

Trace elements status in the terrain of an impounded vehicle scrapyard

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Received: 14 June 2016/Published online: 24 October 2016 © Akadémiai Kiadó, Budapest, Hungary 2016

Abstract The impact of a scrapyard of impounded vehicles in São Paulo state on topsoil was evaluated for As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V, Zn and rare earth elements (REEs). Mass fractions of all elements, except for Co, Cu, Mo and Zn, were higher than reference values. Hot spots were observed for most elements suggesting vehicular source. The geoaccumulation index showed moderate pollution of As. The enrichment factor pointed to a significant enrichment of As, Mo and Pb. The normalization of REEs to Earth's crust values indicated a positive anomaly of Ce. The results indicate a potential risk to the soil quality of the scrapyard.

Keywords Vehicle scrapyard · Soils · Potentially toxic elements · Neutron activation analysis

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Introduction

Urban soil contamination varies considerably depending on different anthropogenic activities within city perimeters. However, one of the most common sources of pollution present in most cities is vehicular. Over the past decade, worldwide vehicle production has increased rapidly and tends to continue to rise due to demand. The Brazilian scenario is no different. The number of licensed vehicles has increased by 118 % over the last decade, totaling a fleet of 89 million vehicles in 2015 [1]. Rapid demographic and spatial transformation is proving to be a challenge for cities in developing countries, especially small- and medium-size cities, where capacity is typically inadequate to cope with the increase of vehicles.

Impounded vehicle scrapyard (IVS) overcrowding has become a problem in many Brazilian cities. Brazilian law states that apprehended vehicles must not remain longer than 90 days in an impound yard. However, in spite of this, they remain longer than that and suffer from weathering action. Mostly, the ground of these areas is not impermeable. The main sources of pollution are liquid residue spills, leachates produced by rainwater leaching and particulate material resulting from vehicle decomposition.

Metals and some metalloids are important pollution sources in different parking areas, as reviewed by Revitt et al. [2]. Many metals are present at different levels in leaded and unleaded gasoline, diesel oil, anti-wear substances added to lubricants, brake pads, and tires, as well as emitted by vehicle exhausts. The main components of automobiles are steel materials, including those that contain alloys and are composed by elements such as Al, Co, Cr, Cu, Fe, Mn, Mo and Ni [3].

Environmental impact investigations carried out on the end-of-life vehicles (ELV) reveal that Cd, Cu, Pb and Zn, as

well as waste oil, brake liquid and lubricants were the main contaminants [4]. The originated fluids and fragments can penetrate the soil profile, resulting in progressive degradation of soil quality around scrapyard vehicle areas [5].

Metals are non-degradable in soil, and their high toxicity and persistent nature in the environment, even at low levels, may result in long-term cumulative health effects, making them priority pollutants [6].

Several authors studied metal contamination in soils under and in the vicinity of discarded vehicle scrapyards [3–6], mechanic workshops and vehicle dismantlers [7–9]. Most of them observed moderate to high contamination by Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn in the top layer of soil (0–10 cm), decreasing with depth.

Many of the above mentioned studies occurred in developing countries [3, 4, 6, 7] where the fate of ELV has little or no regulation, differently of what occurs in Europe [10, 11]. Mechanical or physical recovery techniques allow recycling up to 75 % of ELV, leaving a 25 % residual automotive shredder residue (ASR), classified as hazardous waste [12].

In Brazil, in spite of the increasing number of IVS, the consequent soil metal contamination has still received little attention. Makara et al. [13] evaluated the levels of Cd, Pb, Ni, Zn, Cu and Cr in the deposit area of abandoned vehicles without soil sealing, in the metropolitan region of Curitiba–PR, and reported Cr and Ni contamination in the soil. Previous studies related to vehicle emissions pointed to an increase of cerium levels in road soils [14]. More recently, nanoparticles of cerium oxide have been used as fuel additives as an alternative to MMT (methylcyclopentadienyl manganese tricarbonyl) [15]. Information concerning rare earth elements (REEs) in IVS is also scarce.

Therefore, studies on metal contamination in soils of Brazilian vehicle impound scrapyards may provide valuable information to support remediation procedures, as well as encourage improvements in the management practices of these areas.

