Trace metals and PAHs in topsoils of the University campus in the megacity of São Paulo, Brazil

CHRISTINE L.M. BOUROTTE[1], LUCY E. SUGAUARA[2], MARY R.R.
DE MARCHI[2] and CARLOS E. SOUTO-OLIVEIRA[1]

[1]Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080 São Paulo, SP, Brazil
[2]Grupo de Estudo em Saúde Ambiental e Contaminantes Orgânicos, Departamento de Química
Analítica, Instituto de Química, Universidade Estadual Paulista "Júlio de Mesquisa Filho"/UNESP,
Campus Araraquara, Rua Prof. Francisco Degni, 55, 14800-970 Araraquara, SP, Brazil

Abstract: The aim of this study is to discuss the concentration distribution, composition and possible sources of trace metals and 13 PAHs in topsoils of the University campus, in the city of São Paulo, the largest city of South America. Mineralogy and granulometry of topsoils (0-10 cm) samples, were determined and As, Ba, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, V, Zn, Hg, Pt, Pd and PAHs concentrations were quantified in the bulk fraction. The average clay content of soils was 221 ± 61.8 g kg^{-1} and total carbon was low (mean of 25 g kg^{-1}). Concentrations of metals were generally lower than the reference value established by the São Paulo State Environmental Agency and other studies in the São Paulo urban area, except for Cd, Ni, Pb, Cr and Zn. The mean concentration of the sum of 13 PAHs was 0.33 mg kg^{-1} and fluorene, indeno(1,2,3-cd) pyrene, anthracene, pyrene and benzo(ghi)perylene were the most abundant compounds. PAHs and trace metals variability were constrained in PMF analysis and showed an association with exhaust and non-exhaust vehicular emissions. The results also pointed out a spatial pattern in the campus area related to traffic conditions and intensity and terrain slope.

Key words: urban topsoils, trace metals, PAHs, PMF.

INTRODUCTION

The urban environment is a worldwide concern since the concentration distribution and the geochemistry of contaminants in urban environment (atmosphere, dust, soil, water and vegetation) need a better understanding (Wong et al. 2006). According to the United Nations (2014), more than half of the world's population is living in urban areas and is exposed to a complex mixture of pollutants. Soils in urban areas are submitted to intense anthropogenic activities related to civil construction, industrial activities and vehicular traffic that are responsible for their degradation and chemical contamination by direct disposal of contaminant to the soils. Dry and wet atmospheric deposition is also an important source for contaminants in urban soils and street dust (Tanner et al. 2008). Soil pollution by metals and other compounds such as Polycyclic Aromatic

Correspondence to: Christine Laure Marie Bourotte
E-mail: chrisbourotte@usp.br
ORCid: https://orcid.org/0000-0002-2821-1059

Hydrocarbons (PAHs) has been described in several studies and different urban contexts principally performed in northern hemisphere (Werkenthin et al. 2014, Orecchio 2010, Nadal et al. 2004, Jensen et al. 2007, Haugland et al. 2008, Mielke et al. 2004, Manta et al. 2002, Madrid et al. 2002, Charlesworth et al. 2011, Alekseenko and Alekseenko 2014) and Asia (Zhang et al. 2006, Zuo et al. 2007, Chung et al. 2007, Ray et al. 2008, Agarwal 2009, Jiang et al. 2009, Liu et al. 2010). In South America, fewer studies have been published in urban areas (Morton et al. 2001, Morcelli et al. 2005, Ribeiro et al. 2012, Figueiredo et al. 2011, Fujiwara et al. 2011, Bourotte et al. 2009, Netto et al. 2006).

Toxic substances such as trace metals or persistent organic pollutants like PAHs in the soil-atmosphere interface are of concern since they accumulate in topsoil horizons and may be re-suspended and inhaled causing risk for human health and ecosystems. Wilcke (2007) also pointed out that PAHs as a complex mixture in topsoils are originated from two main sources: the background condition with a biological component and anthropogenic processes through atmospheric deposition. Since little information exists on the occurrence and distribution of metals and PAHs in Brazilian soils in urban areas, the aim of this study is to discuss the distribution of trace metals and PAHs concentration and their possible sources of topsoils in the campus of the University, a green area of the São Paulo city. To this end descriptive statistics and Positive Matrix Factorization (PMF) analysis, a statistical approach to identify contaminant sources, were performed using spatial variability of PAHs and trace metals concentrations.

MATERIALS AND METHODS

STUDY AREA AND SAMPLING SITES

The metropolitan region of São Paulo is the world's fourth largest city and the biggest metropolis in South America. This agglomeration of 21 million inhabitants is in an area of 8,051 km^2 of which 18.7% are in the municipality of São Paulo (23º32'51"S, 46º38'10"W). The greater portion (66%) of the municipality of São Paulo is an urban area and accounts with a population of 11 million of inhabitants and a fleet of 8.5 million of vehicles, composed of 70.5% of cars, 13% of light trucks, 3% of trucks and buses and 13.5% of motorcycles (DETRAN 2017). The climate is humid subtropical, with a dry season during winter (June-August) and a wet season during summer (December-February), an annual temperature average of 18.7ºC and an annual average precipitation of 1410 mm (IAG-USP 2016).

The sampling site is located in the western region of São Paulo city, on the *campus* of the University of São Paulo, at the left bank of the Pinheiros river (Figure 1). The campus area can be divided into two main topographic zones: a flat one in the north, corresponding to the flood plain of the Pinheiros river, now channeled, and a steepest one at the south with dense vegetal cover. Sedimentary formations occur in a great area of the campus: the São Paulo Formation and the Itaquaquecetuba Formation. The first one outcrops at the "prefeitura" and the Chemical Institute area. The second one occurs in the north part of the campus and close to the Olympic streak. These formations are related to fluvial deposits (meandering river and braided fluvial system deposits) and are constituted by conglomerates, sandstones and claystones. Quaternary alluvial deposits occur in the Olympic streak area. The bedrock is mainly constituted of granitic rocks, gneisses and migmatites and outcrops in the south and southeast areas of the campus where the topography is steeper (790 m) and locally in the northwest area of the campus (Av. Prof. Lineu Prestes, close to IPEN and the universitary Hospital). A more detailed description of the geological aspects of the São Paulo sedimentary basin and campus area can be found in Riccomini and Coimbra (1992), Iritani
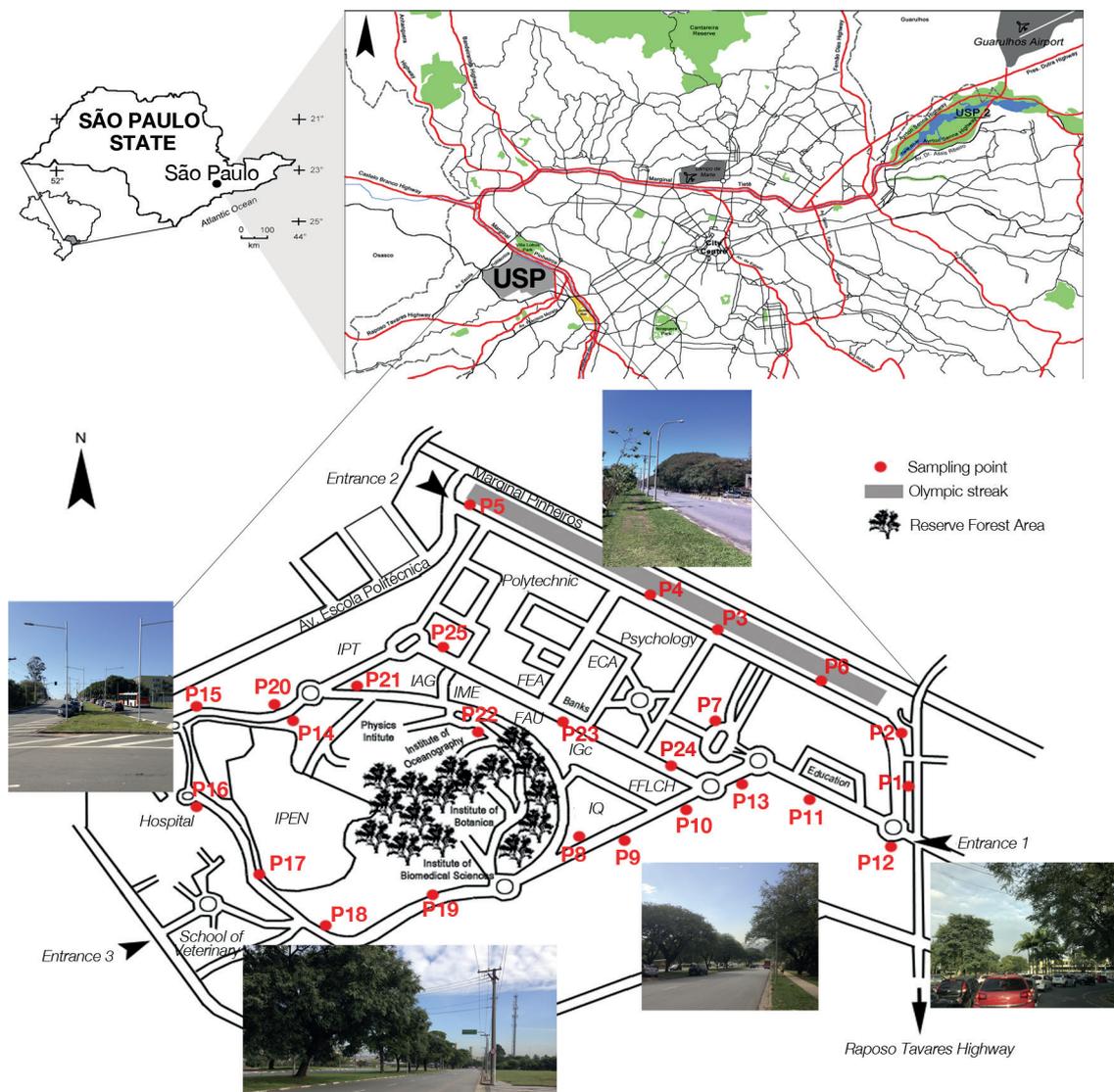
Figure 1 - Topsoil sampling sites located at the *campus* (green area) of the University of São Paulo, in the west zone of the São Paulo city.

