EVALUATION OF Co AND Cr MOBILITY IN SOIL PROFILES COLLECTED IN A SCRAPYARD OF IMPOUNDED VEHICLES

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ABSTRACT

The number of motor vehicles in urban environments has increased dramatically in the past years. As a result, so has the number of impounded and end-of-life vehicles. Car wastes can have a very high metal content, which can cause important environmental impacts to the soil where these vehicles are kept. Most Brazilian vehicle impound scrapyards are currently operating at their maximum capacity and soils may have become contaminated by past or current vehicle handling practices. Most of these areas do not present an impermeable surface. The level of soil contamination with heavy metals depends on the type of soil, climate and management practices. Metals, such as Co and Cr, that are present in many auto-parts, may be considered potentially toxic elements in these areas. The aim of this study was to evaluate Co and Cr levels and behavior in soil profiles located in a scrapyard of impounded vehicles of Ribeirão Pires-SP city. For this purpose, samples from distinct horizons of three soil profiles were collected. Element concentrations were determined by Instrumental Neutron Activation Analysis (INAA). Soil parameters such as pH, organic matter content and clay, silt and sand percentage were also determined. The obtained data were statistically analyzed in order to establish correlations between elemental concentrations and the impounded vehicles scrapyard soil. Soil acidity showed to be the most remarkable property for Cr and Co mobility through soil profile.

1. INTRODUCTION

Worldwide automobiles production has sharpy increased over the past decade and cities have had to cope with a large number of new vehicles in order to adapt to this increase. In developing countries, such as Brazil this demand for spatial transformation may prove to be difficult and vehicle mobility, parking and storage have become a challenge. An example of this situation can be observed at impounded vehicles yards, where overcrowding has become a problem in many Brazilian cities. Brazilian law states that the apprehended vehicles must not remain longer than 90 days in impound yards. However, in spite of this, they remain longer than that and suffer from weathering action. As most of these areas do not present an impermeable surfaces, superficial soil, ground water and superficial water are exposed to contamination. Liquid residues by spill or by rain water leaching and particulate material by vehicle decomposition result in diverse sources of pollution.

Metals are commonly used in combination and/or alloyed with other products and the automobile industry is one of the largest metal consumers. The main components of automobiles are steel materials, including alloy steels that contain alloying elements such as chromium [1] and cobalt.

According to Ohno *et* al [1] a car-part composition of a middle class passenger car, excluding tires and glass, has a total unit mass of 943 kg and 6.35 kg of chromium. In vehicle motor, for example, Cr is present in hydraulic cylinder blocks. Chromium plating is employed to make products shiny, attractive, and wear and tear-resistant and utilizes chromic (VI) acid (CrO_3 or H_2CrO_4) baths, which yield a very hard, brilliant, and wear and corrosion-resistant coating [2].

Chromium soil contamination generally enters the body via inhalation and ingestion. Inhalation of Cr-III or Cr-VI can cause shortness of breath, coughing, ulcerations of the septum, bronchitis, decreased pulmonary function, and pneumonia. Cr-III appears to be less toxic than Cr-VI. Inhalation of Cr-VI is known to cause human lung cancer. Chromium ingestion can yield ulcers in the stomach and small intestines, and anemia. Animal studies have indicated the potential for male reproductive system damage [3].

Recently, Co has also been largely used in several alloys due to its resistance to corrosion and abrasion. Co oxide is used as coating material because it has a very unique blue color [4]. Recently, Co has also been largely used as a component of electric vehicle batteries. According to Castro *et* al [5] the electric car Tesla Roadster has 21 kg of Co per unit.

Cobalt occurs in two oxidation states in soil, Co-II and Co-III, but Co-II is the dominant is soil solution [6]. Acute human and animal inhalation exposure to cobalt can yield significant decreases in lung function due to congestion and hemorrhaging. Chronic inhalation exposure can produce respiratory system irritation, asthma, decreased lung function, pneumonia, and fibrosis. It may also lead to heart, liver, and kidney damage. Human ingestion of cobalt can yield nausea, vomiting, and diarrhea. Animal exposure studies have yielded similar results [7].