The aim of this study was to evaluate topsoil samples from a local Brazilian IVS for potentially toxic elements (PTEs), such as As, Ba, Co, Cr, Cu, Mo, Ni, Pb, V and Zn, and REEs.

Materials and methods

Study area and sampling strategy

This study was carried out at an IVS located in the city of Ribeirão Pires, a municipality in the metropolitan region of São Paulo state, Brazil $(23^{\circ}42'S; 46^{\circ}25'W)$ (Fig. 1). The 15,017.74 m² study area has a subtropical, moist climate with rainy summers and dry winters, June, July and August being the driest months. The entire city and its surrounding areas are protected watersheds. The city has a total of 119,644 inhabitants, with a population density of approximately 1140 inhabitants km⁻² [16]. The city is at 800 m above sea level.

The study area is partially occupied by the ruins of an old chemical plant, closed in the 1970s. Since the 90s, most of the site has been used as an impoundment area for the municipality administration. The IVS does not present an impermeable surface and the majority of vehicles are parked directly on the soil. The site is located in a predominantly residential, urban area with vegetation.

All samples, at all sampling points contained soil with demolition waste, such as brick, tiles, steel, wood, plastic, glass, asphalt fragments, rubbers and also auto parts pieces. Such waste materials, derived from construction and demolition debris, are typical of urban soils [17].

Forty soil samples (0–20 cm depth) of approximately 2 kg were collected during the dry season, in May 2013, with a manual stainless steel drill. Three subsamples collected at each point produced a composite sample, following a grid of approximately 15×5 m. The schematic map of the sampling points is presented in Fig. 2. Samples were stored in airtight polyethylene bags, labeled and taken to the laboratory for analysis.

Sample treatment and characterization

Samples were dried at 40 $^{\circ}$ C and sieved (<2 mm), to eliminate waste material, which represented less than 10 % of the total. Before and after sieving samples were



Fig. 1 Impounded vehicle scrapyard (IVS) schematic localization



Fig. 2 Schematic representation of the sampling points

disaggregated, homogenized, quartered. The samples were characterized for soil texture, pH, organic matter (OM) and cation exchange capacity (CEC) (pH 7), sum of bases (SB), base saturation (V %) and H+Al, according to Camargo et al. [18]. Samples were ground using a mechanic agate ball mill in order to obtain a fine and homogeneous powder.

Table 1 presents the analytical results of the soil scrapyard physicochemical characterization. Most of the samples consisted of neutral soils with a pH ranging from 4.5 to 7.9 (mildly acidic to alkaline) and with an average of 7.4. The samples had 50–326 g kg⁻¹ of clay, with an average of 186 g kg⁻¹, with high sand content between 406 and 785 g kg⁻¹ and, in general, contained average silt, averaging 250 g kg⁻¹. The texture range varied from loam to sandy-clay-loam, with a predominance of sandy-loam soils. This type of soil has a lower potential for retaining contaminants compared to clay soils. OM content varied greatly, ranging from 6 to 28 g kg⁻¹, with an average of 11 g kg⁻¹. The CEC, which expresses capacity of the soil to retain cations, was on average 240.4 mmol_c dm⁻³. Base saturation (V %) ranged between 62 and 97 %.

Instrumental neutron activation analysis (INAA)

Mass fraction of As, Ba, Co, Cr, Zn and most REEs (La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, and Sc) were determined by Instrumental Neutron Activation Analysis (INAA). Approximately 100 mg of each sample and the geological reference materials basalt BE-N (IWG-GIT), granite GS-N (IWG-GIT) and SOIL-7 (IAEA; used for analytical quality control), were accurately weighed, sealed in polyethylene bags and irradiated, approximately, for 8 h at a thermal neutron flux of 10^{12} n cm⁻² s⁻¹ at the IEA-R1 reactor of

Table 1 Physicochemical properties of soil samples (n = 40)

Variable	Mean	Median	Min	Max	SD
pН	7.4	7.6	4.5	7.9	0.8
$(g kg^{-1})$					
Sand	564	570	406	785	74
Silt	250	235	104	494	86
Clay	186	176	50	326	69
OM	11	9	6	26	5
(mmol _c dm ⁻	⁻³)				
H + Al	9	8	6	28	4
Κ	2	1	1	12	2
Ca	209	198	23	510	114
Mg	21	21	5	59	11
SB^{a}	232	217	29	571	125
CEC ^b	240	224	45	578	123
(%)					
V ^c	97	97	62	99	9
Fe ₂ O ₃	5.38	5.22	2.00	9.48	1.89
MnO	0.046	0.039	0.019	0.128	0.024

