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Chromium, Cobalt and Nickel Contents in Urban Soils of Moa, Northeastern Cuba

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Abstract Iron, chromium, cobalt and nickel concentration levels in urban soil samples collected from Moa city (Holguín province), northeastern Cuba were determined. Both chromium and nickel contents exceed the Dutch Intervention Value soil quality standard in 2.8–5.4 and 1.3–3.3 times, respectively. Furthermore, cobalt content exceeds the Target Value in 1.3–1.8 times. Metal-to-Iron normalization predicts a natural origin for nickel and cobalt (Enrichment Factor <1), and also a moderate chromium enrichment (Enrichment Factor = 1.5–4.0) in all studied stations. The application of the Urban Environment Entropy Model show that residential area located near to industrial area is slightly affected by industrial chromium emissions and not affected by cobalt and nickel possible emissions. A chromium speciation in soil samples is recommended in order to evaluate the real impact of the current chromium content in Moa urban soils to local urban and suburban agricultures.

Keywords Urban soils · Heavy metals · Pollution · Environmental entropy · Cuba

In urban areas, soil environmental quality is closely related to human health. Humans, and particularly small children, are adversely affected by high concentrations of many heavy metals. Due to their active digestive systems, children have higher heavy metal absorption rates which, given the connection between this system and the circulatory system, can lead to imbalances in the blood composition. Heavy metals that accumulate within our bodies can also affect the central nervous system, cause poisoning, and act as co-factors of many other illnesses (Goyer 1997; Finkelstein et al. 1998; Brewster and Perazella 2004; Navas-Acien et al. 2007). Furthermore, heavy metal contents in the urban soil tend to increase with vehicular emissions (Surthland et al. 2000; Mielke et al. 2010), industrial residues (Schumacher et al.1997), the atmospheric deposition of dust and aerosols (Simonson 1995), and other industrial sources such as metallurgical industries and thermoelectric centers (Diawara et al. 2006; Biasioli et al. 2007).

The particular geological characteristics of the Moa municipality (Holguín province, Northeast Cuba), characterized by ultrabasic igneous rock (serpentine) abundance, justify the location and exploitation of the biggest Ni mines of the country. It is due to this that near Moa city [63 027 population, 23% – children (CNSO 2009)] are located some Ni + Co and Cr processing plants, which emissions most likely might end up in the city, or at least up to a certain percent. In that sense, the aim of this study is to investigate the concentrations of iron (Fe), nickel (Ni), cobalt (Co) and chromium (Cr) in the surface urban soils throughout Moa city, and to evaluate the soil environment quality in terms of metal contamination.

Materials and Methods

Surface soils (0–10 cm) were sampled at representative sites from Moa city (Fig. 1) during the same journey. Composite samples, consisting of four soil cores, were collected at each site (approximately 1 × 1 m). This

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Fig. 1 Location of studied stations in Moa city

sampling strategy was adopted in order to reduce the possibility of random influences from urban wastes, and to investigate trace metal concentrations in representative soils: industrial (St. 1–4) and residential (St. 5–7). All samples were collected with a spatula and kept in PVC packages and dried at 50°C. 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 heavy metal concentrations were estimated by X-Ray Fluorescence Analysis (XRF) using the Certified Reference Materials (CRM) IAEA-SL-1 "Lake Sediment" (Dybczynski and Suschny 1974), IAEA-Soil-5 (Dybczynski et al. 2007), IAEA-356 "Polluted Marine Sediment" (IAEA 1994), BCR-2 "Basalt Columbia River" (Wilson 1997) 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 a 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 et al. (Quevauviller and Marrier 1995):

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

where C_X – experimental value, C_W – certified concentration value and σ is the standard deviation of C_X. On the basis of

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

Metal	Certified value	Measured value*	SR (%)	L_D ($mg.kg^{-1}$)
Cr	60	59 ± 4	10	22
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

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

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 (Pszonicki 1984) is presented in Table 1. All heavy metals (Cr, Fe, Co and Ni) determined by XRF are "excellent" ($SR \leq 25\%$) and the obtained results shows a very good correlation (R = 0.9999) between certified and measured values.

The metal enrichment was assessed by normalizing the results to a reference metal, using the Enrichment Factor parameter (Schropp et al. 1990):

$$EF = (X/Y)_{sample} \Big/ (X/Y)_{background}$$

where X is the concentration of potentially enriched metal and Y is the concentration of the reference metal. If the EF value of an element is close to unity, it means that its observed concentration in samples can be considered as crustal material. An enrichment value higher than unity indicated non-crustal contribution on the corresponding element concentration. Taking into account the geology of the studied area, the (Turekian and Wedepohl 1961) results for ultrabasic igneous rocks were used as background values. In order to assess the possible anthropogenic impact, the use of Fe to normalize the trace metal contaminants is recommended (Mucha et al. 2003). Iron is abundant in the environment and is scarcely influenced by anthropogenic inputs due to the natural high levels of this element (Villares et al. 2003).

