Spatial distribution and contamination assessment of heavy metals in street dust from Camagüey city (Cuba) using X-ray fluorescence

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Abstract
Concentrations of Cr, Co, Ni, Cu, Zn, Pb and Fe in the street dust from Camagüey city were studied by X-ray fluorescence analysis. The mean Cr, Co, Ni, Cu, Zn and Pb contents in the urban dust samples (97 ± 30, 14 ± 2, 35 ± 36, 94 ± 26, 199 ± 87 and 42 ± 29 mg.kg-1 dry weight, respectively) were compared with mean concentrations in other cities around the world. Spatial distribution maps indicated the same behaviour for Cr–Ni and Pb–Zn–Cu, respectively, whereas the spatial distribution of Co differs from other heavy metals. The metal-to-iron normalization, using Cuban average metal soil contents as background, showed that street dusts from Camagüey city are moderately or significantly Zn-Pb enriched in those areas associated with heavy traffic density and metallurgic plant location. However, the calculation of the potential ecological risk index shows that metal content in Camagüey street dust does not represent any risk for the city population.

Key words: *heavy metals; Cuba; X-ray fluorescence analysis; dusts; pollution; health hazards; roads; spatial distribution; concentration ratio*

Distribución espacial y estudio de la contaminación por metales pesados en polvos urbanos de la ciudad de Camagüey (Cuba) 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 polvos urbanos de la ciudad de Camagüey. Los contenidos medios de metales pesados en las muestras de polvos urbanos (97 ± 30, 14 ± 2, 35 ± 36, 94 ± 26, 199 ± 87 y 42 ± 29 mg.kg-1 en peso seco respectivamente) son comparados con las concentraciones medias determinadas en otras ciudades del mundo. Los mapas de distribución espacial indican comportamientos similares para Cr–Ni y Pb–Zn–Cu respectivamente, en tanto la distribución espacial de Co difiere del resto de los metales. La normalización a un metal de referencia, empleando como fondo los valores medios de concentraciones de metales pesados cubanos, mostró que los polvos urbanos de la ciudad de Camagüey tienen un enriquecimiento moderado o significativo de Zn y Pb en aquellas áreas que están asociadas a una elevada densidad del tráfico automotor y a la ubicación de plantas metalúrgicas. El cálculo del índice de riesgo ecológico potencial mostró que el contenido de metales pesados en los polvos urbanos de Camagüey no representa riesgo alguno para su población.

Palabras clave: *metales pesados; análisis por fluorescencia de rayos X; polvo; polución; riesgos para la salud; carreteras; distribución espacial; tasa de relevancia; Cuba*

Introduction

Street dust usually consists of soil, deposited airborne particles, construction materials and soot or fumes discharged from industries, waste incinerators or vehicles, among others. Its composition is, in essence, a sensitive indicator of urban environmental quality, providing valuable information beyond the single analysis of urban air, water or soil samples [1]. Metals in dust can accumulate in human fatty tissue and internal organs via direct inhalation, ingestion and dermal contact absorption [2-3], causing risk to human health because of their toxicity and non-degradability, especially for children who are more sensitive than adults [4-6]. In Cuba, the assessment of heavy metal content in urban soils and the evaluation of its impact on human health and on urban agriculture started recently [7-14]. However, heavy metal content in urban dust from a Camagüey city has not been reported yet.

Camagüey, a city with a population of 324 989 inhabitants, from which 16.3 % are children [15], is one of the oldest Cuban cities, where some metallurgic plants are located, and, due to their geographical position, an important vehicular maintenance center, which may represent a significant heavy metal emission source into the environment. Furthermore, in 2015 Camagüey celebrated the 500 anniversary of the city foundation. On this special occasion, important restoration works were performed in urban areas in the last few years. Therefore, the main objective of this study was to investigate the contents and spatial distribution of heavy metals in Camagüey street dusts to estimate both their potential risks as well as sources of pollution.