Studies on soil contamination at scrapyards of impounded vehicles are scarce, especially in Brazil, where there is no knowledge of such studies to date. Few studies on Co and Cr soil contamination at auto-repairs workshops, discarded vehicles scrapyards, vehicle dismantlers and car battery processing workshops have been reported [8-11]. However, the majority of these studies [8-10] were performed in top soils only, not in total soil profiles. Therefore, the aim of this study was to assess the vertical profile distribution of Co and Cr at scrapyard of impounded vehicles of Ribeirão Pires city and correlate them with some relevant soil characteristics.

2. MATERIALS AND METHODS

2.1 Site description

This study was carried out inside a scrapyard of impounded vehicles situated in the city of Ribeirão Pires, a municipality in the metropolitan region of São Paulo state, Brazil (23°70′S; 46°43′W). The 15,017.74 m^2 study area has a subtropical, moist climate with rainy summers and dry winters, in which June, July and August are the driest months. All the city extension is considered as fountainhead protection area. The city has a total of 119,644 inhabitants, with a population density of approximately 1,140 inhabitants km^{-2} [12].

The study area is partially occupied by the ruins of an old chemical industry, closed in the 1970's. Since the 90's, most of the site is used as an impoundment area for the municipality administration. The impound yard does not present an impermeable surface and the majority of vehicles are parked directly on soil top. The site is located in a predominantly residential, urban area with vegetation. The surrounding roads have light traffic and recently (2014) a new intensive traffic road called "Rodoanel Mário Covas" has been in operation and is located 500 m from the yard. Nearby there is also a metropolitan rail train line and a small river (São Caetaninho River).

2.2 Sample collection

The sampling area was selected according to vehicles positions. One of the soil profiles collected was located before the vehicle storage area (PA), which appears unaffected by vehicle influence, in relation to its slightly elevated position. The other two were located in the storage area (PB and PC), which is considered to be affected by parked vehicles. The sampling area is presented in Figure 1.
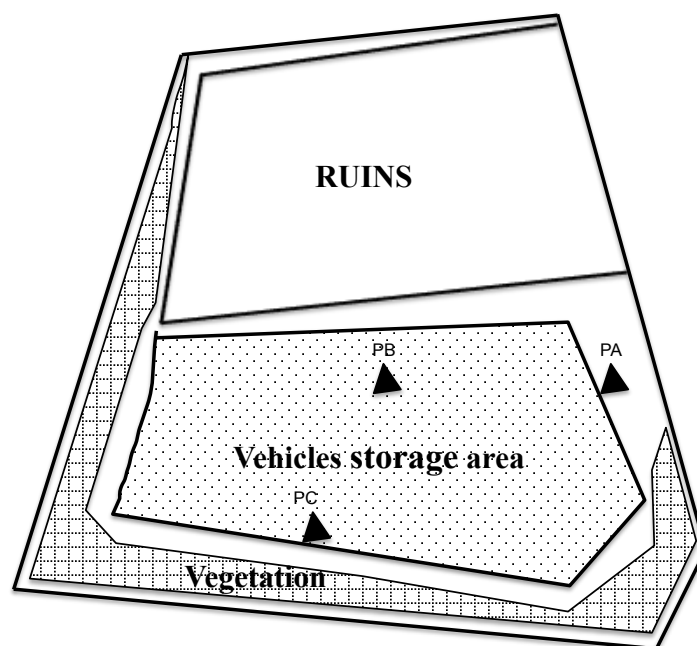

Figure 1: Sampling position representation.

Samples were collected by using plastic core catchers of 2 inches each. A Macro-Core sampler (a mechanical probing machine) was used to reach a residual soil horizon depth. Samples were collected from distinguished mineral horizons, which could easily be identified in each profile.

