Co, Ni, Cu, Zn and Pb 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", BCR-2 *"Basalt Columbia River"*, SGR-1 *"Green River Shale"* 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 multi channel analyzer. A ^{238}Pu (1.1 GBq) excitation source with ring geometry was used. All spectra were processed with WinAxil code [18]. Detection Limits were determined according to Padilla et al. [19] (in concentration units) as LD = 3σ/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 hours). The accuracy was evaluated using the SR criterion, proposed by McFarrell [20]:

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

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 ≤ 25 % = excellent; 25 < SR ≤ 50 % = acceptable, SR > 50 % = unacceptable. The analysis of five replica of the CRM IAEA Soil-7 is presented in table 1. All metals (Cr, 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.

Table 1. XRF analysis of CRM Soil-7*, SR values and detection limits

Metal	Certified value	Measured value*	SR (%)	LD (mg.kg^{-1})
Cr	60.0	60.3 ± 1.6	6	12
Fe (%)	2.57	2.68 ± 0.8	11	9
Co	8.9	9.2 ± 0.8	21	6
Ni	26	22 ± 4	16	7
Cu	11.0	10.3 ± 0.6	15	6
Zn	104	94 ± 5	20	5
Pb	60	59 ± 2	12	4

* - Mean ± SD, n=5, in mg.kg^{-1}, DW.

In order to assess the possible metal pollution in topsoils, the element enrichment was estimated by normalizing the results to a reference element, using the enrichment factor (EF) calculated as: EF = $(C_x/C_{Fe})_s/(C_x/$

$C_{Fe})_{BV}$, where $(C_x/C_{Fe})_s$ is the ratio of the concentration of a test element to the concentration of iron in the sample and (Cx/CFe)BV is the same ratio but with a background soil [21]. Due the absence of previous baseline or background studies, the results for Earth crust [22] were used as background values (BV). EF values were interpreted as suggested by Birch: EF < 1 indicates no enrichment, EF < 3 is minor enrichment, EF = 3–5 is moderately enrichment, EF = 5–10 is moderately severe enrichment, EF = 10–25 is severe enrichment, EF = 25–50 is very severe enrichment and EF > 50 is extremely severe enrichment [23].

On the other hand, to assess soil contamination degrees and to estimate their possible impact on human health, the integrated pollution index (IPI) [24] and the enrichment index (EI) [25] were calculated for each studied farm. 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 metal concentration (C_i) to the geometric means of background concentration (BV_i) of the corresponding metal:

$$PI = C_i / BV_i$$

Soils are to be classified as low contaminated (IPI ≤ 1.0), moderate contaminated (1.0 < IPI ≤ 2.0) or high contaminated (IPI > 2.0).

The EI was calculated by averaging the ratios of element concentrations to the permissible level (PL). The permissible level was obtained from the threshold of the element concentration in soils above which crops produced were considered to be unsafe for human health [1, 25]. Taking into account that element enrichments can come from anthropogenic inputs or natural geological sources, all studied metals were selected to calculate the EI by using the following equation:

$$EI = \frac{1}{n}\sum_{i=1}^{n} \frac{C_i}{PL_i}$$

An enrichment index of more than 1.0 indicates that, on average, metal concentrations are above the permissible levels (PL) for agricultural soils.

Results and Discussion

Concentrations of Cr, Fe, Co, Ni, Cu, Zn and Pb in the farm topsoils (0-10 cm) of the vicinity of Antillana de Acero are presented in table 2. The concentration ranges of Cr, Co, Ni, Cu, Zn and Pb were 54-186, 15-39, 19-137, 50-945, 91-7739 and 21-731 $mg.kg^{-1}$ dry weight, with mean values of 99, 23, 69, 193, 1057 and 131 $mg.kg^{-1}$ respectively. Mean concentrations of the heavy metals in the farm soils decreased following this order: Zn > Cu > Pb > Cr > Ni > Co; Cr, Co and Ni mean contents were all comparable to the Earth crust values, while for Cu, Zn and Pb which mean contents were 1.9, 6.8, 4.2, 21.8 and 4.4 fold higher than their corresponding background values. The concentrations of Cr, Ni, Cu, Zn and Pb varied greatly (see figure 2), while Co concentrations were quite homogeneous across the studied area. The comparison with metal contents reported for soils from the vicinity of other smelters worldwide (table 3) shows that the results from Cotorro farm soils are within the same usual range, except for Zn and Pb.