Materials and Methods

Thirty street dust samples (each weighting approximately 150 g) were collected from different locations (St.) in the highly urbanized region of Camagüey during the same journey (Fig. 1). Samples were collected close to recreational centers (St. 1, 5, 7, 8, 16), parks (St. 6, 12, 13, 14), schools (St. 17, 21, 22, 25, 26), hospitals (St. 9, 10, 15, 30), factories (St. 4, 11, 20, 24, 29), hotels (St. 3, 19), metallurgical plants (27, 28), residential areas (St. 18, 23) and in the railway station (St. 2). Each sample was collected by gently sweeping an area of about 16 m^2 in the street crossroad using a plastic hand broom and transferred to a clean, self-sealed polyethylene bag. In the laboratory, samples were first dried at 35 °C and large rock, metallic and plastic pieces and organic debris were removed before sieving. The fractions smaller than 2 mm were ground to a fine powder (< 63 μm) in an agate mortar. The pulverized samples were newly dried at 35 °C until obtaining a constant weight. For analysis, samples 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.

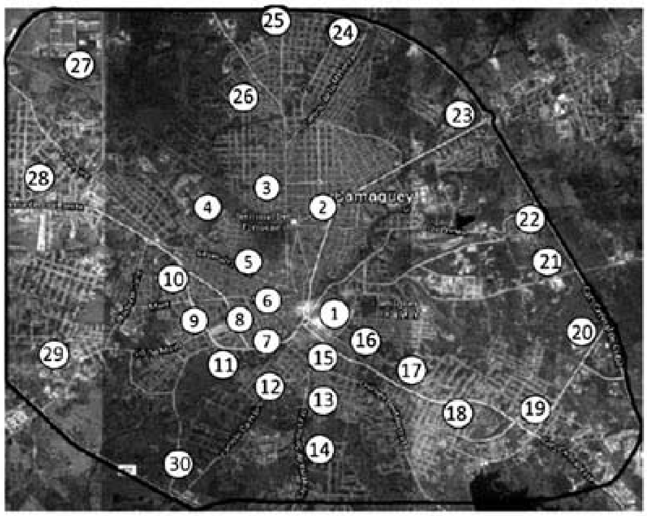

Figure 1. Location of the studied stations in Camagüey city.

The Cr, Co, Ni, Cu, Zn and Pb concentrations were estimated by X-Ray Fluorescence Analysis (XRF) using the experimental array and methodology described in [7, 10]. The spatial distribution maps of all studied heavy metals in urban street dust from Camagüey city were generated with ArcGIS software.

The accuracy was evaluated using the SR criterion, proposed by McFarrell [16]:

$$SR = \frac{|C_x - C_w| + 2\sigma}{C_w}.100\,\%$$

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.

To assess the possible metal pollution in urban dust, 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 studied element to the concentration of iron in the sample and $(C_x/C_{Fe})_{BV}$ is the same ratio but with a background soil [17]. Due to the absence of previous baseline or background studies, the average heavy metal content reported for Cuban soils [18] were used as background values (BV). Six contamination categories are recognized on the basis of the enrichment factor: EF < 1 corresponds to non-enrichment, EF = 1–2 states deficiency to minimal enrichment, EF = 2–5 moderate enrichment, EF = 5–20 significant enrichment, EF = 20–40 very high enrichment and EF > 40 extremely high enrichment [19, 20].

Table 1. XRF analysis of CRM Soil-7, SR values and Detection Limits (L_D)

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.

Potential ecological risk index (RI) originally introduced by Hakanson [21] is also calculated to assess the degree of heavy metal pollution in street dust, using the following equations:

$$RI = \sum_{i=1}^{n} E_i \quad (1)$$

$$E_i = T_i f_i \quad (2)$$

$$f_i = \frac{C_i}{B_i} \quad (3)$$

where, RI is the sum of the all give risk factors for heavy metals, Ei is the monomial potential ecological risk factor, Ti is the metal toxic factor and the values for each element are in the order of Zn = 1 < Cr = 2 < Cu = Co = Ni = Pb = 5. fi is the metal pollution factor, Ci is the concentration of metals in the street dust, and Bi is a reference value for metals. Different RI classifications of metal pollution are low ecological risk (RI ≤ 150), moderated ecological risk (150 ≤ RI < 300), considerable ecological risk (300 ≤ RI < 600) and high ecological risk (RI ≥ 600) [21].

