Bull Environ Contam Toxicol (2012) 88:182–186
DOI 10.1007/s00128-011-0505-7

Assessment of Metal Pollution in Soils From a Former Havana (Cuba) Solid Waste Open Dump

O. Díaz Rizo · M. Hernández Merlo · F. Echeverría Castillo · J. O. Arado López

Received: 10 August 2011 / Accepted: 19 December 2011 / Published online: 29 December 2011

Abstract Concentrations of cobalt, nickel, cooper, zinc and lead in the top-soils (0–10 cm) from a former Havana solid waste open dump were estimated by X-ray fluorescence analysis. The mean metal contents in the dump topsoil samples (in mg kg^{-1}: 8.4 ± 2.7 for cobalt, 50 ± 27 for nickel, 252 ± 80 for copper, 489 ± 230 for zinc and 276 ± 140 for lead) were compared with mean concentrations from Havana urban soils and from other solid waste disposals around the world. The comparison with Dutch soil quality guidelines showed a serious cooper contamination and a slight contamination with the rest of determined metals. The values of the integrated pollution index (mean index = 3.5) indicated that dump soils are highly contaminated by metals, and the enrichment index values shows that metal concentrations on the studied locations are above the permissible levels for urban agriculture.

Keywords Urban soils · Metal pollution · Solid waste dump · Havana · Cuba

It is well known that solid waste disposals (SWDs) (open dumps, landfills, sanitary landfills or incinerators) represent a significant sources of metals released into the environment (Bretzel and Calderisi 2011; Waheed et al. 2010; Ferré-Huguet et al. 2007). The main recipient of SWD is the soil, which can be contaminated by these metals then bioaccumulate in plants and animals, eventually making their way to humans by way of the food chain or contamination of waters (Acosta et al. 2011; Gupta et al. 2010; Krishna and Govil 2007).

Havana has the largest and most developed system of urban agriculture in Cuba. Over 5,000 popular gardens have been developed throughout all Havana's 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. For many years, the main SWD in Havana was the open dump, popular named as "Cayo Cruz", located in the surrounding of the Havana harbor. During more than 100 years, in Cayo Cruz was deposited around the 80% of the solid waste (industrial, domestic, etc.) of the city. Nowadays however, Cayo Cruz is one of the vacant plots available for urban agriculture. The purpose of the present study was to determine the current relative amounts of metals in top-layer soils collected from Cayo Cruz and furthermore, to assess the possible health risks derived from a future agriculture use of this land.

Materials and Methods

Top soils (0–10 cm) were collected at 16 stations in Cayo Cruz SWOD during the same day (Fig. 1). Composite samples, consisting of four soil cores, were collected at each site (approximately 1 × 1 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 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.

O. Díaz Rizo (✉) · M. Hernández Merlo · F. Echeverría Castillo · J. O. Arado López
Instituto Superior de Tecnologías y Ciencias Aplicadas, Ave. Salvador Allende y Luaces, POB 6163, 10600 La Habana, Cuba
e-mail: odrizo@instec.cu