Additionally, the Urban Environment Entropy (UEE) Model (Ouyang et al. 2008) was applied to assess the impact induced by Cr, Ni and Co levels in residential soils to the Moa city population. Knowing the concentration of a potential pollutant and also its standard or background concentration value, the UEE value for this pollutant can be calculated as:

$$UEE_i = (\pm)\frac{\Delta E_i}{U}$$

where, ΔE_i stands for the percentage of the difference between the measured value of the *i*th pollutant and its standard or background value; U is the temporal urbanization level of the sampling location. Here, the (Turekian and Wedepohl 1961) results for ultrabasic igneous rocks were also used as background values. The child percentage in Moa population was used as urbanization level, being them the most likely fraction of the population to be affected by heavy metal pollution.

Results and Discussion

The average Cr, Fe, Co and Ni concentrations determined by XRF in Moa city urban soils are shown in Table 2. The highest chromium and nickel concentrations were recorded in the nearest to the industrial area residential station 5, while Co concentration is practically uniform through all studied stations. It has been found before that Cr and Ni are inherited from parent rocks. Particularly, soil on serpentines contains high Cr and Ni concentrations (Kabata-Pendias and Pendias 1992). Due to the lack of an official Cuban guideline for proper concentrations of heavy metals in 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) (Swartjes 1999). 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. According to Dutch classification, the Moa city urban soils can be considered as *"seriously contaminated"* with Cr and Ni and *"slightly contaminated"* with Co.

Table 2 Average concentrations for heavy metals determined in Moa city urban soils

Metal	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7	TV[a]	IV[a]
Cr	1823 ± 93	1737 ± 92	1366 ± 84	1056 ± 75	2052 ± 98	1804 ± 94	1582 ± 89	100	380
Fe (%)	3.5 ± 0.1	3.4 ± 0.1	4.8 ± 0.5	4.2 ± 0.1	3.0 ± 0.4	3.6 ± 0.2	4.5 ± 0.5	–	–
Co	12 ± 1	12 ± 2	16 ± 2	14 ± 2	14 ± 1	14 ± 1	16 ± 2	9	240
Ni	419 ± 84	489 ± 65	272 ± 77	355 ± 42	701 ± 35	569 ± 45	311 ± 42	35	210

Mean ± SD, n = 4, mg kg^{-1}, except Fe

[a] Target Value (*TV*) and Intervention Value (*IV*) in mg kg^{-1} (Swartjes 1999)

Table 3 Chromium, cobalt and nickel enrichments in Moa city urban soils

Metal	Station 1	Station 2	Station 3	Station 4	Station 5	Station 6	Station 7
Cr	3.1	3.0	1.7	1.5	4.0	2.9	2.0
Co	0.2	0.2	0.2	0.2	0.3	0.2	0.2
Ni	0.6	0.7	0.3	0.4	1.1	0.7	0.3

Calculated using Cr, Co and Ni average concentrations in mg kg^{-1} and Fe concentration in %

Table 4 UEE values for Cr, Co and Ni in Moa residential stations

Metal	Station 5	Station 6	Station 7
Cr	1.2	0.6	−0.05
Co	−3.9	−3.9	−3.9
Ni	−2.8	−3.1	−3.7

On the other hand, calculating the Enrichment Factor using Fe as reference metal for Cr, Co and Ni and (Turekian and Wedepohl 1961) results for ultrabasic igneous rocks as background (Table 3), a different result is obtained. Here, according to Birch classification (Birch 2003), the natural Co and Ni origin is confirmed (EF < 1), meanwhile Cr origin is anthropogenic (EF > 1). Thus, the Moa city urban soils can be considered, according to this criterion, as not contaminated with Co and Ni, independently their relative high content values, and moderately contaminated with Cr. The observed decrease of the Cr enrichment in the residential area as the distance to the industrial zone increases makes us believe that the Cr input must be associated with atmospheric discharges from a Cr processing plant.

The results of Urban Environment Entropy values for Cr, Co and Ni contents in residential soils are listed in Table 4. At sampling sites 5 and 6, only Cr UEE values were positive. Moreover, their absolute values were relatively low. On the other hand, Co and Ni UEE values in all studied residential stations so as the Cr UEE value in the station 7 (fairest from industrial area) were negative. Thus, Moa residential soil quality is slightly affected by industrial chromium emissions at these sites and not affected by the possible Co and Ni emissions.

Urban agriculture in Cuba has rapidly become a significant source of fresh food production for the urban and suburban populations (Altieri et al. 1999). This system of urban agriculture has been developed and managed along agroecological principles, which eliminate the use of synthetic chemical pesticides and fertilizers, emphasizing diversification, recycling, and the optimal use of local soils. As well known, soil Cr mobility to plants depends on its oxidation state (from +2 to +6) (Kabata-Pendias and Pendias 1992). Due to this fact, in order to evaluate the soil Cr real impact to Moa urban agriculture, a soil Cr speciation is recommended.

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