J Radioanal Nucl Chem
DOI 10.1007/s10967-011-1260-2

Metals and semi-metals in street soils of São Paulo city, Brazil

Andreza P. Ribeiro · Ana Maria G. Figueiredo · Regina B. Ticianelli · Georges M. Nammoura-Neto · Natália C. Silva · Mauricio H. Kakazu · Guilherme Zahn

Received: 2 June 2011

Abstract São Paulo is the largest city in Brazil and South America with about 20 million inhabitants in the metropolitan area, more than nine million motor vehicles and intense industrial activity, which are responsible for increasing pollution in the region. Nevertheless, little is known concerning metal and semi-metal content in the soils of this metropolitan region. This type of information could be extremely useful as a fingerprint of environmental pollution. The present study determined the elements As, Ba, Co, Cr, Sb, and Zn concentrations in soils adjacent to avenues of highly dense traffic in São Paulo city to assess their levels and possible sources. The analytical technique employed was Instrumental neutron activation analysis. The results showed, except for Co, concentration levels higher than the reference values for soils of São Paulo, according to the Environmental Protection Agency of the State of São Paulo guidelines. When compared to similar studies in other cities around the world, São Paulo soils presented higher levels, probably due to its high density traffic and industrial activity. The concentrations obtained for As and Cr indicate anthropogenic origin. The high levels of the traffic-related elements Ba, Sb, and Zn in soils nearby high density traffic avenues indicate they may originate from vehicular exhausts.

Keywords Urban soil · Metals · São Paulo · Neutron activation analysis

A. P. Ribeiro · A. M. G. Figueiredo (✉) ·
R. B. Ticianelli · G. M. Nammoura-Neto ·
N. C. Silva · M. H. Kakazu · G. Zahn
Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP, Av. Prof. Lineu Prestes 2242, Cidade Universitária, São Paulo, SP 05508-000, Brazil
e-mail: anamaria@ipen.br

A. P. Ribeiro
Oceanografia Física, Química e Geológica, Instituto Oceanográfico, Universidade de São Paulo, Praça do Oceanográfico, 191, Cidade Universitária, São Paulo, SP 05508-120, Brazil

Introduction

Urban environment pollution is a key issue in almost every metropolitan area in the world; economical and populational growth, heavy traffic and industrial emissions lead to contamination of air, water and soil, with a negative impact on the health of the population [1]. Metals are often used as pollution tracers and, although they occur naturally in soils, their levels are generally higher in the urban environment due to anthropogenic activities. Vehicular emissions are derived of hydrocarbons (HC), nitrogen oxides (NOx) and carbon monoxide (CO) that are released into the environment. Moreover, the automobiles are also responsible for the release of particulate matter into the atmosphere which presents high concentrations of several metals (traffic-related elements, such as Ba, Cu, Pb, and Zn) derived of fuel oil and other vehicular system devices [2]. There has been an increasing interest in urban geochemistry of potentially toxic elements. Soils of urban areas gather materials of different compositions and origins. The manner in which these materials are like to interact with each other is poorly understood [3]. It has been recognized that, in urban areas, anthropogenic pressures often contribute to soil disturbance and to the enrichment of certain elements [4]. Studies of urban soils are available for a number of cities [1, 2, 4–16] and numerous studies have identified anthropogenic signatures, particularly for Pb, Cu, and Zn, associated with soil management and urban systems [17].

São Paulo, with about 20 million inhabitants distributed over 8000 km^2 in the metropolitan area, a huge industrial park and approximately, one vehicle for every two inhabitants, presents severe pollution problems. Recently, some studies have researched the concentration of metals in soils of public parks in São Paulo [18], but little is known concerning the soils that border the city's most important traffic corridors.

This study presents the results obtained for some potentially toxic elements (As, Ba, Co, Cr, Sb, and Zn) in soil samples collected along the most important traffic arteries of São Paulo city.