 $^{\rm a}$ SB—Sum of bases, equal to exchangeable Ca + Mg + K

 $^{\rm b}$ Cation exchange capacity (millimol of charge per dm $^{\rm 3}),$ equal to SB + H + Al

^c V—Base saturation, equal to V (%) = (100 SB)/CEC

IPEN. The induced gamma-ray activity was measured in a gamma-ray spectrometer consisting of a Ge-hyperpure detector and analysed by CANBERRA S-100 system software, which locates peak positions and calculates the energies and net areas. The detector used had a resolution (FWHM) of 1.9 keV for 1332 keV gamma rays of ⁶⁰Co. Counting was divided in two series: the first one 7 days after irradiation and the second one 15 days after irradiation. Counting times varied from 1 to 2.5 h.

X-ray fluorescence (XRF)

Aliquot samples were separated to produce 40 mm diameter pressed pellets, by mixing a 9 g sample with 1.5 g of wax powder in a mechanic mixer and then pressing it with a semi-automatic press. The loss on ignition was measured for all samples. Fe_2O_3 , MnO, Cu, Mo, Ni, Pb, V and Y were determined by XRF using a Philips sequential spectrometer, model PW 2404. The details of the procedure and data quality control are described elsewhere [19].

Quality control

The accuracy of the results was verified by the analysis of the certified reference materials SOIL-7 (IAEA) in INAA, and GSS-2 and GSS-5 (soil, IGGE, China) in XRF. The analytical uncertainties of the XRF method including measurement precision and trueness, varies between 3 and 10 % relative (95 % confidence interval) depending on element abundance. For INAA analysis, the results obtained for the measured reference materials also showed good agreement with the reference values. For all analyzed elements the relative deviation of the determined values from the reference values was below 10 %. The estimated relative expanded uncertainties, with a 95 % confidence level (k = 2), were less than 10 % for all elements.

Statistical analysis

Pearson correlation analyses were performed using Stat-Plus version 5 [20]. Levels of statistical significance are expressed as p < 0.05. Principal component analysis (PCA), a multivariate statistical method based on principal component scores, was performed to evaluate multivariate relationships using Statistica 7.0 software program [21].

Geoaccumulation index

Soil contamination by some PTEs was assessed by using the geoaccumulation index (I_{geo}) [22] according to Eq 1:

$$I_{\text{geo}} = \log_2\left(\frac{C_{\text{n}}}{1.5B_{\text{n}}}\right) \tag{1}$$

where C_n is the total concentration of an element in the tested soil and B_n is the respective element concentration in the Earth's crust [23]; the constant 1.5 compensates for fluctuation of natural and minor anthropogenic origin. The calculated result was compared to the seven classes proposed by Müller [37]; $I_{geo} < 0$, unpolluted; $0 < I_{geo} \le 1$, unpolluted to moderately polluted; $1 < I_{geo} \le 2$, moderately polluted; $2 \le I_{geo} \le 3$, moderately to heavily polluted; $3 < I_{geo} \le 4$, heavily polluted; $4 < I_{geo} \le 5$, heavily to extremely polluted; $I_{geo} > 5$, extremely polluted.

Enrichment factor

PTEs contamination was also evaluated by enrichment factor (EF) values. This method is based on the standardization of an element tested against a reference element, as proposed by Loska et al. [24], based on the equation suggested by Buat-Menard and Chesselet [25], according to Eq. 2:

$$EF = \frac{\frac{C_{n(sample)}}{C_{ref(sample)}}}{\frac{B_{n(background)}}{B_{ref(background)}}}$$
(2)

where $C_{n(\text{sample})}$ is the mass fraction of the target element in the soil sample; $C_{\text{ref (sample)}}$ is the content of a reference element in the soil sample; $B_{n(\text{background})}$ is the mass fraction of the target element in the reference environment and $B_{ref(background)}$ in the mass fraction of the reference element in the reference environment. In the present study, scandium was used as the reference element, according to previous studies [26] and the reference environment used was the Earth's crust [23]. The calculated result was compared to the five categories as proposed by Sutherland [27]; EF < 2 no or minimal pollution; EF 2–5 moderate pollution; EF 5–20 significant pollution; EF 20–40 very strong pollution; and EF > 40 extreme pollution.