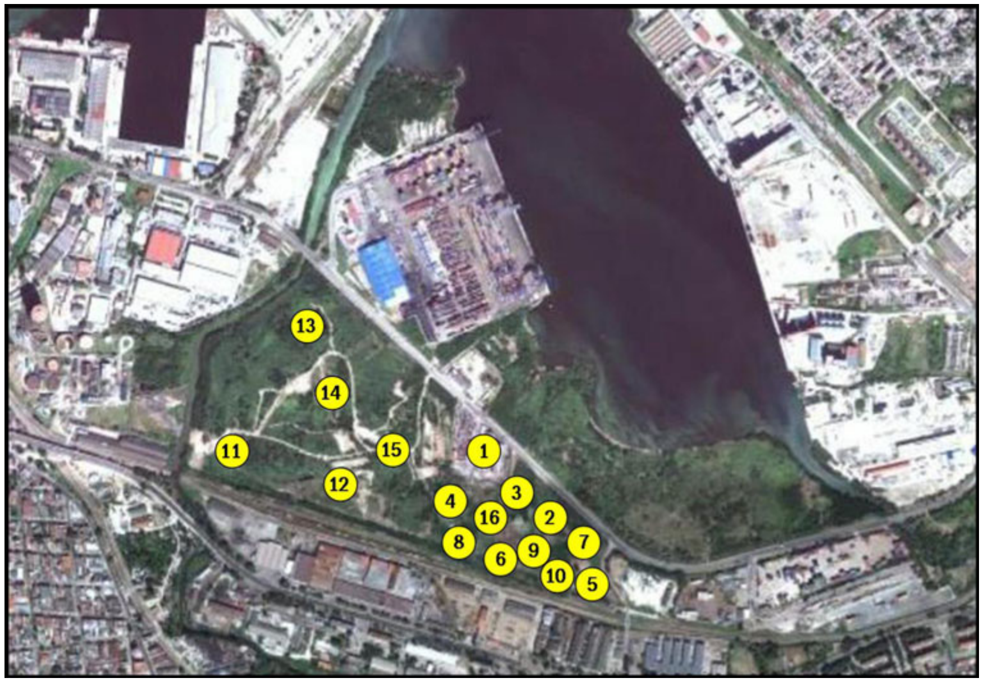

Fig. 1 Location of the studied stations within Cayo Cruz SWOD

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", 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 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 Ph and Marrier 1995):

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

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 metals (Co, Ni, Cu, Zn and Pb) determined by XRF are "excellent" ($SR \leq 25\%$) and the obtained results shows a very good correlation (R = 0.999) between certified and measured values.

In order to assess the soil contamination degrees and to estimate the possible impact to the human health, the integrated pollution index (IPI) (Sun et al. 2010; Chen et al. 2005) and the enrichment index (EI) (Lee et al. 1998) were calculated for each studied station. 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 metal concentration to the geometric means of background concentration of the corresponding metal:

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

Metal	Certified value	Measured value	SR (%)	L_D (mg kg^{-1})
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}

$$PI = C_i/S_i$$

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 for the Havana un-urbanized areas: 14.8 for Co, 58 for Ni, 83 for Cu, 151 for Zn and 28 for Pb (Díaz Rizo et al. 2011), and soils are to be classified as *low contaminated* ($IPI \leq 1.0$), *middle contaminated* ($1.0 < IPI \leq 2.0$) or *high contaminated* ($IPI > 2.0$).

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 to be unsafe for human health (Kabata-Pendias and Pendias 2001; Lee et al. 1998). Taking into account that element enrichments can come from anthropogenic inputs or natural geological sources, all determined metals were selected to calculate the EI by using the following equation:

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

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

Results and Discussion

Determined concentration values of Co, Ni, Cu, Zn and Pb in former Havana SWOD using XRF are presented in Table 2. The concentration value represents an average of the four subsamples independent determinations for each station. Mean, median and range of metal concentrations over the survey area are also shown in Table 2. The distribution of concentrations was skewed by a small number of small values (stations 3 and 11, see Fig. 2). The extent of this skewness is clearly visible by the differences between the mean and the median values. The difference (expressed as a percentage of the median value) was larger for Ni (14%), Pb (11%) and Zn (10%) and smaller for Cu

Table 2 Metal mean (±SD, n = 4, in mg kg^{-1}) concentrations in Cayo Cruz SWOD and its comparison with different SWDs at the world