Results and Discussion

Concentrations of Cr, Fe, Co, Ni, Cu, Zn and Pb in the street dusts of Camagüey city, together with soil background values (BV), are presented in table 2. The concentration ranges of Cr, Co, Ni, Cu, Zn and Pb were 41–278, 8–26, 7–168, 25–72, 84–553 and 16–401 $mg.kg^{-1}$, with mean values of 126, 15, 66, 36, 222 and 63 $mg.kg^{-1}$ respectively. Mean concentrations of the heavy metals in urban soils decreased following this order: Zn>Cr>Ni>Pb>Cu>Co; they were all comparable to the background values with the exception of Zn and Pb, the mean contents of which were 2.5 and 1.8 fold higher than its corresponding background values, respectively. The concentrations of Cr, Ni, Zn and Pb varied greatly, while Co and Cu concentrations were quite homogeneous across the city. The comparison with metal contents reported for other similar population cities worldwide (table 3) shows that those from Camagüey streets dusts results are within the same range.

Table 2. Metal concentrations in urban street dusts from Camagüey city and background values (BV) (in $mg.kg^{-1}$, except for Fe)

Metal	Concentrations					BV [18]
	Min.	Max	Median	Mean	SD	
Cr	41	278	121	126	48	463.2
Fe (%)	1.9	5.5	3.4	3.6	0.7	4.3
Co	8	26	15	15	4	31.4
Ni	7	168	61	66	36	294.2
Cu	25	72	32	36	12	83.7
Zn	84	553	212	222	84	90.7
Pb	16	401	50	63	13	34.6

Table 3. Metal concentrations in urban street dusts from Camagüey city and background values (BV) (in $mg.kg^{-1}$, except for Fe)

Location	Cr	Co	Ni	Cu	Zn	Pb	Reference
Camagüey. Cuba	126	15	66	36	222	63	Present study
Isfahan, Iran	82	14	67	182	707	393	[22]-
Xi´an, China	154	40	32	62	391	152	[23]
Otawa, Canada	43	8.3	15	66	113	39	[24]
Aman, Jordan	29	32	66	139	351	271	[25]
Kavala, Greece	232	N/A	68	172	355	387	[26]
Kayseri, Turkey	29	17	45	37	122	75	[27]
Coventry, England	N/A	N/A	130	226	386	47	[28]
Rio do Janeiro, Brazil	202	N/A	74	291	2612	369	[29]

N/A – not available

Table 4 depicts the correlation coefficient matrix, listing the Pearson's correlation coefficient. A very significant correlation ($p < 0.01$) was found between Cr and Ni ($r = 0.64$), while significant correlation ($p < 0.05$) was also found between Cu and Zn ($r = 0.38$), Cu and Pb ($r = 0.28$) and Zn and-Pb ($r = 0.40$). The high correlations between dust metals may reflect that these heavy metals had similar sources.

Table 4. Pearson's correlation coefficients between metal elements (n = 30)

Metal	Cr	Co	Ni	Cu	Zn	Pb
Cr	1					
Co	-0,04	1				
Ni	0,64*	-0,03	1			
Cu	0,02	-0,02	-0,03	1		
Zn	-0,04	-0,04	-0,03	0,38**	1	
Pb	-0,03	-0,02	-0,03	0,28**	0,40**	1

Level of significance: *p≤0.01, **p≤0.05.

The spatial distributions of Cr, Co, Ni, Cu, Pb and Zn in the street dusts of Camagüey city are represented in Fig. 2. It is evident that the Cr–Ni and Pb–Zn-Cu spatial distribution characteristics are similar, while Co distribution is unique. That fact is in line with the determined Pearson's factors.