2.3 Soil preparation and characterization

Samples were dried at 40ºC and sieved (< 2 mm). Before and after sieving samples were homogenized and quartered. A fraction of each sample was characterized. Soil texture, pH, organic matter, cation exchange capacity (CEC) (pH 7), sum of bases (Ca^{2+}, K^+, Mg^{2+}), H+Al

and P analysis were performed in Campinas Agronomic Institute (IAC), from São Paulo state. The methods used in chemical and physical analysis were described by Camargo *et* al. [13]. The texture of each sample are given in Table 1 along with the encoding of the different profiles and samples. It is important to notice that during sampling some soil samples presented an unexpected characteristic, such as dark color and strong odor. The samples that had these characteristics were: PB-0.85, PC-1.75 and PC-3.60.

Table 1: Soil texture, encoding and sampling depth

Sampling Point	Sampling Depth (m)	Encoding	Clay <0.002 mm	Silt 0.053 – 0.002 mm	Total Sand 2.00 – 0.053 mm	Texture
			(g kg⁻¹)			
PA	0.75	PA-0.75	178	145	680	Sandy loam
	1.30	PA-1.30	277	241	482	Sandy clay loam
	2.10	PA-2.10	278	222	500	Sandy clay loam
	2.70	PA-2.70	127	293	580	Sandy loam
PB	0.50	PB-0.50	100	108	792	Sandy loam
	0.85	PB-0.85	256	136	608	Sandy clay loam
	1.45	PB-1.45	100	102	798	Sandy loam
PC	1.00	PC-1.00	202	267	531	Sandy clay loam
	1.75	PC-1.75	168	306	526	Sandy loam
	3.60	PC-3.60	178	331	491	Loam

2.4 Elemental determination by INAA

Samples were ground using a mechanic agate ball mill in order to obtain a fine and homogeneous powder. Elemental concentrations were determined by Instrumental Neutron Activation Analysis (INAA). Unfortunately, PC-3.60 sample was heavily involved by a dark color residue with a greasy aspect that interfered with the grinding to reach the appropriate grain size for INNA. 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) were accurately weighed and sealed in polyethylene bags and were irradiated approximately for 8 hours at a thermal neutron flux of 10^{13} n cm^{-2} s^{-1} at the IEA-R1 reactor of 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 counting were divided in two series: the first one seven days after irradiation and the second one 15 days after irradiation. The counting times varied from 1 to 2.5 hours.

2.5 Statistical Analyses

Pearson correlation analysis were performed using StatPlus version 5 [14]. The strength of the correlations was categorized in our study as follows: r<0.20 represents very weak correlations; r between 0.20 and 0.39 weak correlations; r between 0.4 and 0.69 modest correlations; and r>0.69 strong correlations. Levels of statistical significance are expressed as *$p<0.05$ and **$p<0.01$.

3.   RESULTS

3.1 Chemical characteristics of soil

The results of pH, exchangeable cations, CEC and organic matter contents are presented in Table 2.

Table 2: Soil chemical characterization

Sample	O.M. (g dm^{-3})	pH	P (mg dm^{-3})	K$^+$	Ca^{+2}	Mg^{+2}	Al^{+3}	H$^+$ + Al^{+3}	S.B.	C.E.C.^{a}	V% (%)
							(mmolc dm^{-3})				
PA-0.75	7	5.1	10	5.6	19	5	<LD^b	31	29.6	60.6	49
PA-1.30	6	5.9	2	1.3	16	4	<LD	12	21.3	33.3	64
PA-2.10	6	4.5	3	0.6	13	3	<LD	20	16.6	36.6	45
PA-2.70	6	4	3	0.5	4	1	<LD	109	5.5	114.5	5
PB-0.50	11	6.1	39	2.2	78	8	<LD	16	88.2	104.2	85
PB-0.85	27	4.2	5	2.1	10	1	<LD	109	13.1	122.1	11
PB-1.45	6	4.3	5	0.2	2	0	<LD	28	2.2	30.2	7
PC-1.00	9	7.1	12	1.3	87	16	<LD	10	104.3	114.3	91
PC-1.75	30	4.7	24	4.4	87	6	<LD	58	97.4	155.4	63
PC-3.60	6	4	3	0.5	4	1	<LD	109	5.5	114.5	5