(1993) and Porsani et al. (2004). Natural soils originate from this lithology but have been affected by anthropogenic activities related to building and pavement construction. The campus is also a green area (4.3 km^2) used as a park for practice and sporting events during weekends or holidays. Green areas and gardens cover about 25% of the campus area and native vegetation is preserved in a reserve forest area of 10ha. Important avenues with intense traffic of light- and heavy-duty vehicles surround the campus. The area is also inside a commercial and residential zone of the city and some small manufacturing activities (metallurgy, cement and food manufacturing). Surrounding the campus, arterial streets (speed limit of 50 km/h) and "marginal Pinheiros" (a peripheral road with a higher speed limit of 90 km/h) with circulation of all vehicles types (cars, trucks, buses, motorcycles). On the campus, cars and buses flow all day. During rush hours, heavy circulation and stop and go-traffic increase at the three main entrances of the campus.

SAMPLING METHODS AND PREPARATION

Topsoils (0-10 cm) were sampled in a 5 m² area where 6 subsamples were mixed to obtain a bulk sample at each sampling point. The characteristics of each area such as proximity of parking areas, main streets, bus stops and green areas conditioned the sampling point locations (Figure 1). The distance between the sampling point and the road varied from 1 to 5 m and 80% of sampling points were close to a bus stop. In each sampling point, a total of 1 kg of sample was collected and stored in plastic bags until preparation and analysis. Sampling was performed from July to August 2012 (winter dry season) totalizing 25 samples.

Samples were air-dried at room temperature and sieved through a 2 mm mesh nylon sieve to remove stones, roots, leaves or any other greater materials. All samples were homogenized and divided by a successive quartering method to provide a representative sample. This fraction (<2 mm) was divided into several aliquots for laboratory analyses. Samples were grinded to fine powder in an agate mortar for acid digestion and X-Ray Diffraction analyses. Element concentrations in the digest extracts were quantified by ICP-MS.

ANALYTICAL METHODS

Size fraction analyses consisted to the separation of sedimentology classes into 0.5ϕ intervals between 2.00 and 0.0062 mm and into intervals of 1ϕ for silt and clay classes.

Topsoil mineralogy was determined by X-Ray powder Diffraction analysis (XRD). Diffraction patterns were obtained using a Bruker D8 diffractometer coupled with a LYNXEYE detector operated at 40kV, current of 40mA, a Cu source (Kα radiation), with a step mode of 0.02° (2θ) ranging from 2° to 65° and counting time of 0.5s per step.

Total Carbon was also quantified in soil samples (LECO, CHN 1000 model) according to the methodology established by Andrade et al. (2009).

Analyses of total elemental composition were carried out after hot acid digestion (Aqua Regia) of 0.5g of samples and quantified by ICP-MS at ACME Analytical Laboratories, accredited by ISO/IEC 17025. The Aqua Regia digestion provides partial results for most elements since it not attacks silicate minerals and it is generally used to estimate the mobility, behavior and element availability to plants. Major elements (as oxide forms) and 53 trace elements were quantified in soil samples but, for trace metals, arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), vanadium (V), zinc (Zn), mercury (Hg), platinum (Pt) and palladium (Pd) will be discussed. The accuracy and precision of analyses were determined by using duplicate samples, blank samples and standard reference materials. The relative percent difference varied from 7% to 17% and standard recoveries ranged between 97% and 108%.

Polycyclic Aromatic Hydrocarbons (PAHs) were extracted by an Accelerated Solvent Extraction System (ASE350, DIONEX Corporation) according to the following procedure: 2 static cycles of 10 min each using dichloromethane at a temperature of 100ºC and a pressure of 100 bars. Each cell was filled with 4g of soil mixed with diatomaceous earth that promotes a better homogenization of the sample, humidity retention, and interaction with solvent. After clean up through solid phase extraction cartridge (Bakerbond SPE silica gel) and elution with cyclohexane and cyclohexane-dichloromethane (4:1) mixture, the extracts were concentrated in a gentle N_2 (analytical grade) flux and solvent changed with 1 mL of acetonitrile (HPLC grade) for quantification by High Performance Liquid Chromatography with Fluorescence detection (HPLC-FLU) (Fujita 2009). Thirteen PAHs (Acenaphthene-ACE, Fluorene-FLU, Phenanthrene-PHE, Anthracene-ANT, Fluoranthene-FLT, Pyrene-PYR, Benzo(a)

anthracene-BaA, Chrysene-CRY, Benzo(b)fluoranthene-BbF, Benzo(k)fluoranthene-BkF, Benzo(a)pyrene-BaP, Dibenzo(a,h)anthracene-DahA, Benzo(ghi)perylene-BghiP, Indeno(1,2,3-cd)pyrene-IND) were quantified by HPLC-FLU (Varian 920LC model) with a 250 mm x 4.6 mm x 5 mm column (Supelcosil LC PAH), in the GRESCO Laboratory (Institute of Chemistry-UNESP). The accuracy and precision of analyses were determined by using blank samples and standard reference materials (NIST SRM1649a Urban dust). Recoveries ranged between 70% and 107%. Compounds with lower recoveries have not been considered.

DATA ANALYSIS

For PAHs, potential carcinogenic risk exposure for adult and children were calculated considering the toxic and mutagenic equivalent factors (BaP_{TEF} and BaP_{MEF}, respectively), that is the toxicity of PAHs relative to BaP. Exposition through inhalation, ingestion and dermal contact routes was also evaluated through the Incremental Lifetime Cancer Risk model (ILCR). Calculation details were obtained from the studies of Ha et al. (2016) and Peng et al. (2011). For BaP_{TEF} and BaP_{MEF} calculation, we considered PAHs with higher molecular weight *i.e.* BaA, CHRY, BbF, BkF, BaP, IND, DahA and BghiP, according to Jung et al. (2010).

Multivariate data analysis was performed using the Positive Matrix Factorization (PMF) model (version 5.0), an operational system from the United States Environmental Protection Agency (US-EPA). This model was developed to source apportionment analysis in environmental studies, which consider the error of instrumental measurements. It is a multivariate analysis technique used in the evaluation and modeling environmental data set such as in lake and river sediments (Bzdusek et al. 2006, Comero et al. 2014, Yu et al. 2015), soils (Vaccaro et al. 2007, Syed et al. 2017, Guan et al. 2018). The analysis was performed for elemental and PAHs concentrations. The number of factors was adjusted to obtain the best $Q_{theory} \approx Q_{robust}$ and physical validity of the model. Estimation of the goodness of the model fit was achieved by minimal values of Q and a scaled residual between −2 and +2, following the recommendations of Reff et al. (2007).

The spatial distribution study of metals and PAHs was performed by ArcGIS 10 mapping software.