Results and discussion

Total PTEs concentration in the IVS

Figure 3 presents the analytical results obtained for the measured PTEs of the IVS superficial soil, as well as the reference values for soils in São Paulo provided by the Environmental Protection Agency of the State of São Paulo [28] and the Dutch guideline values for soil [29]. The Dutch guidelines were chosen, as the model used by São Paulo State environmental agency to obtain guidelines values was based on that developed by the Netherlands National Institute of Public Health and Environment [30].

The São Paulo State Quality Reference Value (SP-QRV) and the Dutch target values (Dutch-TV) represent the amount of an element in the soil, which defines clean soil. The São Paulo State Prevention Value (SP-PV) is the mass fraction of an element that causes no damage to soil and groundwater quality. This level indicates a soil capable of maintaining its primary functions, protecting the ecological receptors and groundwater quality, and was determined based on ecological receptors assays. The Dutch intervention values (Dutch-IV) for soil represent the amount of an element in the soil or groundwater from which direct or indirect potential risks to human health can occur.

The mean values of As, Co, Cr, Cu, Mo, Ni, Pb and Zn contents in IVS soil comply with the Dutch-TV. However, only Co, Cu, Mo and Zn comply with SP-QRV. As, Ba, Cr, Ni and Pb contents exceeded SP-QRV, as these reference values are more restrictive than the Dutch-TV. Individual values of PTEs content in the soil have varied widely and, in some hotspots, Co, Cr, Cu, Mo, Ni, Pb and Zn values exceeded the SP-PV and Dutch-TV. Arsenic highest content values also exceed SP-PV. The mean values of Ba and V contents exceeded Dutch-TV. The Ba mean contents also exceeded SP-PV. None of the results has exceeded the intervention value for residential land use from São Paulo State guideline, and for this reason, these values were not presented in Fig. 3. In some hotspots, Ba content exceeds Dutch-IV. Total contents PTEs rank in the of following order: Ba > V > Cr > Zn > Pb > Cu > Ni > As > Co > Mo.



Fig. 3 Total content of PTEs in the soil samples; The Dutch target values (Dutch-TV), The Dutch intervention values (Dutch-IV) []; Quality reference value (SP-QRV), Prevention value (SP-PV) established for soil and groundwater in the state of São Paulo according to CETESB []

Most studies on PTEs in IVS or vehicle related areas are focused on Co, Cr, Cu, Ni, Pb and Zn, and there is little information on As, Ba, Mo and V concentrations.

Arsenic content varied from 3.1 to 19.1 mg kg⁻¹, with an average of 8.5 mg kg⁻¹. This value is lower than the reported value (62.08 mg kg⁻¹) obtained in topsoils from a scrapyard of discarded vehicles in Guangzhou (China) [4]. Although As can be found in car batteries, fuel, glass and alloys, the obtained value is also lower than reported values in other studies in the metropolitan region of São Paulo, such as São Paulo city topsoils adjacent to avenues [31], 12.5 mg kg⁻¹.

Barium is applied widely in many auto-part manufacturing materials, such as plastic, rubber, electronics, steel, glass, pigments and diesel fuel [32]. However, Ba assessments in IVS or similar areas are scarce. The same occurs for V and Mo. Vanadium is the major trace metal in petroleum products, especially in the heavier fractions [33] and Mo can be applied in vehicle as an alloy component, vehicle exhaust catalysts, fuel, oil additives, brake lines and batteries [34]. Barium, Mo and V levels varied from 149 to 790 mg kg⁻¹, 14 to 153 mg kg⁻¹, <1 to 5.8 mg kg⁻¹, respectively. Cobalt, Cr, Cu, Ni, Pb and Zn mass fraction levels obtained in this study were compared with similar studies in vehicle related activity areas (Table 2). The obtained mean values for almost all elements were lower than the values reported for Araucária city IVS [12], except for lead. In general, these PTEs contents are lower in IVS than in other vehicle related activities, such as scrapyards of discarded vehicles or mechanic workshops, probably due to the fact that in these areas soil quality is more vulnerable to leaking, split or particles influence, since vehicles are constantly being manipulated.