Table 2. Metal concentrations in soils from studied farms and background values (BV) (in $mg.kg^{-1}$ DW, except the indicated)

Farms	Cr	Fe (%)	Co	Ni	Cu	Zn	Pb
1	76	6.8	23	115	945	7739	232
2	87	5.9	21	61	75	95	39
3	136	12.2	39	137	287	1139	75
4	115	7.5	25	57	81	122	46
5	109	10.4	34	100	194	856	55
6	55	2.6	16	19	91	187	731
7	97	4.5	15	43	52	94	24
8	54	5.7	20	39	64	138	32
9	71	4.7	15	39	50	91	21
10	186	9.6	33	76	88	107	52
Mean	99	7.0	23	69	193	1057	131
St. Dev.	41	3.0	10	38	275	2377	220
Earth crust [22]	100	5.0	25	75	55	70	13
TVa	100	-	9	35	36	140	85
IVa	380	-	240	210	190	720	530
PLb	100	-	50	75	100	300	100

a – Dutch target and intervention values [26]
b – Permissible Levels for agricultural soils [1]

Table 3. Metal concentrations in smelter topsoils worldwide (in $mg.kg^{-1}$)

Location	Cr	Co	Ni	Cu	Zn	Pb	Reference
Cotorro. Cuba	99	23	69	193	1057	131	Present study
Beijing, China	65,9	NA	25,1	24,7	90,5	31,1	[2]
Shenyang, China	NA	NA	NA	527,93	912,45	81,2	[27]
Surat, India	176,1	51,3	50,7	137,5	115,7	NA	[28]
Wuxi, China	58.6	NA	NA	40.4	112.9	46.7	[29]
Sudbury, Canada	NA	NA	757	836	79	75	[3]
Bagnoli, Italy	368	11	69	97	143	36	[30]

NA – not available

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 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 [26]. According to the Dutch classification (figure 2), the soils from farms 1 and 3 can be considered as "seriously contaminated" with Ni, Cu and Zn, farm 5 with Ni, Cu and Zn and farm 6 with Pb, due to surpluses in their corresponding intervention values.

Furthermore, metal enrichment estimated for the studied soils (figure 3) using the enrichment factors (EF), shows that soils from farms 2, 4, 7–10 are practically not enriched with the determined metals (EF $\leq$ 3), i.e., its origin must be from natural sources. On the other hand, soils from farm 1 are extremely severe enriched by Zn (EF = 81), severely enriched by Cu (EF = 12.7) and Pb (EF = 13.2); soils from farm 3, 5 and 6 are moderately severe enriched by Zn (EF = 6.7, 5.9 and 5.1 respectively), while soils from farm 6 are also extremely severe enriched by Pb (EF = 108), due to the former location in this area of an small Pb smelter. Its can be observed that most metal enriched soils are in those farms, where their location coincide with the prevalent wind direction in the studied zone (1, 3, 5 y 6). Thus, the fallout of the smelter