Two Pb-Zn-Cu hot-spots are located in the centre of city and in the western area. As it is well known, lead, copper and zinc have been identified as typical "urban" metals for which the usual sources are traffic (i.e. vehicular emissions) and other industrial sources such as metallurgical industries and thermo-electric plants [30]. Despite the wide use of lead-free fuels since 2000 in Cuba, Pb is not liable to transfer, resulting in its accumulation in urban soil due to pollution from previous decades [31]. Taking into account that urban soil is one of the

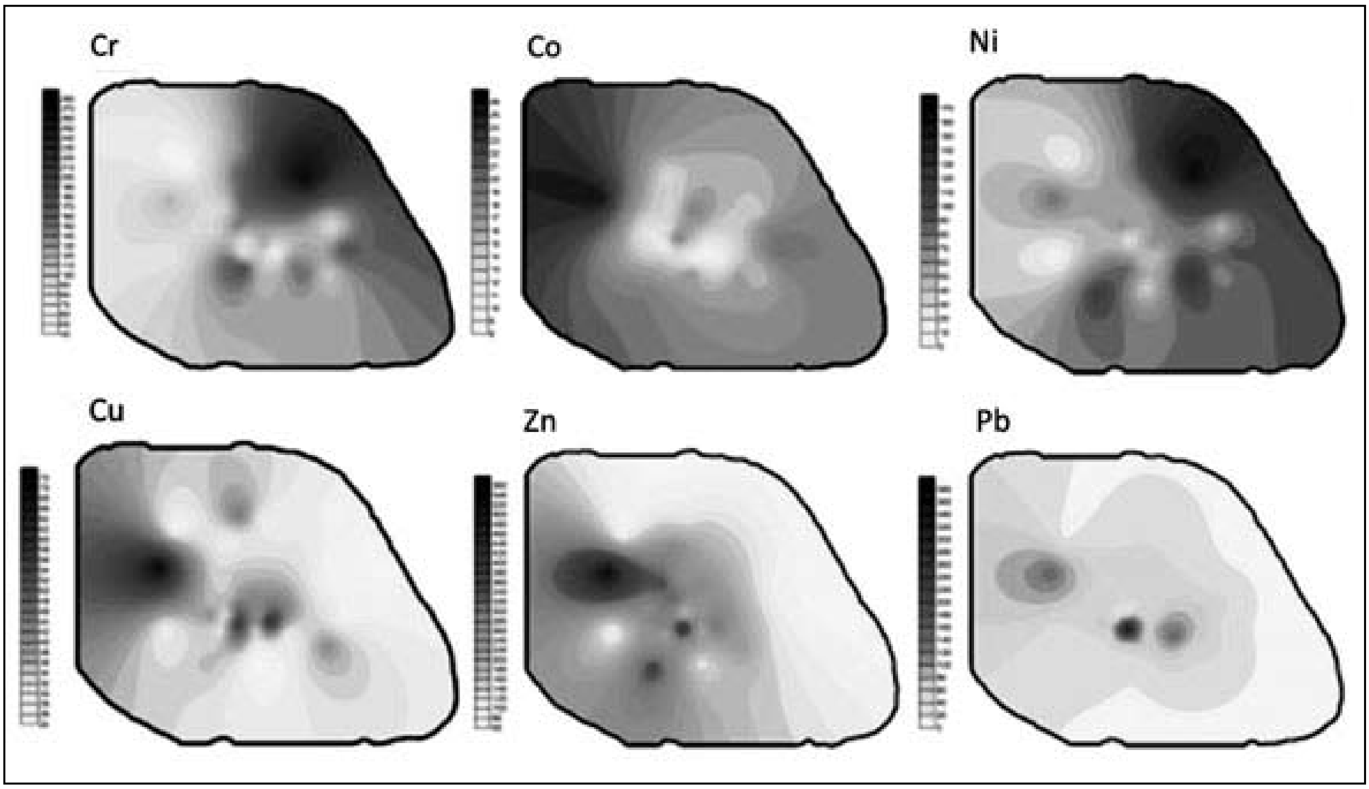

Figure 2. Spatial distribution of heavy metal concentrations determined in Camagüey street dusts.

main street dust components [1], the hot-spot area of Pb, Zn and Cu located in the centre of the city (highest traffic zone of the city) must be mainly associated with heavy traffic density. The second Pb-Zn-Cu hot-spot area is shown in the metallurgical plant location (station 28) and must be associated with plant emissions.