Experimental

Sampling

Urban soil sampling locations were carefully selected to represent a cross-section of high traffic density in São Paulo City (Fig. 1). The most important traffic arteries of São Paulo city were studied. Seven avenues with high density traffic altering between constant speed and stop-and-go traffic were selected. Two of the main arteries run along the two main rivers that cut across the city (Pinheiros and Tietê rivers) and are considered to be the most congested of South America, with about 4,00,000 vehicles/day. The Marginal Pinheiros Avenue is second in traffic in South America, with 3,00,000 vehicles/day [19]. The type of vehicles which circulate in these avenues is distributed as follows: 80% cars, 17% trucks and 3% buses. This translates into 20% commercial vehicles, which is most uncommon in other countries, where the commercial vehicle fleet usually accounts for about 5% of the circulating vehicles. These avenues can be characterized as high-constant speed traffic driving style, since there are no traffic lights, traffic circles or roundabouts. However, this fact does not prevent huge rush hour traffic jams or stop and go traffic. The other avenues in this study are among the biggest avenues in the city, and present high density traffic, with different traffic pattern and style.

The distance between the sampling points was from 3 to 5 km, providing 110 samples in 36 points all over the city's metropolitan region. Areas of 1 m^2, forming a rectangular grid, were sampled. The sampling took place from the grass strip 15 cm next to the asphalt up to 115 cm from the roadway. Composite samples were prepared, from three samples, collected at each point of the rectangle. The sampling depth was from 0 to 5 cm, since most of the metals are accumulated in the soil surface [5]. A polyethylene tube with 4 cm diameter was used to collect the samples, which were placed in air-tight polythene bags, labeled, and brought to the laboratory for analysis.

Soil properties

Soil samples from São Paulo avenues were neutral or sub-acid pH (pH between 6 and 7). The content of organic matter in the soil ranged from 4 to 6%. Only two samples (one point in the Marginal Pinheiros Avenue and one point

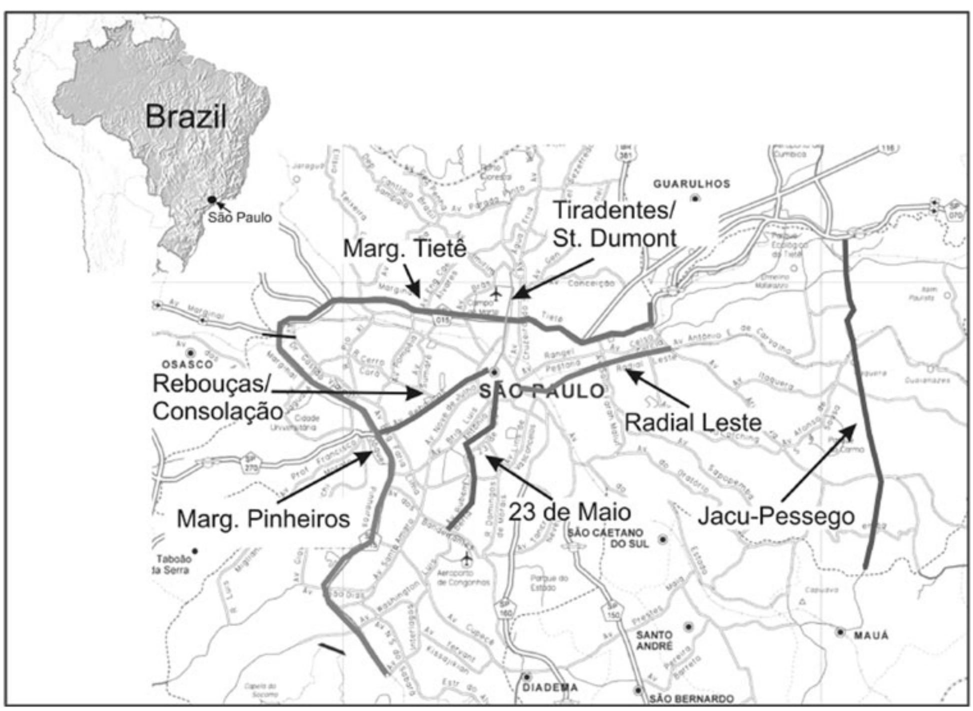

Fig. 1 Main high density traffic arteries in São Paulo City

Table 1 Results obtained for the reference material soil-7 (IAEA)

Element	Mean[a] ± SD	Recommended value	Relative error, %
As	13 ± 2	13.4	0.4
Ba	150 ± 8	159	5.7
Co	8.5 ± 0.3	8.9	5.0
Cr	65 ± 2	60	8.0
Sb	1.6 ± 0.2	1.7	4.0
Zn	106 ± 6	104	2.0

[a] $n = 6$

in Jacu Pêssego and Rebouças/Consolação Avenues) presented organic matter of about 2%. The content of clay-size particles ranged from 40 to 50%, characterizing loam sandy clay soils.