RESULTS AND DISCUSSION

SOIL CHARACTERISTICS

Soil texture was predominantly medium to fine with a great variation of sand, silt and clay content and showing sandy loam, sandy clay loam and loam textures. The results of particle size analysis showed that average clay content was 221±61.8 g kg^{-1}, average silt and sand contents were 267±61.9 g kg^{-1} and 511±95.5 g kg^{-1}, respectively. P22 showed the lowest silt (95.7 g kg^{-1}) and clay (81.8 g kg^{-1}) and highest sand (823 g kg^{-1}) content values whereas P23 showed the highest silt (374 g kg^{-1}) and clay (328 g kg^{-1}) and lowest sand (298 g kg^{-1}) content. Quartz pebbles were found in topsoils at P3, P4 and P5 sites, which are close to the Olympic streak and may characterize a layer related to the landfilling of old sand pits. We also found gravel mixed to topsoil at P18 site, and plastic fragments mixed to concrete construction fragments at P22 site.

X-Ray Diffraction results showed that primary minerals such as quartz, mica and feldspars constituted topsoil mineralogy associated with kaolinite and gibbsite. In some samples, iron oxides (hematite/goethite), other clay minerals, amphibole and rutile were also identified.

MAJOR AND TRACE ELEMENTS, TOTAL CARBON

Descriptive statistics of major elements, trace elements and soil Total carbon (C) concentrations are presented in Table I. As expected for tropical

TABLE I
Major and trace elements and C$_{tot}$ content in topsoils (min. - minimum; max.- maximum; std. - standard deviation).

MAJOR ELEMENTS					TRACE ELEMENTS				
	mean	std.	min.	max.		mean	std.	min.	max.
	(g kg^{-1})					(mg kg^{-1})			
Al	80.5	12.8	43.2	103	**As**	5.14	1.64	2.10	8.70
Si	305	21.0	274	368	**Ba**	48.5	14.7	30.8	75.5
Fe	33.1	6.54	18.0	49.4	**Cd**	0.59	0.60	0.18	2.96
K	6.95	2.30	2.91	11.4	**Co**	3.73	2.63	1.60	14.6
Ca	2.42	0.97	1.14	4.93	**Cr**	42.1	23.8	24.6	153
Mg	1.27	0.63	0.66	3.79	**Cu**	19.5	5.48	11.8	31.3
Na	1.36	0.64	0.67	3.19	**Mo**	0.91	0.26	0.45	1.59
P	0.45	0.09	0.26	0.61	**Ni**	11.2	15.3	4.50	66.6
Mn	0.25	0.09	0.16	0.54	**Pb**	40.8	14.1	17.4	75.9
Ti	5.09	0.86	3.26	6.83	**Sb**	0.32	0.11	0.13	0.56
					V	63.4	15.7	26.0	91.0
C$_{tot}$	25.1	6.30	15.3	39.8	**Zn**	94.6	50.8	38.5	275
						(µg kg^{-1})			
					Hg	79.0	40.0	22.0	197
					Pt	2.80	1.87	1.00*	7.00
					Pd	8.04	7.55	5.00*	40.0

*value is corresponding to half the limit detection value (2.00 and 10.0 µg.kg^{-1} for Pt and Pd, respectively).

soils, Si, Al and Fe predominated in topsoil composition. Si varied between 273.8 g kg^{-1} and 367.9 g kg^{-1}, Soil total carbon content was low (<25 g kg^{-1} on average).

The order of trace metal concentration measured in topsoils was: Zn>V>Ba>Cr>Pb>Cu>Ni>As>Co>Mo>Cd>Sb. Trace metal concentrations showed a great variation between sampling point for most of the metals (Figure 2). However, these concentrations did not exceed the quality reference values established by the São Paulo State Environmental Agency (CETESB 2014), except for As, Pb, Zn, Cr and Hg in most sampling points and for Co, Cd, Ni, Sb only in few points. Some metal concentrations (Cd and Ni) exceed the Prevention Values established by CETESB.

Trace metal concentrations measured in this study were lower than trace metal concentrations in natural and urban Brazilian and World soils (Table II), except for Cu, Pb, Zn, As and V. Also, Zn concentrations in this study were higher than those reported to urban green parks topsoils from São Paulo city. Comparing topsoil trace metal concentrations at the campus with those obtained from urban forest soils in the São Paulo city (PEFI) and in natural soils of the Serra do Mar State Park (Cunha) (Bourotte 2009), Cu, Ni, Zn and Pb showed higher concentrations. For reference values of Cd, Co, Cr, Cu, Ni, Pb and Zn concentration in background soils from the São Paulo State, we chose data from Fadigas et al. (2006), who compiled trace elements concentrations in several typical soils of the São Paulo State. Average concentrations for Zn and Pb in our study soils are 3.2 and 2 times higher, respectively, than these background values. The concentrations in our study soils were similar for Cr and lower for Ni, Co and Cd. Results also
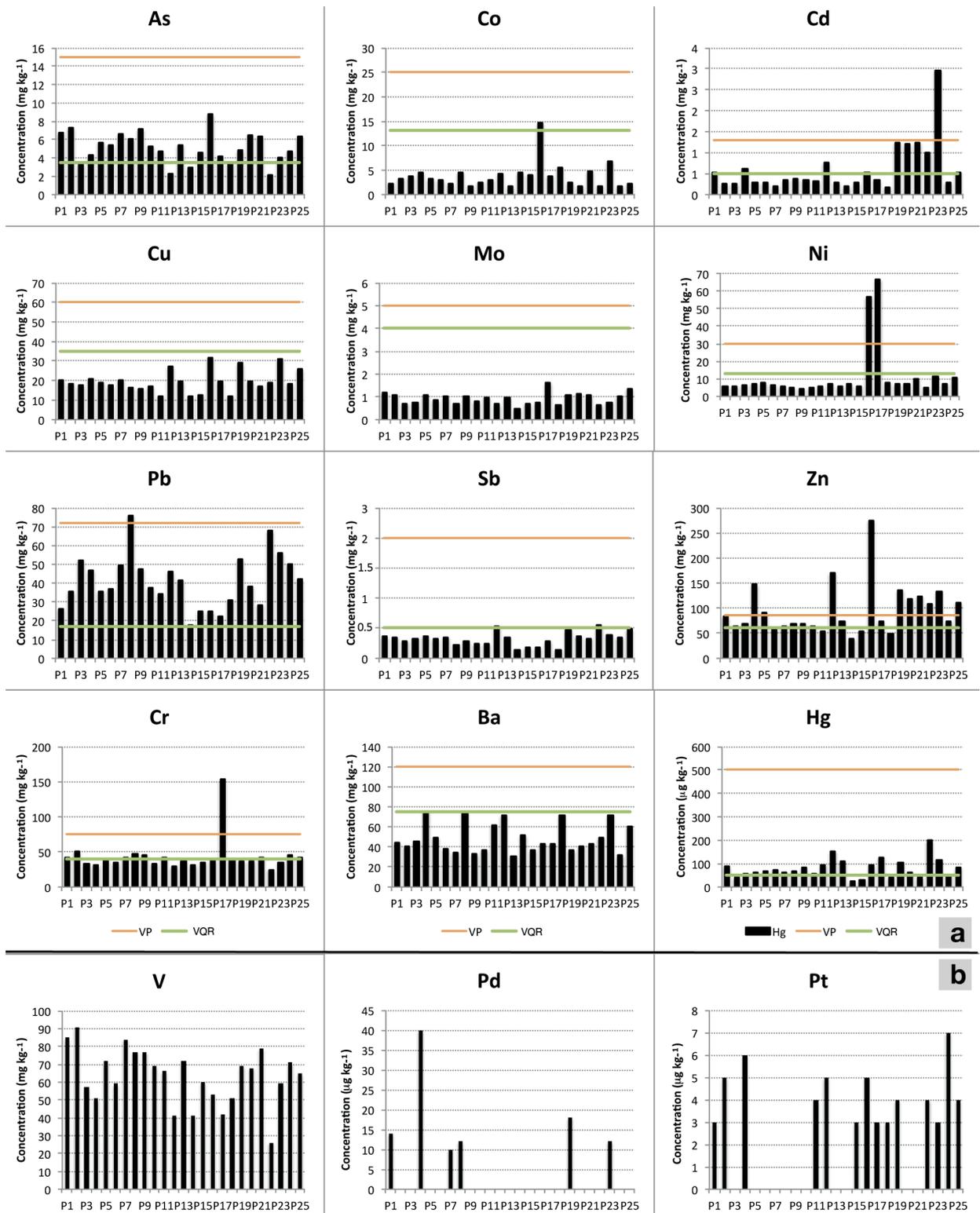
Figure 2 - a) Variation of trace metals concentration (mg kg^{-1}) in superficial soils and comparison with the Quality Reference (VQR) and Prevention values (VP) established by CETESB (2014). **b)** Variation of vanadium concentration (mg kg^{-1}), platinum and palladium concentration (µg kg^{-1}) in topsoils (No Quality Reference Values or Prevention Values have been established by CETESB for these trace metals).

showed an enrichment of Cu and Zn in topsoils with respect to rock basement (Table II).