Furthermore, metal enrichment in street dusts (Fig. 3) using the enrichment factors (EF), shows that Camagüey urban dusts are not enriched with Cr, Co and Ni (EF < 1) and only street dusts from a few of the studied stations shows a minimal Cu enrichment (station 16), a moderate Zn-Pb enrichments (stations 7-9, 11-13, 15 and 28) and a significant Zn-Pb enrichment (stations 16-17). The highest Zn-Pb enrichments (7.4 and 6.3, respectively) were determined in station 16. This behaviour is in correspondence with the observed Pb-Zn-Cu hot-spot areas (Fig. 2).

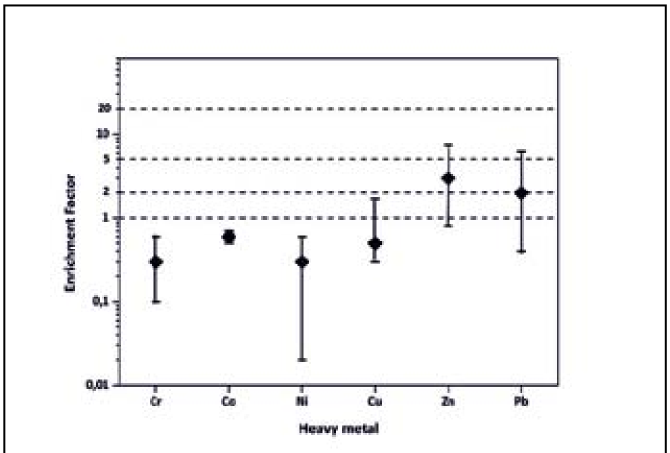

Figure 3. Enrichment factors determined for studied dusts of Camagüey city (dashed lines show the classification ranges established in [19, 20]).

To quantify the overall potential ecological risk of determined metals in street dust, RI was estimated as the sum of all calculated risk factors (Fig. 4). RI values in all studied stations are less than 150. Therefore, according to Hakanson classification [21], metal content present in dust from Camagüey city represents a negligible ecological risk to its population. The highest RI value (42.4) was determined in the location of a metallurgic plant (St.28).

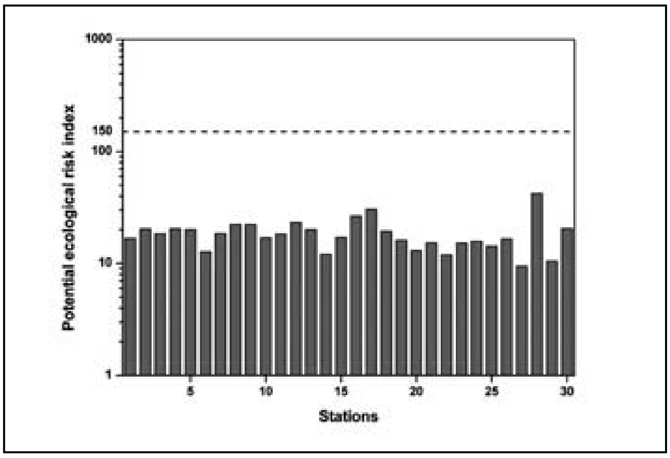

Figure 4. Potential ecological risk indices (RI) in the street dusts of Camagüey city.

Conclusions

Concentrations of six heavy metals (Cr, Co, Ni, Cu, Zn and Pb) in street dust from Camagüey city were determined by XRF analysis. The metal spatial distribution allowed to identify two Pb-Zn-Cu hot-spots areas, associated with the highest traffic zone of the city and with a metallurgic plant location, respectively. Independently of the moderate or significant Zn-Pb enrichment in the mentioned areas, the metal content in Camagüey street dusts does not represent a risk for the health of the city population.

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