Analytical procedure

Once in the laboratory, samples were dried at 40 °C and sieved through plastic-only sieves into fractions lower than 2 mm—before and after sieving, the samples were homogenized, quartered and grinded in an agate mortar.

For the analysis process, approximately 100 mg of each sample was placed in a pre-cleaned inert plastic bag and weighted; samples were then placed inside an aluminum vessel, together with the standard reference materials soil 7 (IAEA), GS-N and BE-N (GIT-IWG), and irradiated for 8 h at a thermal neutron flux of 10^{12} n $cm^{-2}s^{-1}$ in the IEA-R1 nuclear reactor. The reference materials GS-N and BE-N were used as standards (literature values), in the comparative INAA method. The samples were then counted twice using an HPGe detector; the first counting series was performed after 7 days of the irradiation and the second one 15 days after irradiation; the counting times varied from 1 to 2 h, and gamma-ray spectra were analyzed using the VISPECT software in order to obtain the gamma peak areas. The quality of the determinations was assessed by the analysis of the certified reference materials soil-7 (IAEA). The results showed good accuracy (relative errors to certified values <5% for most of elements) and acceptable precision (relative standard deviations <15%) (Table 1).

Results and discussion

The results obtained for each of the sampling points are presented in Table 2, together with the Environmental Protection Agency of the State of São Paulo guiding values [20], as well as reference values [21]. As can be observed in Table 2, all elements, except Co, presented concentration values higher than the Quality Reference Values for São Paulo soils. For As and Ba, mean values are close to Intervention Value, considering the Environmental Protection Agency of São Paulo guidelines, but are below the Dutch intervention value, except in one point of the Marginal Tietê Avenue. Intervention values used by the Dutch government are based on a detailed study by the Dutch National Institute for Public Health and Environmental Protection concerning the human toxicological effects of soil contaminants [11]. For Cr and Zn, mean values are close to or below the Prevention Value, except for Zn in the Marginal Tietê Avenue. Zn concentration values higher than the intervention value of the Dutch soil guidelines were observed in some points of the Marginal Pinheiros and Marginal Tietê Avenues, reaching a concentration level of 1,669 mg kg^{-1}. It has been suggested that a common group of metallic elements accumulates in urban soils as a result of anthropogenic activities (i.e., Ba, Cd, Co, Cu, Mg, Pb, Sb, Ti, and Zn) [9]. Zn accumulation is due mainly to the wear and tear of certain automobile materials and parts during driving. Monaci et al. [22] emphasized that Ba and Zn are new tracers of vehicle emission, instead of Pb. Organometallic compounds containing barium and calcium have been used to reduce diesel smoke and 85–95% of the metal is emitted as particulates in the vehicle exhausts [18]. The presence of Cr may be associated to vehicular emissions and to industrial activities, and also as consequence of incineration of urban waste [23]. Antimony is used in many brake linings up to at least 5–7% by weight, as Sb_2S_3 [24], and several studies have shown that Sb concentrations are elevated close to major roads, both in soils and in air [25, 26].

The factorial analysis (FA) with extraction principal components for data sets (Table 3), applying the varimax-raw rotation normalized, corroborates these conclusions. Two principal components were considered, which accounted for about 76% of the total variance. The matrix of the components for data set indicated that Zn and Ba presented good correlation and were associated in the first component (F1), with a factor loading of ≥0.88, followed by Co, Sb, and Cr, with a factor loading ≥0.60. These results indicate that Ba and Zn are originated from vehicular exhausts. Since As was only included in F2 (factor loading 0.93), its origin may be due to other anthropogenic

Table 2 Concentration values compared to guiding values for São Paulo soil [20] and reference values [21] (mg kg^{-1})