^{a}Cation exchange capacity, equal to exchangeable Ca + Mg + K + H + Al
^{b}LD – limit of detection

It is important to determine soil pH on studies of metal mobility, such as Co and Cr, because mobility is strongly related to soil acidity. The pHs of the samples were generally acidic, with the lowest values found in the deepest horizons. The pH values were higher in PB and PC top horizons reaching neutrality. The statistical analysis presented in Table 3, indicated a negative modest correlation (r = -0.56, *p=0.05) between pH and depth.

The C.E.C values did not obey the same pattern at the distinct profiles. Referring to the supposed unaffected PA profile, one can notice that the most acid sample consistently contain more H+Al than the superficial samples. These cations are mainly responsible for C.E.C increase at the bottom of this profile and are generally associated to soil colloids. The highest C.E.C was found in PC-1.75, where the higher value of Ca^{+2} and the higher value of organic matter were also found. PB-0.85 also presented high contents of C.E.C and organic matter. The association between C.E.C and O.M. was confirmed with a positive strong correlation (r

=0.74, p=0.01) and CEC was positively modestly correlated with H+Al (r = 0.53, p=0.01) and with Ca^{+2} (r = 0.61, p=0.05), Table 3.

Table 3: Pearson correlation coefficients between relevant soil properties and Cr and Co concentrations.

	Depth	Co	Cr	O.M.	pH	P	K	Ca	Mg	H + Al	C.E.C.	Clay	Silt
Co	-0.25*												
Cr	-0.49*	0.85$^{n.s}$											
MO	-0.15	-0.09*	-0.25*										
pH	-0.56*	0.72**	0.73**	-0.22*									
P	-0.46*	0.17	0.36*	0.32*	0.40*								
K	-0.42*	0,13	0.53*	0.43*	0.07	0.39*							
Ca	-0.35*	0.61*	0.76**	0.38*	0.66*	0.78**	0.34*						
Mg	-0.41*	0.90$^{n.s}$	0.89$^{n.s}$	-0.02	0.90$^{n.s}$	0.45*	0.19	0.83$^{n.s}$					
H + Al	0.38*	-0.30*	-0.36*	0.48*	-0.69**	-0.24	0.00	-0.34*	-0.52*				
C.E.C.	-0.01	0.34*	0.42*	0.74**	0.04	0.49*	0.33*	0.61*	0.33*	0.53*			
Clay	0.01	-0.06	-0.11	0.11	0.07	-0.51*	-0.04	-0.21*	0.00	-0.06	-0.22*		
Silt	0.15	0.05	-0.10	0.37*	0.00	0,25*	-0.51*	0.32*	0.08	0.32*	0.52*	-0.32*	
Sand	-0.44*	-0.16	-0.24*	-0.15	-0.09	0.42*	0.05	-0.06	-0.18	-0.07	-0.13	-0.76**	0,08

n.s – not significant; * significant at p<0,05; **significant at p<0,01.

3.2 Cobalt and chromium concentration results

Cobalt concentration through the three profiles was illustrated in Figure 2. Highest values of Co concentrations were obtained at the most superficial horizon of PC, 15.90 mg kg^{-1}, and the lowest value was found at PB-1.45, 1.69 mg kg^{-1}. The quality reference value established by the Environmental Protection Agency of the State of São Paulo, the local regulatory environmental agency, for Co at superficial horizons is 13 mg kg^{-1} [15]. There was a remarkable difference between concentrations at the superficial horizon of PA and PC, indicating some interference favoring the increase of Co concentration at PC that is around three times higher than value found at PA. Cobalt concentration behavior through profiles PA and PB observed were similar.