Stations	Co	Ni	Cu	Zn	Pb
1	12.3 ± 0.8	43 ± 4	326 ± 4	754 ± 7	316 ± 4
2	7.6 ± 0.8	42 ± 4	252 ± 3	498 ± 6	316 ± 4
3	14.3 ± 0.7	16 ± 5	129 ± 2	78 ± 3	14 ± 1
4	6.7 ± 0.5	45 ± 4	191 ± 3	446 ± 5	503 ± 5
5	7.9 ± 0.7	61 ± 4	185 ± 3	370 ± 5	213 ± 3
6	10.2 ± 0.7	37 ± 4	376 ± 4	631 ± 6	308 ± 4
7	8.5 ± 0.8	46 ± 4	273 ± 3	638 ± 6	400 ± 4
8	7.9 ± 0.7	37 ± 4	323 ± 4	718 ± 7	470 ± 5
9	10.2 ± 0.8	45 ± 4	350 ± 4	631 ± 6	383 ± 4
10	9.4 ± 0.8	49 ± 4	327 ± 4	572 ± 6	361 ± 4
11	6.4 ± 0.3	22 ± 4	104 ± 2	56 ± 3	25 ± 1
12	6.9 ± 0.7	132 ± 5	172 ± 2	226 ± 4	185 ± 3
13	6.5 ± 0.4	78 ± 4	260 ± 3	256 ± 4	194 ± 3
14	11.0 ± 0.8	77 ± 4	261 ± 3	696 ± 6	253 ± 4
15	6.7 ± 0.5	35 ± 4	223 ± 3	743 ± 7	159 ± 3
16	7.0 ± 0.7	38 ± 4	288 ± 3	515 ± 6	323 ± 4
Mean ± SD	8.4 ± 2.7	50 ± 27	252 ± 80	489 ± 230	276 ± 140
Median	7.9	44	261	543	312
Range	6.4–14.3	16–132	104–376	56–754	14–503
Havana urban soils[a]	13.9 ± 4.1	66 ± 26	101 ± 51	240 ± 132	101 ± 161
Dutch TV[b]	9	35	36	140	85
Dutch IV[b]	240	210	190	720	530
Islamabad, Pakistan[c]	10,4	33	51	189	55
Kolkata, India[d]	–	63 ± 17	260 ± 30	540 ± 50	350 ± 40
Pisa, Italy[e]	–	73.4 ± 24.4	68.7 ± 43.3	127 ± 135	39.3 ± 34.8
Newcastle, England[f]	–	30 ± 26	233 ± 77	419 ± 274	350 ± 233
Hangzhou, China[g]	–	54,8 ± 7,4	133 ± 11	626 ± 63	777 ± 49

[a] Díaz Rizo et al. (2011)
[b] Swartjes (1999)
[c] Waheed et al. (2010)
[d] Gupta et al. (2007)
[e] Bretzel and Calderisi (2011)
[f] Rimmer et al. (2006)
[g] He et al. (2006)

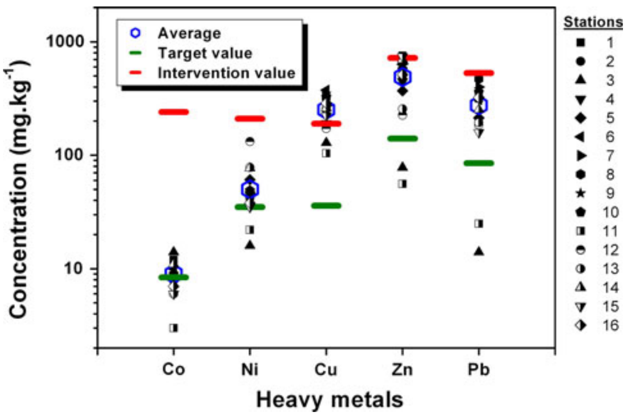

Fig. 2 Soil metal concentrations in Cayo Cruz SWOD

(4%) and Co (7%). A similar picture was obtained from examining the ranges of the concentration values for each element. Proportionally (the maximum value as a multiple of the minimum value) Pb (35) and Zn (13) had the largest ranges, and Co (2) and Cu (4) had the smallest ranges.