In urban areas, soils generally exhibit trace metal content higher than background levels (Wong and Thornton 2006, Manta et al. 2002, Luo et al. 2012, Werkentin et al. 2014, Alekseenko and Alekseenko 2014). Thus, in order to better identify possible metal correlations and sources associated, a statistical analysis has been performed. Spearman correlation was chosen to account for the non-parametric data distributions. The results showed a strong association (>0.5 and significant at $p < 0.050$) between As, Mo, V and Cr; Co, Ni and Ba; Cd, Cu, Sb, Zn, and Hg; Cu, Ni, Sb, Hg, Pt, Pd and Zn; Pb, Sb and Pt.

Automobile catalyzers are the main source of Pd and Pt in roadside soils (Whiteley and Murray 2003, Wiseman and Zereini 2009, Reith et al. 2014). Pt and Pd concentrations ranged between 1.00 to 7.00 µg.kg^{-1} and 5.00 to 40.00 µg.kg^{-1}, respectively. As pointed out by Morcelli et al. (2005) who studied these elements in some road-soils of the São Paulo city, traffic conditions and distance from the road influenced their concentrations in topsoils. In Brazil, automobile catalyzers are in use since 1996 and Morcelli et al. (2005) also pointed out that they contain lower Pt concentrations than European catalytic converters. The strong correlation between Pt and Pd indicated this common vehicle source. Average Pt/Pd ratios obtained in this study were 0.46 that is similar to ratios obtained in other studies (Morcelli et al. 2005, Ribeiro et al. 2012).

Other metals may also be associated with vehicular sources since Cu, Zn and Pb are common constituents of vehicle components. Tire wears, break pads, lubricant oils are also considered as contributors in urban pollution (Davis et al. 2001, McKenzie et al. 2009, Mielke et al. 2001, Thorpe and Harrison 2008, Wiseman and Zereini 2009, Adachi and Tainosho 2004). Element ratios may indicate the contribution of brake dusts and tire wear dusts (McKenzie et al. 2009). In brakes, Cu is enriched

over Zn and Cu/Zn ratio is >1 but Pb, Cd, Cr, Ni/Zn <1. In this study, mean values for Pb/Zn and Cu/Zn were 0.50 and 0.23 respectively. For tire wears, Zn is a tracer (Thorpe and Harrison 2008) and Zn/Cu >1. In this study, the mean value for this ratio was 2.18 and 4.68 for Zn/Cu, which may indicate automobile contribution as a source for these metals. Antimony was also statistically associated with these metals. Varrica et al. (2013) showed that antimony might also be significantly released in urban environment through brake abrasion processes since stibinite (Sb_2S_3) is used in brake linings. Adachi and Tainosho (2004) and Quiroz et al. (2013) also associated this element with brake dusts. Pb is generally attributed to vehicular emissions but since 1989, lead has been banned from gasoline in Brazil and totally eliminated since 1992. The addition of ethanol to gasoline substituted Pb for its anti-knock property. However, although lead concentrations decreased in the urban atmosphere, lead contamination remain as a problem in the urban environment, mostly due to other sources and its accumulation in surface soils and slow release to environment. In São Paulo city, according to Gioia et al. (2010) the isotopic signature of lead showed that 71.6% of Pb is derived from gasoline, even though vehicular emissions have low Pb concentrations. Although Pb, Cu and Zn are usually associated with automobile sources (Zn-tire wears, Cu-brake and vehicle components), other trace metals such as Ni, As, Cd and Cr also accumulated in urban soils. These metals are associated to vehicular emissions, industrial sources and other sources as wood preservatives and pesticides for As. Sternbeck et al. (2002) also associated Cu, Zn, Sb, Ba and Pb to vehicle-derived metals and not to combustion processes.

PAHs

The sum of 13 PAHs in topsoil samples had an average of 0.33 mg kg^{-1} [0.07-1.38 mg kg^{-1}] (Table III) and fluorene, indeno(1,2,3-cd)pyrene, anthracene,

TABLE II

Trace metals concentration values in natural and urban Brazilian and world soils. Concentrations are expressed in mg kg^{-1} except for Pt and Pd whose values are expressed in μg kg^{-1}.

	Cd	Cu	Ni	Pb	Zn	Co	Cr	Sb	As	Ba	Mo	V	Pt	Pd
					(mg kg^{-1})									
[1] World surface soils	1.1	14	18	25	62	6.9	42	0.62	4.7	362	1.8	60	3	2
[2] Brazilian Ferralsols	0.66 ±0.19	65±7.4	18±12	22±9	39±24									
[3] Quality Reference Value (CETESB)	0.50	35.0	13.0	17.0	60.0	13.0	40.0	0.50	3.5	75.0	4.0			
[4] Serra do Mar natural soils (Cunha)		14.0		9.00		2.00	78.0			170.5		137.5		
[5] São Paulo urban forest soils (PEFI)		16.5		10.5	26.0	3.00	65.0		11.5	115.3		148.3		
[6] São Paulo urban soils (12 parks)*					81.5		49		9.63	683.3				
[6] Marginal Pinheiros soils, São Paulo*					467	7.03	87.1	2.76	10.5	459			11.4	58.6
[7] Roadsoils, São Paulo													0.3-17.0	1.1-58.0
[8] Basement rocks at study site		13.0			83.0	15.0	75.0			1590		72.0		
[9] Urban soils, China	0.394	38.2	29.2	45.3	112		76	1.72	11.4					
[10] Urban soils, Mexico													3.1-332.7	2.5-101
[11] Urban park soils, Hong Kong	0.36±0.16	16.2±22.6	4.08±2.51	88.1±62.0	103±91.3	3.55±1.6	17.8±5.92							
[12] Roadside soils, Perth (Australia)													31-153	14-109

TABLE II (continuation)

	Cd	Cu	Ni	Pb	Zn	Co	Cr	Sb	As	Ba	Mo	V	Pt	Pd
					(mg kg⁻¹)									
(13) Roadside soils, Melbourne (Australia)	0.06-0.59	4-12	7-20	16-144	10.4-88.8		18-29							
(14) Urban soils, Xuzhou (China)			34±3.4	37±19.4	169±106		73±8.4							
(15) Urban soils, New Orleans (USA)	2.1	17.6	9.1	174	147		1.9					4.8		
(16) Urban soils, Hungria	0.55 ±0.36	59±78.8	22.6±4.7	15.7 ±8.23	80.2 ±30.9	6.09±2.1	31.3±7.2		7.19 ±2.3					
(17) Urban soils, Palermo (Italy)		63**		202**	138**							58		
(18) Urban soils, Prague	0.26 ±0.04	19.7 ±1.53	11.1 ±1.29	126±8.80	54.8±7.30	2.36±0.6	33±0.62							
(19) Urban soils, Seville (Spain)	1.39±0.16	121±74	27.6±6.0	397±325			121±74							
(20) Urban soils, Chicago (USA)		59.0**	31.0**	198**	235**						5.0**	82.0**		
(21) Urban soils, Toronto (Canada)													8.7	63
(22) Urban soils, Napoli (Italy)													<2-52	<10- 110
This study	**0.59 ±0.6**	**19.5 ±5.48**	**11.2 ±15.3**	**40.8 ±14.1**	**94.6 ±50.8**	**3.73 ±2.6**	**42.2 ±23.8**	**0.32 ±0.1**	**5.14 ±1.6**	**48.5 ±14.7**	**0.91 ±0.3**	**63.4 ±15.7**	**2.80 ±1.87**	**8.04 ±7.55**

* mean value   ** median value.

[1] Kabata-Pendias and Mukherjee 2007; [2] Campos et al. 2003; [3] CETESB 2014; [4] Bourotte 2009, Licht 2005; [5] Figueiredo et al. 2011; [6] Ribeiro et al. 2012, Nammoura et al. 2009; [7] Morcelli et al. 2005; [8] V.A. Janasi (personal communication); [9] Cheng et al. 2014; [10] Morton et al. 2001; [11] Lee et al. 2006; [12] Whiteley and Murray 2003; [13] De Silva et al. 2016; [14] Wang 2013; [15] Mielke et al. 2001; [16] Szolnoki et al. 2013; [17] Manta et al. 2002; [18] Boruvka et al. 2005; [19] Madrid et al. 2008; [20] Cannon and Horton 2009; [21] Wiseman et al. 2016; [22] Cicchella et al. 2003.

TABLE III
Statistics for PAHs concentration in topsoil samples from USP campus in the São Paulo city (min. - minimum; max.-maximum; std. - standard deviation).