The results obtained for REEs are presented in Table 3 In order to evaluate the REEs distribution in samples of the Ribeirão Pires IVS, the results were normalized in relation to UCC values [23] (Fig. 4). The normalized curve indicated high anomalous values of Ce in some points that may suggest an anthropogenic source, such as vehicle exhaust catalysts, fuel or oil additives [15]. Nevertheless, soils rich in amorphous or crystalline Fe and Mn oxides tend to retain up to 70 % of total Ce in soils and consequently, present a positive Ce-anomaly [35, 36].

Table 2 Mean PTE concentration in topsoils (mg kg ^{-1})	of Ribeirão Pires IVS and similar studies in other cities
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Location	Туре	Region	egion Co Cr			Ni	Pb	Zn
Brazil	IVS	This study	6.9	67	24.1	17.2	50	60
		Araraucária [13] ^a	nr	97.29	31.61	34.93	35.92	96.11
Jordan	Scrapyard of discarded	Zarqua [3]	nr	nr	131	nr	307	426
China	a vehicle/dismantler	Guangzhou [4]	nr	182.17	257.85	59.82	568.12	827.84
Spain		Madrid [5]	120	92.2	207.6	246	746.6	934.8
Ghana	Mechanic villages	Kwadaso [7]	nr	nr	20.61	nr	197.24	8.38
Nigeria		Okigwe [9]	nr	26	1281	24.7	1559	nr
		Oriji [9]	nr	19.5	571	24.8	619	nr
		Nekede [9]	nr	16.8	569	18.3	759	nr

nr Not reported

^a Arithmetic mean of reported values [13]

Element Mean (mg kg $^{-1}$)		Median (mg kg ⁻¹)	Min (mg kg ⁻¹)	Max (mg kg^{-1})	SD (mg kg^{-1})	
La	20	19	7	43	10	
Ce	101	87	33	440	64	
Nd	19	19	6	50	11	
Sm	3.9	3.7	2.1	7.4	1.5	
Eu	0.57	0.52	0.35	0.86	0.13	
Tb	0.71	0.7	0.45	1.12	0.16	
Yb	0.4	4.1	2.3	5.0	0.8	
Lu	0.6	0.6	0.4	0.8	0.1	
Sc	14.6	14.1	6.1	26.2	5.1	
Y	27.3	27.7	12.8	39	6.2	

Table 3REEs concentration inRibeirão Pires IVS soil



Fig. 4 REEs normalized curve to UCC

Geoaccumulation index

The I_{geo} was calculated (Fig. 5) and, considering the mean value obtained, the soil from the studied IVS can be classified as: unpolluted for Ba, Co, Cr, Cu, Ni, V and Zn; unpolluted to moderately polluted for Mo and Pb; moderately polluted for As. Some outliers were observed to As, Co, Cr, Cu, Mo and Pb, suggesting a more critical scenario in some hot spots. None or minimum enrichment by Ba, V and Ni was observed, pointing to a geogenic occurrence.

Enrichment factor

The results showed no enrichment for Ba, Co, Cr, Ni and V, suggesting a geo genic source for these elements (Fig. 5). Values indicating a moderate enrichment were obtained for Cu and Zn, and a significant enrichment was observed for As, Mo and Pb.

The elemental concentration data were evaluated by multivariate statistical analysis (PCA) and Pearsons



Fig. 5 Box plot diagram of PTEs index of geoaccumulation and enrichment factor results

Table 4 Results of principal component analysis

	Factor 1	Factor 2	Factor 3
As			0.75
Ba	0.67		
Co	0.63		
Cr	0.87		
Cu	0.72		
Мо		0.82	
Ni	0.78		
Pb			0.59
V	0.76		
Zn		0.57	

correlation (Tables 4, 5) in order to obtain information about PTEs sources in the IVS soil. The PCA results pointed to three components, being responsible for 67 % of the variability of the data. Only factors above 0.5 were considered. The first factor represents 36 % of total data variability and is most probably not related to anthropogenic sources considering the results obtained for I_{geo} and *EF* for Ba, Co, Cr, Cu, Ni and V. The second and third factors represent 29 % of data variability grouping Mo/Zn and As/Pb, respectively. These results indicate an anthropogenic source probably related to vehicular origin, since these elements are commonly associated with auto parts, fuel, grease and oil composition.