Avenues		As	Ba	Co	Cr	Sb	Zn
23 de Maio	Mean	13.6	317	4.0	75.5	4.5	362
	Median	14.0	285	4.1	80.0	3.9	314
	Range	5.8–20.5	195–472	3.5–4.7	48–94	2.7–6.8	194–499
Consolação/Rebouças	Mean	15.9	252	3.5	72.2	2.9	215
	Median	16.3	271	3.2	67.3	2.8	217
	Range	11.6–20.3	105–375	2.5–4.9	51.6–98.0	1.0–4.8	58–396
Tiradentes/Santos Dumont	Mean	8.8	278	3.2	53.7	2.1	188
	Median	8.8	272	3.0	54.0	2.1	184
	Range	3.3–16.0	185–374	2.2–4.9	20.6–102	1.1–3.6	89–333
Marginal Tiete	Mean	15.0	407	6.1	85	2.4	447
	Median	14.4	355	5.9	79	2.3	364
	Range	1.9–57	180–713	3.3–13.3	25–185	0.79–4.2	76–1669
Marginal Pinheiros	Mean	10.5	459	7.0	87.9	2.8	467
	Median	9.0	443	6.4	88.0	2.7	315
	Range	3.3–21.3	352–619	5.3–12	68–107	1.6–4.3	275–925
Jacu Pêssego	Mean	16.2	311	4.1	68.8	1.9	189
	Median	16.8	312	3.9	81.0	1.9	172
	Range	4.1–29	127–549	3.2–6.1	34–92	1.1–2.6	81–320
Radial Leste	Mean	7.9	208	4.0	61	2.6	236
	Median	7.7	206	3.6	58	2.3	217
	Range	2.9–15	111–329	2.8–5.8	30–123	1.0–4.9	117–369
Quality reference value		3.5	75	13	40	0.5	60
Prevention value		15	150	25	75	2.0	300
Intervention value		35	300	35	150	5.0	450
Dutch soil guidelines							
Target value		29	200	20	100	3	140
Intervention value		55	625	240	380	15	720

Table 3 Factorial analysis with extraction principal components (varimax normalized)

Variable	Factor 1 (F1)	Factor 2 (F2)
As	−0.19	0.93
Ba	0.88	−0.26
Co	0.80	0.06
Cr	0.60	0.63
Sb	0.67	0.19
Zn	0.93	−0.01
Eigenvalue	3.11	5.86
% Total variance	1.45	24.17

sources. Anthropogenic sources of As include copper smelting, coal combustion, herbicide, pesticide and rodenticide use, as well as waste incineration, steel/glass production, and pressurized wood production [27]. According to the FA, the Cr sources are associated with the two factor loadings ($F1 = 0.60$; $F2 = 0.63$), which may indicate that Cr derives either from vehicle traffic or other anthropogenic activities.

In general, the highest concentrations were obtained in soils adjacent to the Marginal Pinheiros and Marginal Tietê Avenues (except for Sb). The Pinheiros and Tietê River sediment basins, where these avenues are located, present the most important air pollution problems in the city, since, depending on the season, there is reduced air circulation, with consequent low pollutant diffusion and dispersion [19]. In Fig. 2, the hierarchical dendrogram obtained by cluster analysis is shown. In it, two main groups can be identified. The first group is integrated by Marginal Pinheiros and Marginal Tietê Avenues, while the second can be divided in two sub-clusters: in the first the three downtown avenues are included; the second group includes the Jacu Pêssego and Tiradentes Avenues, further away from the downtown area and with stop and go traffic style. The Marginal Pinheiros and Marginal Tiete Avenues are high-constant speed traffic, with traffic jams during rush hour. The higher concentrations obtained in the Marginal Pinheiros and Marginal Tietê Avenues may be due to the driving style and to the enormous vehicle flux in these avenues. The results obtained in the soils near the