				PAHs		
	n	*mean*	*std.*	*min.*	*max.*	*Prevention Value**
			(mg kg^{-1})			(mg kg^{-1})
Acenaphthene (ACE)	6	0.017	0.015	0.003	0.041	-
Fluorene (FLU)	10	0.102	0.076	0.008	0.208	-
Phenanthrene (PHE)	14	0.001	0.001	0.000	0.003	3.6
Anthracene (ANT)	15	0.060	0.058	0.001	0.164	0.3
Fluoranthene (FLT)	8	0.008	0.005	0.002	0.015	-
Pyrene (PYR)	11	0.043	0.063	0.004	0.220	-
Benzo(a)anthracene (BaA)	15	0.020	0.016	0.004	0.046	0.2
Chrysene (CHRY)	14	0.038	0.020	0.003	0.068	1.6
Benzo(b)fluoranthene (BbF)	15	0.008	0.006	0.001	0.023	0.7
Benzo(k)fluoranthene (BkF)	12	0.036	0.063	0.007	0.234	0.8
Benzo(a)pyrene (BaP)	1	0.275	-	0.000	0.275	0.1
Dibenz(a,h)anthracene (DBahA)	8	0.038	0.027	0.012	0.083	0.2
Benzo(ghi)perylene (BghiP)	11	0.041	0.033	0.004	0.109	0.5
Indeno(1,2,3-cd)pyrene (IND)	9	0.067	0.044	0.013	0.160	0.4
∑PAHs	17	0.329	0.325	0.072	1.379	
∑Low Molecular Weight PAHs	17	0.120	0.096	0.001	0.322	
∑High Molecular Weight PAHs	17	0.209	0.259	0.0000	1.1183	
∑Carcinogenic	17	0.157	0.181	0.0000	0.7767	
∑2-3 rings	17	1.120	0.096	0.001	0.322	
∑4 rings	17	0.080	0.071	0.000	0.318	
∑5 rings	17	0.067	0.139	0.000	0.595	
∑6 rings	17	0.062	0.072	0.000	0.241	

* São Paulo State Environmental Agency - CETESB 2014.

pyrene and benzo(ghi)perylene were the most abundant compounds, accounting for 31%, 20.2%, 18.2%, 12.9%, 12.5% of total PAHs, respectively (Figure 3a). On average, low molecular weight PAHs account for 40% and high molecular weight PAHs for 60% of total PAHs, indicating that high temperature combustion processes are the dominant sources of PAHs (Figure 3b). Benzo(a)pyrene, the most carcinogenic PAHs, has been detected only in one sampling site, exceeding the prevention value recommended by CETESB (2014). The frequency of individual PAHs have shown that anthracene,

benzo(a)anthracene and benzo(b)fluoranthene are the dominant compounds in almost all samples. The sum of carcinogenic PAHs (BaA, CHRY, BbF, BkF, BaP, DBahA, IND) accounted for 44.0±15.5% of the total PAHs, on average (Figure 3c). Higher proportions of 2-3 rings PAHs contributed to the total PAHs (39.8±24.1%) followed by 4-rings PAHs (27.1±13.8%), 5-rings PAHs (17.1±17.7%) and 6-rings PAHs (16.0±12.8%) as shown in Figure 3d.

The comparison of PAHs concentrations in urban topsoils worldwide (Table IV), has shown that values found in this study are lower than in
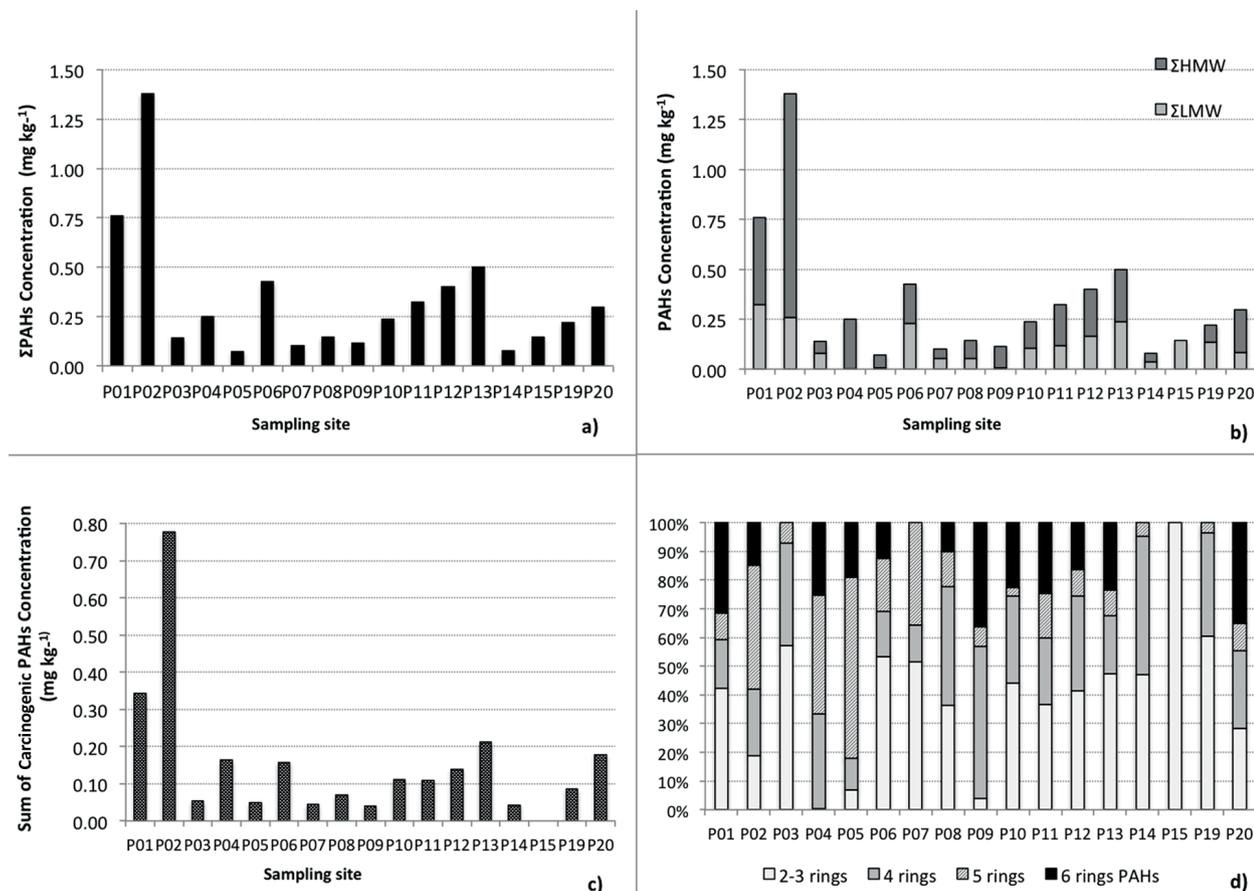
Figure 3 - Variation of **(a)** ∑PAHs concentrations (mg kg^{-1}), **(b)** sum of low (LMW) and heavy molecular weight (HMW) PAHs concentrations (mg kg^{-1}), **(c)** ∑carcinogenic PAHs (BaA, CHRY, BbF, BkF, BaP, DBahA, IND) concentrations (mg kg^{-1}), and **(d)** aromatic ring numbers percentage distribution between sampling sites.

Chinese cities (Beijing - 11.7 millions inhabitants, Dalian - 3.6 millions inhabitants, Shangai - 23 millions inhabitants, Nanjing - 3.6 millions inhabitants, Hong Kong - 7.2 millions inhabitants), Bangkok (5 millions inhabitants) and Dehli (11 millions inhabitants). Concentrations are also lower than cities of the North Hemisphere (Europe and United States). Some authors (Wilcke 2000,Wilcke et al. 1999, 2007, Zhang et al. 2006) have already pointed out this difference between temperate and tropical soils and it is generally attributed to microbial degradation, photo-oxidation and higher volatilization of compounds in tropical climate, which shorten their accumulation time. In addition, emission history in South Hemisphere is shorter and biomass burning and natural background from

biological sources have also been pointed out to explain this difference. Total PAHs concentrations are similar to those obtained in urban surface soils of Huizhou and Zhanjiang (China), Ulsan (South Korea) and Kumasi (Ghana). The comparison with other studies in Brazil is more difficult since they are scarce.

However, the ∑PAHs concentrations are 2 to 5 times higher than natural soils of Amazonian and Mata Atlântica Forests (Cunha) or other regions (Wilcke et al. 1999, 2003, Krauss et al. 2005, Bourotte et al. 2009). Considering the urban forest park (PEFI) located within the urban area of São Paulo city (in the south part of the city), ∑PAHs concentrations are 2.5 times higher than those obtained in this study.

TABLE IV
Comparison of average PAHs concentrations (in mg kg^{-1}) in this study and in world topsoils.