The correlation in our study was defined as follows: 0.6 < r < 0.69 as modest correlation and r > 0.69 as strong correlation. The pH is considered a key parameter in elements mobility in soils, and the results indicated a negative modest correlation (r = -0.62, p < 0.05) between pH and As content. The pH showed no significant correlation with other PTEs. This can be due to the small variation of pH values of the samples (10 %). Only Ba content showed a strong negative correlation with clay content (r = -0.71, p < 0.05). Ba and V presented modest positive correlation with silt fraction (r = 0.69, p < 0.05 and r = 0.66, p < 0.05). Vanadium content also presented modest negative correlation with sand fraction (r = -0.60, r < 0.05). The correlation of Ba and V content with soil fractions may indicate these elements are from natural soil composition. None of the studied PTEs showed modest or strong correlation with OM. Iron oxide strongly correlated to V (r = -0.95, p < 0.05) and modestly correlated to Ba(r = 0.61, p < 0.05). Only Co showed strong correlation with MnO (r = 0.81, p < 0.05).

Conclusions

The mean contents obtained for the PTEs studied did not exceed target/prevention international and local values in most of the analysed samples, except for Ba and V. Nevertheless, some hotspots were observed for all the studied elements, presenting higher levels than target/prevention values, which may indicate a punctual contamination.

In comparison to other reported studies in similar areas, the results here presented lower contents of the PTEs. It should be noted that most of the literature data refers to discarded vehicle scrapyards, mechanic workshops and vehicle dismantlers. In the maintenance or dismantler processes, the vehicles are submitted to much more aggressive actions than just to weathering influences, which is the case of this study. Therefore, occasional fuel, grease or oil leakage, or decomposition of auto parts may explain the observed hotspots instead of a wider contamination spread.

The classification of the analyzed soil according to the I_{geo} index showed that the studied IVS may be considered unpolluted for Ba, Co, Cr, Cu, Ni, V and Zn, unpolluted to moderately polluted for Mo and Pb, and moderately polluted for As. The enrichment factor demonstrated moderate enrichment for Cu and Zn and significant enrichment for As, Mo and Pb. It has been reported that in waste oils contain high Pb values [8] and that Pb, Zn, Cu and As present in waste batteries and discarded vehicle lamps have an important influence in the soil [4]. The molybdenum disulfide is widely used in oil and greases. One can infer that the incorrect disposal of these elements is a potential source of soil contamination.

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Pearson's		As	Ва	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
	pН	-0.62	-0.2	-0.15	-0.2	-0.11	0.2	-0.35	0.06	-0.37	0.08
	OM	-0.10	-0.39	-0.29	-0.08	0.09	0.18	-0.11	-0.01	-0.28	0.15
	CEC	-0.47	-0.19	-0.2	-0.17	0.11	0.18	-0.07	0.02	-0.4	0.31
	Sand	-0.34	-0.13	-0.29	0.11	0.06	-0.08	0.26	0.26	-0.6	0.05
	Silt	0.2	0.69	0.45	0.35	0.23	-0.41	0.12	0.12	0.66	-0.04
	Clay	0.12	-0.71	-0.21	-0.13	-0.40	0.44	-0.07	0.12	-0.17	0.01
	MnO	-0.19	0.35	0.81	0.29	0.29	-0.18	0.22	-0.06	0.33	-0.04
	Fe ₂ O ₃	0.55	0.61	0.43	0.53	0.26	-0.11	0.41	-0.14	0.95	-0.02

Results with $|r| \ge 0.6$ are highlighted in bold

 Table 5 Results of Pearson correlation analysis

No significant correlation was observed for the PTEs concentration and soil characteristics such as pH, OM and CEC. As previously described, the soil was mixed with urban wastes derived from construction and demolition debris. The resultant soils are sandy with an average pH of 7.4. Sandy soils have lower CEC than loamy soils but the higher pH does not favor the metal solution concentration [37].

PTEs contamination in this kind of car scrapyards are considered of environmental concern, since the precarious current vehicle handling practices in developing countries, such as Brazil, represents a potential risk of soil quality.

Acknowledgments We are grateful to Ribeirão Pires Municipality for permission to carry out this project. The author C.N. Lange thanks for the fellowship from the Brazilian Nuclear Energy Comission (CNEN).

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