Cobalt is most mobile under acidic and reducing conditions and it co-precipitates under oxidizing near-neutral or alkaline conditions as Fe and Mn secondary oxides, thus in alkaline conditions the element is immobile [16]. The pH=7.1 at the superficial horizon probably has influenced Co fixation. This assumption could be indicated by the strong positive correlation between Co concentration and pH (r=0.72, p=0.01). A modest positive correlation between Co and exchangeable Ca concentration (r=0.62, p=0.05) was also observed indicating that, probably, Co and Ca are adsorbed in the same charge sites, although a weak correlation (r=0.34, p=0.05) between Co and CEC was observed.
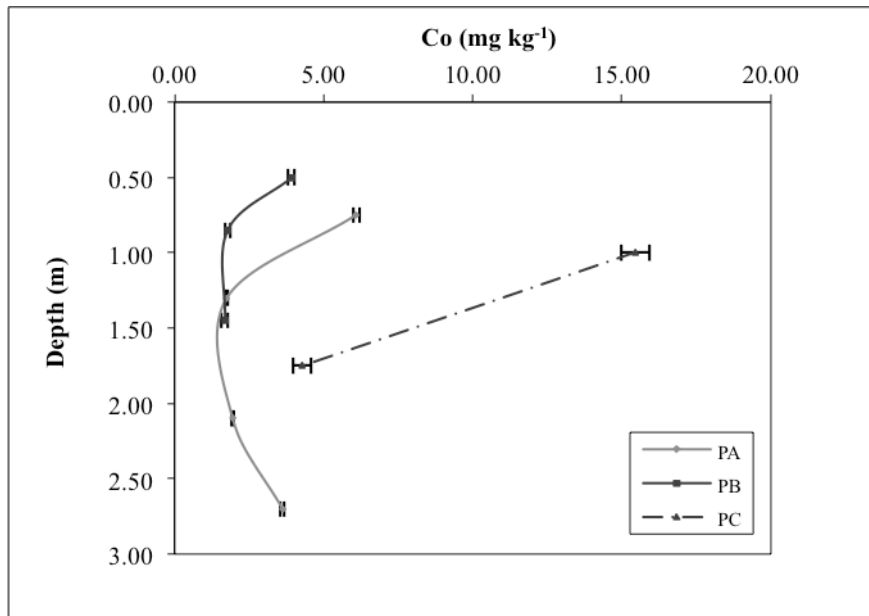
Figure 2: Co concentration through PA, PB and PC profiles.

Chromium concentration through the three profiles was illustrated in Figure 3. Highest values of chromium concentrations were obtained at the most superficial horizon of PC, 68 mg kg^{-1}, and the lowest value was found at PA deepest horizon, 9.6 mg kg^{-1}. The quality reference value established by the Environmental Protection Agency of the State of São Paulo for Cr at superficial horizons is 40 mg kg^{-1} [15]. It is important to notice that at PA, PB and PC chromium concentration decreased throughout the profile. Also remarkable were the differences between concentrations at the superficial horizons of PA and PC, indicating some interference favoring the increase of Cr concentration at PC.
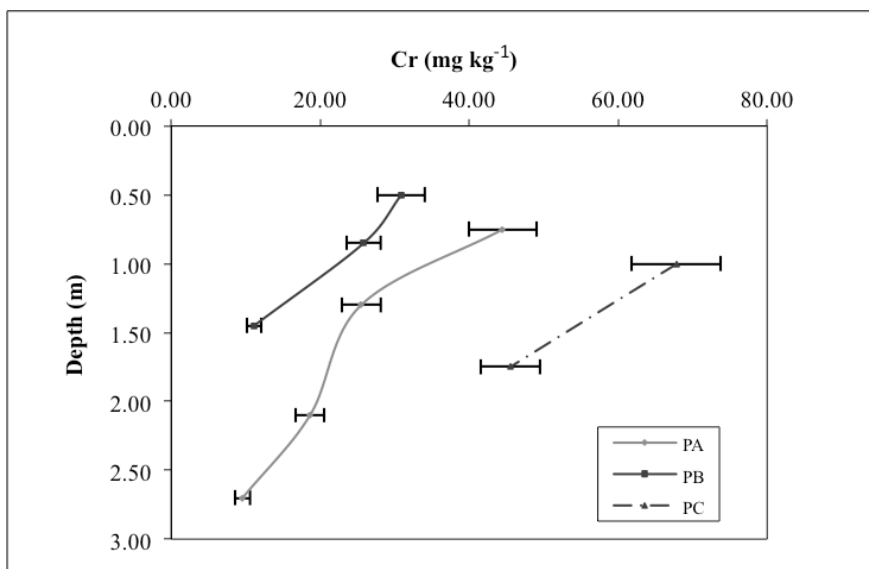