Location	Concentration	Number of PAHs	Area	Reference
São Paulo, Brazil	0.33±0.32 [0.07-1.38]	13	campus of the university (urban green area)	This study
São Paulo, Brazil	0.818	16	urban forest (PEFI)	Bourotte et al. 2009
Cunha, Brazil	0.180	16	natural forest soils	
Uberlândia, Brazil	[0.007-0.390]	20	urban	Wilcke et al. 1999
Manaus, Brazil	0.016-0.038	21	Amazonian forest soils	Krauss et al. 2005
	0.145 [0.015-0.397]	20	Terra Firme, Amazon Basin	
	0.068 [0.029-0.142]	20	Pantanal	
Brazil	0.017 [0.0048-0.035]	20	Cerrado central	Wilcke et al. 2003
	0.115 [0.062-0.143]	20	Mata Atlântica	
	0.023 [0.0071-0.064]	20	Caatinga	
Beijing, China	0.865±0.799		residential	Peng et al. 2013
Beijing, China	1.285±1.848	16	park	Peng et al. 2011
	1.026±0.726		roadside (heavy traffic)	
	0.538±0.340		roadside (light traffic)	
	0.811±0.748		residential	
Beijing, China	1.803±1.824	16	urban soils	Liu et al. 2010
Dalian, China	4.391±4.370	25	garden	Wang et al. 2009
	3.237±2.735		business/residential	
Shangai, China	1.97 [0.083-7.220]	16	urban soils	Wang 2013
Nanjing, China	3.330 [0.059-18]	16	urban soils	Wang et al. 2015
Huizhou, China	[0.0354-0.5345]	16	urban soils	Ma and Zhou 2011
Zhanjiang, China	[0.0095-6.618]	16	urban soils	
Bangkok, Thailand	0.1292	20	urban soils	Wilcke et al. 1999
Shangai, China	6.280	16	roadside soils	Jiang et al. 2009
	2.130	16	park	
Hong Kong, China	0.169 [0.007-0.410]	16	urban soils	Zhang et al. 2006
Ulsan, South Korea	0.390 [0.065-1.200]	16	urban soils	Kwon and Choi 2014
	0.220 [0.092-0.450]	16	rural soils	
Kumasi, Ghana	0.4425±0.5272	22	urban soils	Bortey-Sam et al. 2014
Argentina	0.0075 [0.0017-0.031]	16	soils transect	Wilcke et al. 2014
Dehli, India	4.694±3.028 [1.062-9.652]	16	traffic site	Agarwal 2009
Lisbon, Portugal	1.544	16	urban	Cachada et al. 2012
Viseu, Portugal	0.169	16	urban	
Bayreuth, Germany	37.3	20	roadside soils	Wilcke et al. 2002
Bergen, Norway	6.780	16	urban soils	Haugland et al. 2008
New Orleans, USA	3.731 [0.647-40.692]	16	urban	Mielke et al. 2001
New Orleans, USA	5.100	17	urban soils	Wang et al. 2008
Detroit, USA	7.843	17	urban soils	
London, UK	18	16	urban soils	Vane et al. 2014
Taragona, Spain	0.736	16	urban/residential zone	Nadal et al. 2004
Rouen, France	2.780±0.879	14	urban site	Motelay-Massei et al. 2004
Galsgow, UK	[1.487-51.822]	15	urban	Morillo et al. 2007
Torino, Italy	[0.148-3.410]	15	urban	

PAHs occurrence in soil depends on two major sources: a natural one related to diagenesis of organic matter, biological activities and fires, and another one, associated to high combustion processes and products such as incomplete combustion of fossil fuels, vehicular engine combustion, smelting, waste incinerators. This pyrogenic source usually presents a pattern composed with high molecular weight PAHs. Petrogenic sources of PAHs include unburned petroleum and related products such

as gasoline, kerosene, diesel and lubricating oil. Since the urban area is a complex environment, the identification of PAHs sources is difficult and may be provided by statistical analysis, PAHs profiles and/or PAHs ratios.

There were positive correlations among the concentrations of ANT, BaA, CHRY, BbF and BkF; BaA, CHRY, BkF and BghiP; and CHRY and BghiP which may indicate common sources for these compounds. PHE and IND were negatively correlated. According to Tobiszewski and Namiesnik (2012), PAHs diagnostic ratios are tools used to identify emissions sources. However, diagnostic ratios results must been considered with caution since they may change during transport and environmental degradation processes. According to Mostert et al. (2010), low temperature processes usually produce low molecular weight PAHs whereas high temperature processes such as combustion fuel in engine, usually produce high weight molecular compounds. Thus, in order to identify PAH sources, the LMW/HMW ratios were calculated considering the sum of low PAHs (ACE, FLU, PHE, ANT) and high molecular weight PAHs (FLT, PYR, BaA, CHRY, BbF, BkF, BaP, IND, DBahA, BghiP). The ratios showed that among the sampling sites, 11 sites were affected by pyrogenic sources and 4 sites (P03, P06, P07 and P19) were affected by petrogenic sources. Other PAHs diagnostic ratios are usually used to assess specific sources. Commonly used PAHs ratios are FLU/(FLU+PYR), ANT/(ANT+PHE), FLT/(FLT+PYR), BaA/(BaA+CHRY), IND/(IND+BghiP) only mentioning some of them. Tobiszewski and Namiesnik (2012) also emphasized that ANT/(ANT+PHE) and BaA/(BaA+CHRY) ratios are more sensitive to photodegradation and environmental alterations than FLT/(FLT+PYR) and IND/(IND+BghiP) ratios. In this study, the BaA/(BaA+CHRY) ratio (= 0.36 ±0.2) indicated vehicular emissions/combustion sources which is similar with the values obtained by Bourotte et

al. (2009) in urban forest soils and fine and coarse atmospheric particulate matter (Bourotte et al. 2005), and IND/(IND + BghiP) ratio (= 0.48 ±0.4) also indicated vehicular combustion.

The PAHs ratios indicated predominant combustion source in campus topsoils, which is in concordance with the LMW/HMW ratio results, and with other results for urban soils in São Paulo city (Bourotte et al. 2009). Since PAHs are primarily emitted into the atmosphere and accumulated in surface soil after transport by dry and wet atmospheric deposition (He et al. 2009), it should be interesting taking in account the PAHs concentrations in fine and coarse atmospheric particulate matter collected in the same area by Bourotte et al. (2005). PAHs ratios are similar to those obtained in atmospheric particulate matter and should confirm an atmospheric contribution, although the contamination of topsoils should also result from diffuse and punctual sources of contamination. Most of the samples were collected in the proximity of the street and/or near bus stops inside the campus area, thus mobile sources should directly contribute to the topsoil PAHs input. Lower molecular weight PAHs are more volatile and have a shorter half-life than the heavier compounds. Peng et al. (2012) emphasized that heavy PAHs deposited closer to the source since they are adsorbed on particulate matter and settled according to their size, the larger ones depositing more rapidly than the finer ones, that remain for a longer time in suspension in the atmosphere and may be deposited distant from their source. The main tracers for vehicular emissions are BbF, BghiP and IND, and according to Masclet et al. (1987), diesel exhausts are enriched in FLT, CHRY and PYR, whereas Kulkarni and Venkataraman (2000) also associated FLT, PYR, BbF and BkF to diesel emissions. Abrantes et al. (2009) studied Brazilian light duty diesel vehicle exhausts and characterized both gaseous and particulate phases compositions. The results showed that high molecular weight

PAHs were predominantly adsorbed to soot particles as 100% for BaA, BaP, BghiP, BkF, 98.6% for CHRY, 97.5% for BbF and 96.5% for DBahA. Vehicles circulating in São Paulo city are also significantly fuelled by ethanol and gasohol as an alternative to fossil fuel, and more recently, by biofuel. According to Brito et al. (2013) ethanol was introduced in 1980s but its use has increased since the 2000s. Flexible fuel vehicles that can use either gasohol (a mixture of 20% anhydrous ethanol with gasoline) or pure ethanol included the fleet since 2003. Heavy-duty vehicles compose an older fleet but they are fuelled with a minimum of 5% of biodiesel content since 2010. Tunnel measurements in São Paulo city showed that 3- and 4-rings particle phase PAHs accounted for 24 to 77% of vehicular emissions. PHE, BaA, BbF and DBahA were the most abundant compounds and were associated with light-duty vehicles emissions (Brito et al. 2013). On the other hand, Vasconcellos et al. (2003), in order to characterize particulate matter organic composition in São Paulo tunnels, have associated PYR, CHRY, BaA to gasohol and diesel vehicles exhausts and FLT mainly from light-duty vehicles fuelled with gasohol. Globally, PAHs emissions from ethanol vehicles are on average 92% lower than PAHs emissions from gasohol vehicles and low molecular weight PAHs are the dominant PAHs emitted from light-duty vehicles (Abrantes et al. 2009).