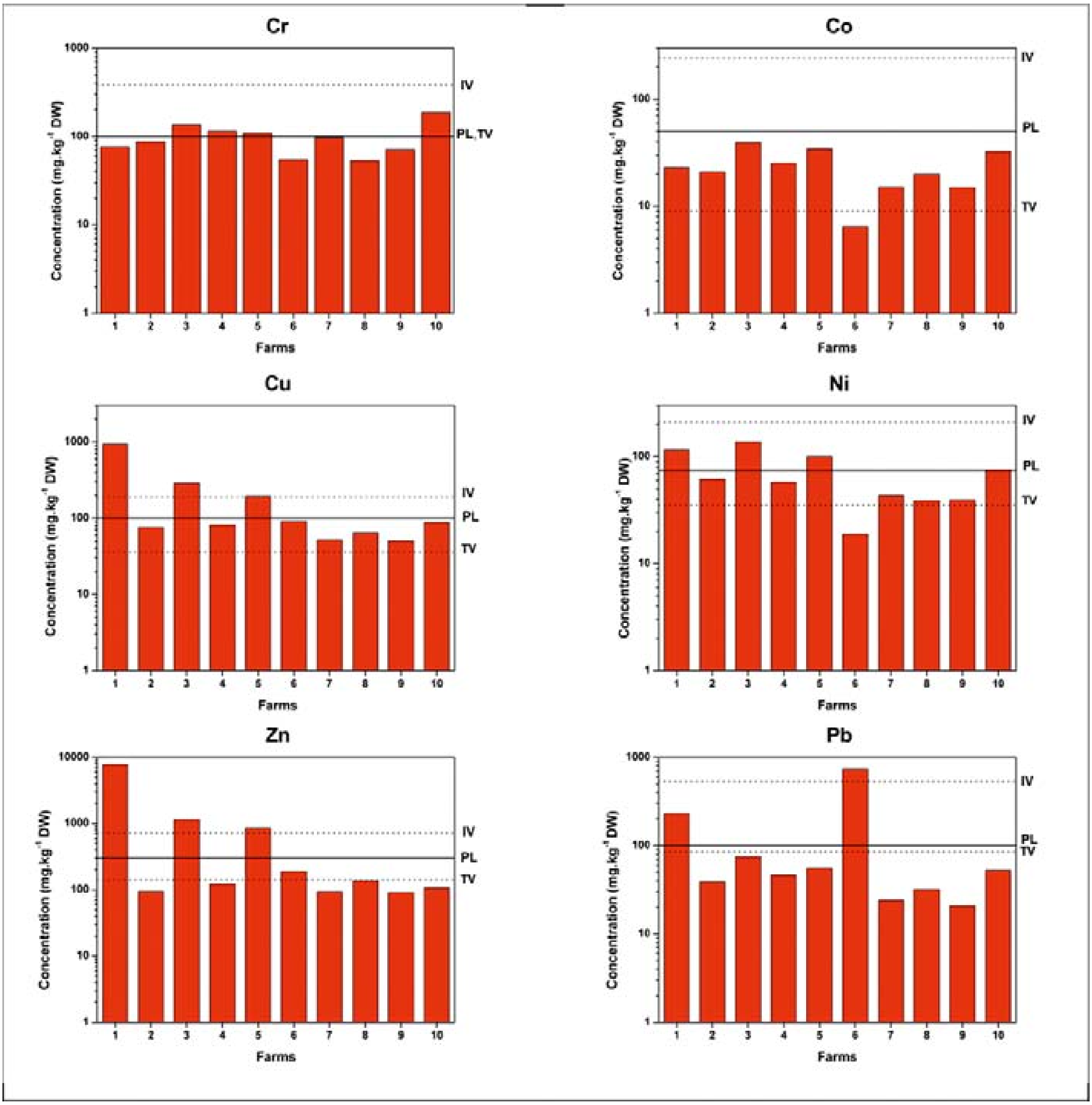

Figure 2. Spatial distribution of metals determined in Cotorro farm soils.

plant emissions must be accumulating in their soils. The exception is farm 2, being its production associated with fruit and timber trees. In that case, the emission fallout will be mainly deposited over tree leaves and not in the farm soil. That must be also the reason why no metal enrichment was determined in farm 7, although it is the nearest to the plant.

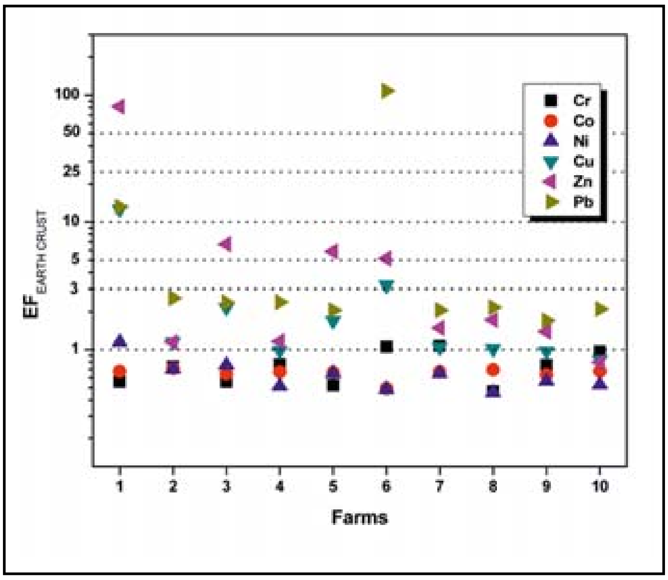

Figure 3. Enrichment factors determined for studied farms of Cotorro town (dashed lines show the Birch's classification ranges).