The comparison with the average metal concentrations recently reported for Havana urban soils (industrial, city parks, school gardens and un-urbanized sites) (Díaz Rizo et al. 2011) shows a concentration ratio lesser than 1.0 for Co and Ni, and between 2.0 and 2.7 for Cu, Zn and Pb. High contents of Cu, Zn and Pb in dump soils may depict their origin due to the type and quantity of the dumped waste including cooked and raw food left outs, domestic cleaning agents and materials, automobile workshops trash and construction and demolition waste. For example, Cu is present in different pigments used in polymer processes; Zn must be associated with the presence of galvanized metal scrap, expired cosmetics and medicines, old building materials, etc.; Pb with lead-based paints, battery parts and galvanised sheets. All of these elements are toxic and are introduced into the environment due to anthropogenic activities so their presence in dump site soil indicates contamination. However, high metal content in SWOD is expected. The comparison with metal contents reported for other SWDs worldwide (Table 2) shows that the obtained for the former Havana SWOD results are in the same range.

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) (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 (see Fig. 2), the former Havana SWOD soils can be considered as slightly contaminated with Co, Ni, Zn and Pb and seriously contaminated with Cu.

Table 3 Integrated pollution index (IPI) and enrichment index (EI) of Cayo Cruz SWOD soils

Station	PI					IPI	Pollution level	EI
	Co	Ni	Cu	Zn	Pb			
1	0.8	0.7	3.9	5.0	11.3	4.4	High	2.0
2	0.5	0.7	3.0	3.3	11.3	3.8	High	1.6
3	1.0	0.3	1.6	0.5	0.5	0.8	Low	0.4
4	0.4	0.8	2.3	3.0	18.0	4.9	High	1.8
5	0.5	1.1	2.2	2.5	7.6	2.8	High	1.2
6	0.7	0.6	4.5	4.2	11.0	4.2	High	1.9
7	0.6	0.8	3.3	4.2	14.3	4.6	High	1.9
8	0.5	0.6	3.9	4.8	16.8	5.3	High	2.2
9	0.7	0.8	4.2	4.2	13.7	4.7	High	2.0
10	0.6	0.8	3.9	3.8	12.9	4.4	High	1.9
11	0.2	0.4	1.3	0.4	0.9	0.6	Low	0.4
12	0.5	2.3	2.1	1.5	6.6	2.6	High	1.2
13	0.4	1.3	3.1	1.7	6.9	2.7	High	1.3
14	0.7	1.3	3.1	4.6	9.0	3.8	High	1.7
15	0.4	0.6	2.7	4.9	5.7	2.9	High	1.4
16	0.5	0.6	3.5	3.4	11.5	3.9	High	1.7
Mean	0.6	0.9	3.0	3.2	9.9	3.5		1.6
SD	0.2	0.5	1.0	1.5	5.0	1.4		0.5
Min	0.2	0.3	1.3	0.4	0.5	0.6		0.4
Max	1.0	2.3	4.5	5.0	18.0	5.3		2.2

Pollution index (PI) and integrated pollution index (IPI) of metals in the soil samples from Cayo Cruz SWOD are listed in Table 3. Based on the criteria mentioned earlier, dump soils are low polluted by cobalt (PI $\leq$ 1) and, in some stations, middle polluted by nickel (1 $<$ PI $\leq$ 3). On the other hand, the results show a high level of pollution by Cu, Zn and Pb (PI $>$ 3) in all stations, except the mentioned stations 3 and 11. The Cu, Zn and Pb pollution levels are so high (mean PI = 3.0 for Cu, 3.2 for Zn and 9.9 for Pb), that the IPI show High Pollution Levels (IPI $>$ 2, mean IPI = 3.5) in all stations, except those also mentioned before.

Enrichment index values bigger than 1.0 in the major part of studied locations (Table 3) indicate that crops produced in these areas will not be safe for human consumption although individual metals could hold the threat of metal toxicity to the plants (Kabata-Pendias and Pendias 2001). Hence, the metal concentrations on the Havana former SWOD are above the permissible levels for agriculture and it selection for urban agriculture is not recommendable.