To evaluate human exposure to carcinogenic PAHs, the toxic equivalence factors (TEFs), mutagenic potency equivalent factors (MEFs) and the incremental lifetime cancer risk (ILCR) were calculated. The values of carcinogenic equivalents (BaP_{TEQ}) for 8 PAHs varied from 0.001 mg kg^{-1} to 9.73 mg kg^{-1} with mean of 1.63 mg kg^{-1}, while the value of mutagenic equivalents (BaP_{MEQ}) ranged from 0.02 mg kg^{-1} to 5.08 mg kg^{-1} with mean of 0.62 mg kg^{-1}. The highest and lowest values were obtained at P2 and P15 site, respectively. $ICLR_{inhalation}$ values ranged between 2.38 10^{-13} and

2.32 10^{-10} with an average of 3.90 10^{-11} for children and 1.51 10^{-12} and 1.47 10^{-9}, with an average of 2.47 10^{-10} for adults. $ICLR_{dermal}$ values ranged between 3.06 10^{-8} and 2.99 10^{-5} with an average of 5.01 10^{-6} for children and 3.46.10^{-8} and 3.38 10^{-5}, with an average of 5.67 10^{-6} for adults. $ICLR_{ingestion}$ values ranged between 6.16 10^{-7} and 6.00 10^{-4} with an average of 1.01 10^{-4} for children and 6.46 10^{-7} and 1.57 10^{-4}, with an average of 1.92 10^{-5} for adults. Higher values were found at P2 site, located at 200 m from the peripheral road and the main access avenue to the campus, and lower ones at P15 site, located at 1.6 km from peripheral road. Comparing our results with other studies, potential risk values are lower than values found in Beijing (Peng et al. 2011), Xi'an-China (Wang et al. 2018) and Turkey (Dumanoglu et al. 2017). Therefore, results showed that ILCR values for inhalation, dermal and ingestion showed very low ($\leq 10^{-6}$) and low ($\leq 10^{-6}$ to $< 10^{-4}$) potential cancer risk for adults and children.

SPATIAL DISTRIBUTION AND SOURCE APPORTIONMENT COMBINING TRACE METALS AND PAHs

The spatial distribution maps of trace metals and total PAHs concentrations were plotted using ArcGIS software and are presented in Figure 4. Dots correspond to concentration at sampling point and their size is proportional to the concentration value. Spatial distribution revealed that most of higher concentration of metals and PAHs are concentrated in the north and southeast part of the campus, in sampling sites (P1 to P6) closer to the peripheral road ("Marginal Pinheiros") and main entrance of the campus ($\approx$150 to 250m). P8, P9, P10, P13, P19 and P20 are located closed to avenue with higher slope and P7 and P16 close to a roundabout. Sb, V and Mo do not show a clear pattern and are homogeneously distributed among the sampling sites. Geographic distribution of Pb and Cu is similar and Ba, PAHs, Pt, Pd and Zn
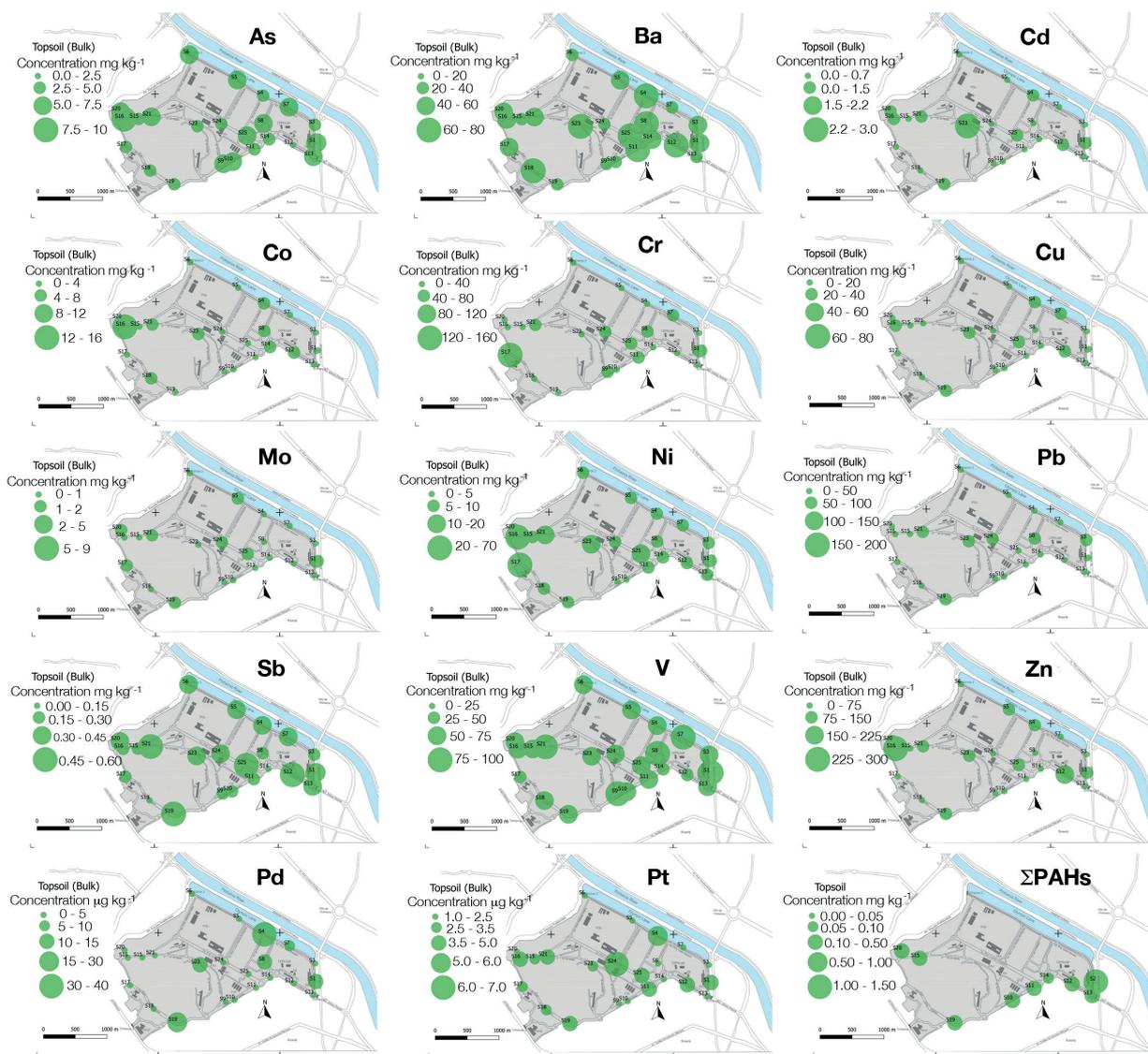
Figure 4 - Spatial distribution maps of trace metals and total PAHs concentrations in University *campus* in the São Paulo city.

concentrations seem to be grouped in the southeast part of the campus area and close to the Olympic streak.

The multivariate data analysis performed for elemental and PAHs concentrations, using the positive matrix factorization (PMF) model obtained four factors (Figure 5). In the first factor, ANT, BaA, CHRY, BbF, BkF, BghiP species were associated with Pt, K and Hg, which may be attributed to vehicular exhaust emissions. In the second factor, PHE and BbF were associated