As it is well known, lead, copper and zinc have been identified as typical "urban" metals for which the usual sources are caused by traffic (i.e. vehicular emissions) and other industrial sources such as metallurgical industries and thermo-electric centers [31]. Despite the wide usage of lead-free fuels since 2000 in Cuba (therefore, Pb is not liable to be transferred, resulting in its accumulation in soils due to pollution from previous decades) and taking into account that farm 1 is located near the National Highway and smelter plant gateway, Pb enrichment and some percentile of determined Zn and Cu enrichments, in soils from this farm, can be associated with traffic, whereas the remaining of the Zn and Cu enrichments must be associated with smelter plant emissions.

The calculated IPI (table 4) shows that highly contaminated soils (IPI $\geq$ 2) correspond to samples from farms 1, 3, 5, and 6. However, a moderate contamination (1.0 < IPI $\leq$ 2.0) is found in soils from farms 2, 4, 8 and 10 due to the obtained metal pollution indexes but, considering the enrichments factors, its origin can be natural (Cr, Co and Ni) and associated with traffic (Pb and some percentile of the Cu and Zn contents). On the other hand, only for farms 1, 3, 5 and 6, enrichment index values higher than one unit were obtained, indicating that crops produced in these areas are not safe for humans [1].

Recent studies have found a very good correlation between heavy metal content in polluted soils and some edible roots (carrot, onion and rabbits) and vegetables (lettuce, cauliflower, etc.) grown in those soils [8,10-11]. Also, the compost usage impact, prepared with wastes of crops cultivated in contaminated soils (regular practice in urban agriculture) may increase the metal absorption by crops [32]. In Cuba, the cultivation (and sale) of mentioned crops and the use of compost are habitual practices in urban agriculture.

Table 4. Integrated pollution index (IPI) and enrichment index (EI) of studied farms topsoils

Farms	PI						IPI	EI
	Cr	Co	Ni	Cu	Zn	Pb		
1	0.8	0.9	1.5	17.2	110.6	17.9	24.8	6.7
2	0.9	0.8	0.8	1.4	1.4	3.0	1.4	0.6
3	1.4	1.6	1.8	5.2	16.3	5.7	5.3	1.9
4	1.2	1.0	0.8	1.5	1.7	3.6	1.6	0.7
5	1.1	1.4	1.3	3.5	12.2	4.3	4.0	1.4
6	0.5	0.3	0.2	1.7	2.7	56.3	10.3	1.6
7	1.0	0.6	0.6	0.9	1.3	1.8	1.0	0.5
8	0.5	0.8	0.5	1.2	2.0	2.5	1.2	0.5
9	0.7	0.6	0.5	0.9	1.3	1.6	0.9	0.4
10	1.9	1.3	1.0	1.6	1.5	4.0	1.9	0.9

Conclusions

In conclusion, we have conducted a thorough examination of the heavy metal content in soils in the vicinity of the steel-smelter plant in Cotorro town, Havana, Cuba. Among the elements studied, we found that farms located in the prevalent wind direction from the smelter plant are severely impacted by the plant emissions, inducing a noteworthy pollution to their soils. On the other hand, the enrichment index values (EI) show that metal concentrations in soils from these farms are above the permissible levels for urban agriculture. Therefore, taking into account that Cuban regulations specify for vegetables (for children consumption) a maximum allowable concentration limit for Pb of 0.3 $mg.kg^{-1}$ FW, for Zn of 10 $mg.kg^{-1}$ FW and for Cu of 5 $mg.kg^{-1}$ FW [33], a follow-up evaluation of metal content in crops cultivated in areas where the highest EI values were detected is strongly recommended.

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