Figure 3: Cr concentration through PA, PB and PC profiles.

The statistical analysis presented in Table 3, indicated a positive strong correlation (r=0.73, *p*=0.01) between Cr concentration and pH. This probably indicates that the highest

concentration found at PC-1.00 was correlated with the distinct pH value (pH=7.1) of this horizon. Chromium mobility is very low under moderately oxidized, reduced and/or neutral conditions. Acidity influences the adsorption of Cr species to clay since, at increasing pH, the presence of organic matter can play a reducing action on toxic Cr^{6+} that converts it into more stable Cr^{3+}. Trivalent Cr co-precipitates with Fe^{3+} as insoluble $Cr(OH)_3$ at high pH values [4] and references therein. Generally, in soils chromate is in a pH-dependent equilibrium with other forms of Cr^{6+} such as $HCrO_4^-$ and dichromate ($Cr_2O_7^{2-}$), with CrO_4^{2-} being the predominant form at pH>6. Cr-III is much less mobile and adsorbs to particulates more strongly. The solubility of Cr^{3+} decreases above pH 4 and above pH 5.5 complete precipitation occurs [16].

Chromium concentration has also showed positive strong correlation with exchangeable Ca concentration (r=0.76, *p*=0.01), indicating that, probably, Cr and Ca are adsorbed in the same charge sites. This assumption could be reinforced by the modest positive correlation (r=0.42, *p*=0.05) between Cr and CEC.
A negative weak correlation between Cr and H+Al was observed (r=-0.36, *p*=0.05) that also likely occurs due to weathering trough profiles favoring accumulation of acid-forming cations, such as Al^{3+}, increasing the potential acidity on deepest horizons.

3. CONCLUSIONS

Summarizing, although the study was conducted in a small area (around 15,000 m^2) it was possible to notice soil heterogeneity among the three soil profiles. Alterations on soil properties have led to distinct retention and mobility behavior of Co and Cr through the profiles. The cause of this heterogeneity should be further investigated in future studies, so as the presence of the oiled residue described in previews sections of the present study. The main alteration occurs in soil pH, which, as it was observed through correlation analysis, plays an important role in Co and Cr mobility, especially at PC superficial horizon, which presented the highest values of concentration of both elements and the highest value of pH. Both elements concentration values obtained were above quality reference values established for São Paulo State, but none was above the prevention values which may indicate that vehicles do not represent as a worrisome source of Co and Cr for soil considering the geochemical condition herein described.

ACKNOWLEDGMENTS

REFERENCES

1. H. Ohno, K. Matsubae, K. Nakajima, Y. Kondo, S. Nakamura, T. Nagasaka. Toward the efficient recycling of alloying elements from end of life vehicle steel scrap". *Resources, Conservation and Recycling*, **V.100**, 2015, Pages 11-20.
2. A. Baral and R. D. Engelken. "Chromium-based regulations and greening in metal finishing industries in the USA". *Environmental Science & Policy*, **V.5 (2)**, 2002, Pages 121-133.