References

Acosta JA, Faz A, Martínez-Martínez S, Arocena JM (2011) Enrichment of metals in soils subjected to different land uses

in a typical Mediterranean environment (Murcia City, southeast Spain). Appl Geochem 26:405–414
Altieri MA, Companioni N, Cañizares K, Murphy C, Rosset P, Bourque M, Nicholls CI (1999) The greening of the “barrios”: urban agriculture for food security in Cuba. Agric Hum Values 16:131–140
Bretzel FC, Calderisi M (2011) Contribution of a municipal solid waste incinerator to the trace metals in the surrounding soil. Environ Monit Assess 182:523–533
Chen TB, Zheng YM, Lei M, Huang ZC, Wu HT, Chen H, Fan KK, Yu K, Wu X, Tian QZ (2005) Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere 60:542–551
Díaz Rizo O, Echevarría Castillo F, Arado López JO, Hernández Merlo M (2011) Concentrations of heavy metals in urban soils of Havana city, Cuba. Bull Environ Contam Toxicol 87:414–419
Ferré-Huguet N, Nadal M, Mari M, Schuhmacher M, Borrajo MA, Domingo JL (2007) Monitoring metals near a hazardous waste incinerator. Temporal trend in soils and herbage. Bull Environ Contam Toxicol 79:130–134
Gupta D, Chatterjee JM, Ghosh R, Mitra AK, Roy S, Sarkar M (2007) Elemental uptake of radish grown near a municipal solid waste dumping site by EDXRF. J Radioanal Nucl Chem 274(2):389–395
Gupta D, Chatterjee JM, Ghosh R, Mitra AK, Roy S, Sarkar M (2010) Radioisotope-induced EDXRF investigation of elemental uptake in cauliflower grown at MSW-contaminated site. X-ray Spectrom 39:364–371
He PJ, Xiao Z, Shao LM, Yu JY, Lee DJ (2006) In situ distributions and characteristics of heavy metals in full-scale landfill layers. J Hazard Mater B137:1385–1394
Kabata-Pendias A, Pendias H (2001) Trace elements in soils and plants, 3rd edn. CRC, New York, pp 10–20
Krishna AK, Govil PK (2007) Soil contamination due to heavy metals from an industrial area of Surat, Gujarat, Western India. Environ Monit Assess 124:263–275
Lee JS, Chon HT, Kim KW (1998) Migration and dispersion of trace elements in the rock–soil–plant system in areas underlain by black shales and slates of the Okchon Zone, Korea. J Geochem Explor 65:61–78
Padilla R, Markowicz A, Wegrzynek D, Chinea E, Bamford SA, Hernández D (2007) Quality management and method validation in EDXRF analysis. X-ray Spectrom 36:27–34
Quevauviller Ph, Marrier E (1995) Quality assurance and quality control for environmental monitoring, VCH, Weinheim
Rimmer DL, Vizard CG, Pless-Mulloli T, Singleton I, Air VS, Keatinge ZAF (2006) Metal contamination of urban soils in the vicinity of a municipal waste incinerator: one source among many. Sci Total Environ 356:207–216
Sun Y, Zhou Q, Xie X, Liu R (2010) Spatial, sources and risk assessment of heavy metal contamination of urban soils in typical regions of Shenyang, China. J Hazard Mater 174:455–462
Swartjes AF (1999) Risk-based assessment of soil and groundwater quality in the Netherlands: standards and remediation urgency. Risk Anal 18(6):1235–1249
Waheed S, Siddique N, Hamid Q, Chaudhry MM (2010) Assessing soil pollution from a municipal waste dump in Islamabad, Pakistan: a study by INAA and AAS. J Radioanal Nucl Chem 285:723–732
WinAxil (2005) WinAxil code.Version 4.5.2. WinAxil, CANBERRA MiTAC