Fig. 2 Cluster analysis

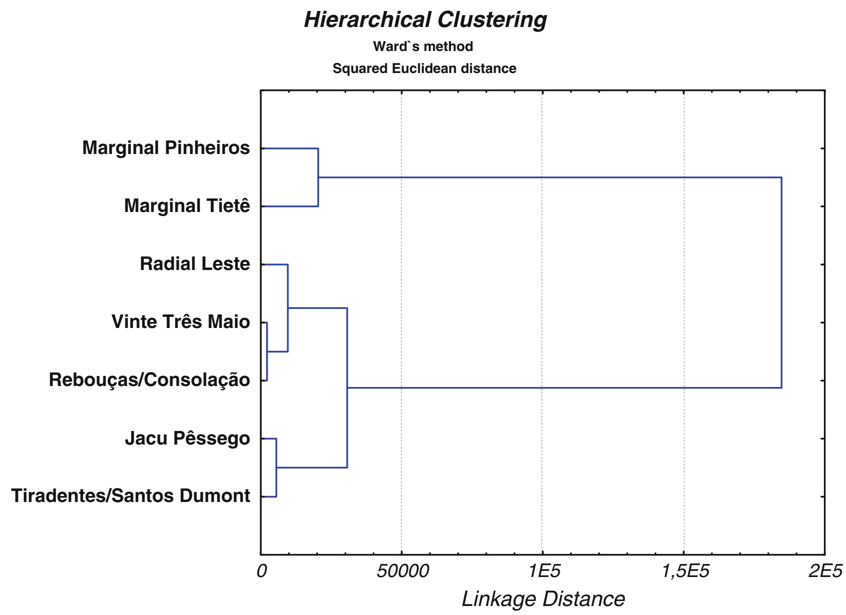

Table 4 Mean metal concentration in soils adjacent to main avenues of São Paulo city (mg kg^{-1}) and similar studies in other cities

	Ba	As	Co	Cr	Sb	Zn
São Paulo topsoils adjacent to avenues	319	12.5	4.5	72	2.7	300
São Paulo urban parks [18]	189	17		70	3.5	125
Other cities in the world						
Madrid [5]	369	–	6.42	74.7	–	210
Naples [1]	–	–	–	11		251
Palermo [6]	–	–	–	39	3.7	151
Mediterranean city, Spain [7]				19.18		21.57
Hong Kong [8]	–	–	3.55	17.8	–	103
Glasgow[a] [9]	–		–	37		179
Aveiro[a] [9]				9		37
Aberdeen, Scotland [10]	204		6.2	22.9		113.2
Oslo [11]	131	5.48	9.98	32.5		160
Berlin [12]		5.1		35		243
México[a] [13]				116		219

[a] Median

downtown avenues confirm previous studies in São Paulo, one employing biomonitors for atmospheric metal pollution [24], and another in urban park soils of the city [18], which have demonstrated that the concentrations of the traffic-related elements Pb, Zn, Cu, and Sb are higher in the central region of the city, where there is more intense traffic.

A comparison of the concentration levels obtained in this study with the concentrations obtained in São Paulo park soils and with similar studies in other cities is in Table 4.

Most studies on metals in urban soils are focused on Cr, Cu, Ni, Pb, and Zn, and there is little information on As, Ba, Co, and Sb concentrations. Table 2 shows that soils nearby São Paulo avenues have higher concentrations than most of the other cities reported. Zn and Cr values were similar to the concentration levels of Mexico City, which is also a very populous and polluted city. Higher values for Zn and Ba were observed when compared to São Paulo public parks soils. As mentioned before, these two elements are traffic derived. Thus, this may indicate that road traffic is a significant source of these contaminants to nearby soils. It should be remembered that soil pollution by heavy metals is generally concentrated in the first few meters to tens of meters on either side of the road pavement and then sharply decreases with distance from the road [14].

Some park soils of São Paulo, mainly in those located in the central region of the city, are also very affected by traffic activities, and present higher concentrations than the quality reference value for São Paulo soils.

Conclusions

The concentration levels of Ba, Sb, and Zn in São Paulo urban soils are high as a result of intense urban traffic along main traffic arteries. As and Cr also presented higher concentrations than reference values indicating anthropogenic sources. Cobalt concentration levels did not exceed target values.

When compared to similar studies in other cities around the world, São Paulo soils presented higher levels, probably due to its high density traffic and industrial activity. As expected, the Marginal Pinheiros and Marginal Tietê Avenues presented the highest concentrations as they are among the world's most dense traffic arteries.

The results obtained in this study are the first of its kind in São Paulo, and can contribute to an assessment of urban soil contamination in São Paulo city.

Acknowledgment The authors thank The Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for financial support.