3. A. A. Jennings. "Analysis of worldwide regulatory guidance values for the most commonly regulated elemental surface soil contamination". *Journal of Environmental Management*, **V. 118**, 2013, Pages 72-95.

4. S. Albanese, M. Sadeghi, A. Lima, D. Cicchella, E. Dinelli, P. Valera, M. Falconi, A. Demetriades, B. D. Vivo. "GEMAS: Cobalt, Cr, Cu and Ni distribution in agricultural and grazing land soil of Europe". *Journal of Geochemical Exploration*, **V. 154**, 2015, Pages 81-93.

5. B. H. R. D. Castro, D.C. Barros, S.G.D. Veiga. "Baterias automotivas: panorama da indústria no Brasil, as novas tecnologias e como os veículos elétricos podem transformar o mercado global". *BNDES Setorial,* **V. 37***, 2013, Pages 443-496.

6. M. B. McBride. *Environmental Chemistry of Soils.* New York: Oxford University Press, 1994.

7. A. A. Jennings. "Analysis of worldwide Regulatory Guidance Values for less frequently regulated elemental surface soil contaminants". *Journal of Environmental Management*, **V. 128**, 2013, Pages 561-585.

8. M. A. P. Balderas, L. J. Cajuste, J. A. L. Fuente, A. A. Vázquez. "Suelos agrícolas contaminados por metales pesados provenientes de depósitos de vehículos de desecho". *Terra Latinoamericana,* **V.21 (4)**, Pages 449-459.

9. M. A. Hamzeh, A. Aftabi, M. Mirzaee. "Assessing geochemical influence of traffic and other vehicle related activities on heavy metal contamination in urban soils of Kerman city, using a GIS-based approach". *Environ Geochem Health*, **V.33**; 2011, Pages 577–594.

10. A. C. Martín, V. C. Rivero, M. T. L. Marín. "Contamination by heavy metals in soils in the neighbourhood of a scrapyard of discarded vehicles". *The Science of the Total Environment*, **V.212**, 1998, Pages 145-152.

11. M. A. Nwachukwu, H. Feng, J. Alinnor. *"*Assessment of heavy metal pollution in soil and their implications within and around mechanic villages*".* *Int. J. Environ. Sci. Tech*, **V.7 (2)**, 2010, Pages 347-358.

12. IBGE – Instituto Brasileiro de Geografia e Estatística, Diretoria de Pesquisas, Coordenação de População e Indicadores Sociais. "Estimativas da população residente com data de referência 1 de julho de 2014". *Diário Oficial da União*, 28/08/2014. Available at: http://www.ibge.gov.br/home/estatistica/populacao/estimativa2014/estimativa_tcu.shtm

13. O. A. Camargo, A. C. Moniz, J. A. Jorge, J. M. A. S. Valadares. *Métodos de Análise Química, Mineralógica e Física de Solos do Instituto Agronômico de Campinas*. Campinas: Instituto Agronômico, 1986, 94 p. (Boletim Técnico, 106).

14. AnalystSoft Inc., StatPlus:mac - statistical analysis program for Mac OS. Version v5. Available at: www.analystsoft.com/en/. 2015.

15. CETESB. "Decisão de Diretoria n° 195-2005-E, de 23 de novembro de 2005. Dispõe sobre a aprovação dos Valores Orientadores para Solos e Águas Subterrâneas no Estado de São Paulo - 2005, em substituição aos Valores Orientadores de 2001, e dá outras providências". *Diário Oficial do Estado [de] São Paulo, Poder Executivo, São Paulo, 3 dez. 2005*. Seção 1, **V. 115 (227)**, Pages 22- 23. Retificação no DOE, 13 dez. 2005, v.115 (233, Page 42. Available at www.cetesb.sp.gov.br.

16. B. J. Alloway. *Heavy metals in soils*. London: Blackie and Son, 1990.