References

1. Imperato M, Adamo P, Naimo D, Arienzo M, Stanzione D, Violante P (2003) Environ Pollut 124:247–256
2. Ljung K, Selinus O, Ottabong E (2006) Sci Total Environ 366:749–759
3. Bullok P, Gregory PJ (1991) Soils in the urban environment. British Society of Soil Science, Natural Conservancy Council, Oxford
4. Madrid L, Diaz-Barrientos E, Ruiz-Cortés E, Reinoso R, Biasoli M, Davidson CM, Duarte AC, Gremasn H, Hossack I, Hurthouse AS, Kralj T, Ljung K, Otabbong E, Rodrigues S, Urquhart GJ, Ajmone-Marsan FJ (2006) Environ Monitor 8:1158–1165
5. De Miguel E, De Grado MJ, Llamas JF, Martín-Dorado A, Mazadiego LF (1998) Sci Total Environ 215:113–122
6. Manta DS, Angelone M, Bellanca A, Neri R, Sprovieri M (2002) Sci Total Environ 300:229–243
7. Acosta JA, Faz A, Martinez–Martinez S (2010) Environ Monit Assess 169:519–530
8. Lee CS, Li X, Shi W, Cheung SC, Thornton L (2006) Sci Total Environ 356:45–61
9. Rodrigues S, Urquhart G, Hossack I, Pereira ME, Duarte AC, Davidson C, Hursthouse A, Tucker P, Roberston D (2009) Environ Chem Lett 7:141–148
10. Paterson E, Sanka M, Clark L (1996) Appl Geochem 11:129–131
11. Tijhuis L, Brattli B, Saether OM (2002) Environ Geochem Health 24:67–94
12. Birke M, Rauch U (2000) Environ Geochem Health 22:233–248
13. Morton-Bermea O, Hernandez E, Martinez-Pichardo E, Soler-Arechalde AM, Lozano Santa-Cruz R, Gonzalez-Hernandez G, Beramendi-Orosco L, Urrutia-Fucugauchi J (2009) Geoderma 151:121–125
14. Guney M, Onay TT, Copty NK (2010) Environ Monit Assess 164:101–110
15. Sialelli J, Davidson CM, Hursthouse AS, Ajmone-Marsan F (2011) Environ Chem Lett 9:197–202
16. Ajmone-Marsan F, Biasioli M (2010) Water Air Soil Pollut 213:121–143
17. Pouyat R, Yesilonis I, Russel-Anelli J, Neerchal N (2007) Soil chemical and physical properties that differentiate land-use and cover types. Soil Sci Soc Am 71:1010–1019
18. Figueiredo AMG, Enzweiler J, Camargo SP, Sígolo JB, Gumiero FC, Pavese AC, Milian FM (2009) J Radioanal Nucl Chem 280: 419–425
19. Braz JT, Vianna Jr EO (1996) Generalidades sobre a poluição na cidade de São Paulo e suas bacias de sedimentação. São Paulo: Companhia de Engenharia de Tráfego, Notas Técnicas, NT 196-A/96
20. CETESB (2005) Companhia de Tecnologia de Saneamento Ambiental. Qualidade do ar no Estado de São Paulo—Série Relatórios. http://www.cetesb.sp.gov.br/Ar/publicacoes.asp
21. Department of Soil Protection, Netherlands (1994). The Netherlands soil contamination guidelines, Netherlands intervention values for soil remediation 1994. Reference #DBO/07494013, Amsterdam
22. Monaci F, Moni F, Lanciotti E, Grechi D, Bargagli R (2000) Environ Pollut 107:321–327
23. Ng SL, Chan LS, Lam KC, Chan WK (2003) Environ Monitor Asses 89:221–232
24. Garg B, Cadle SH, Mulawa PA, Groblicki PJ, Laroo C, Parr GA (2000) Environ Sci Technol 21:4463–4469
25. Cal-Prieto MJ, Carlosena A, Andrade JM, Martinez ML, Muniategui S, Lopez-Mahia P, Prada D (2001) Water Air Soil Pollut 129:333–348
26. Sternbeck J, Sjodin A, Andréasson K (2002) Atmos Environ 36:4735–4744
27. Giacomino A, Malandrino M, Abollino O, Velayutham M, Chinnathangavel T, Mentasti E (2010) Environ Pollut 158:416–423