with Co, Ba, Pd, Pt, Ca, Mg and K, which may be associated with terrigeneous (natural soil contribution), traffic polluted dust resuspension and vehicular exhaust catalysts. Only heavy PAHs species were associated in the third factor (FLT, PYR, BkF, DBahA, BghiP), which may indicate diesel exhaust emissions adsorbed to dust. IND and most of metals are associated in the factor 4 (As, Cu, Mo, Pb, Sb, V, Zn, Cr, Hg, Fe, Al, S, SiO_2), which may be associated with brake source and traffic polluted dust resuspension. As discussed before,
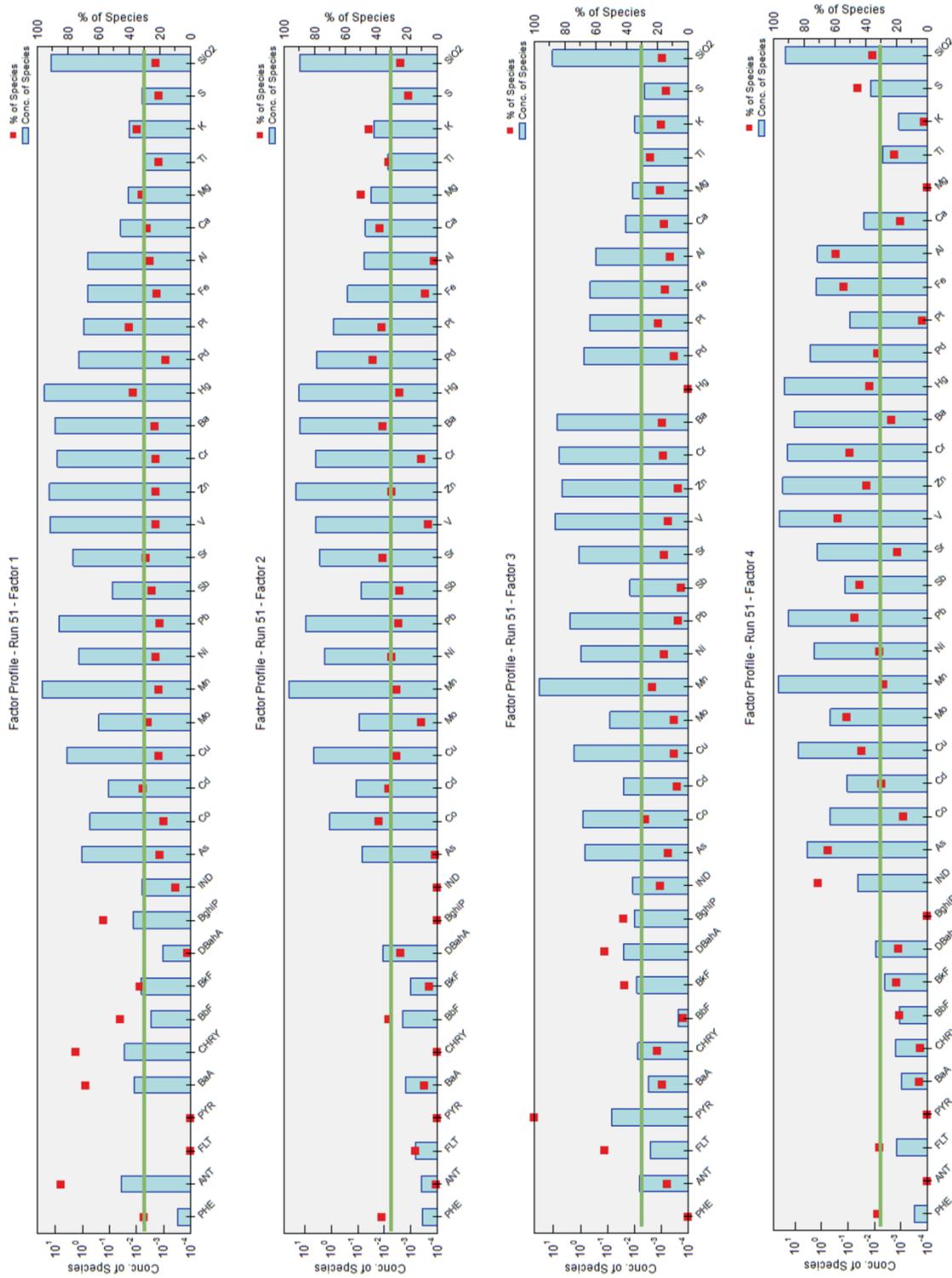
Figure 5 - Results of Positive Matrix Factorization model indicating 4 factors for source apportionment combining PAHs and metals in topsoil samples: Factor 1 – vehicular exhaust emissions, Factor 2 – Soil and traffic polluted dust resuspension, Factor 3 – Diesel exhaust emissions, Factor 4 – Brake source and traffic polluted dust resuspension. Each factor profile is represented by respective bar diagram and their main contribution associated with the map of the campus area.
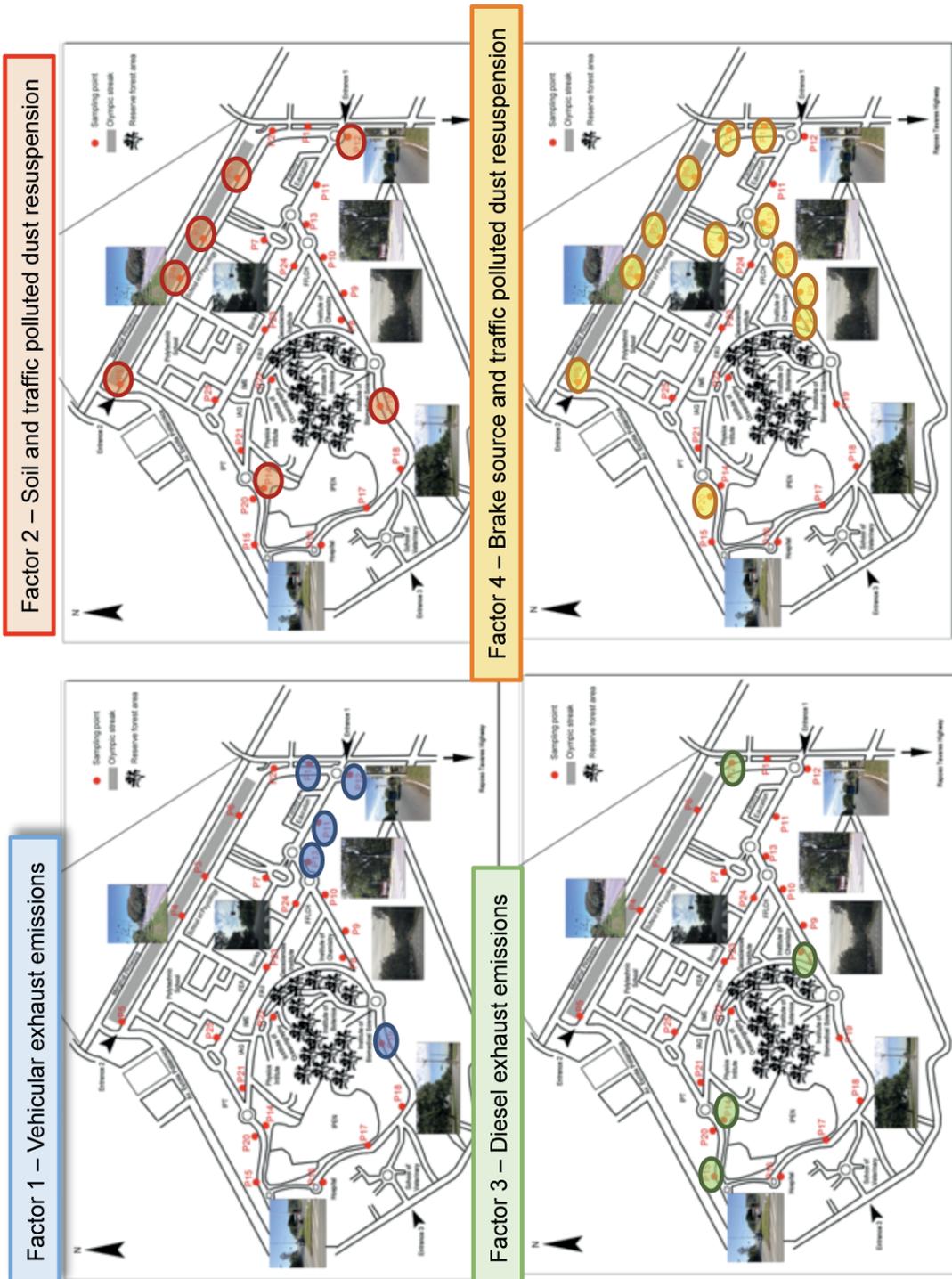
Figure 5 (continuation).

most of these elements are indicative of brake lining materials and road vehicle brake abrasion dust. Iijima et al. (2007) explained that potassium titanate is added to improve heat resistance and wear characteristics, Cu fiber and barium sulfate are usually used to improve control braking characteristics and braking abrasion generate fine particles (< 3 μm) that may be easily resuspended and deposited in adjacent road topsoils.

These factors clearly showed the contribution of traffic through vehicular exhaust emissions from the tail pipe but also non-exhaust emissions derived from road dust re-suspension and direct emissions from brakes, tires, discs pads and other vehicular components due to corrosion and abrasion.

It can also be observed that some trace metals and PAHs are more frequently higher in three main zones of the campus: near the university Hospital (and a roundabout); in the main avenue with higher slope and at the main entrance of the campus, that might be explained by traffic conditions and higher frequency of braking and acceleration also due to higher traffic during rush periods. De Silva et al. (2016) studied roadside soils of Melbourne and pointed out that vehicular speed, road age and traffic intensity are the main factors for metal accumulation in soils. Nearby the main entrances of the campus, the sampling points are close to high traffic avenues outside the campus and consequently higher traffic intensity. These zones of the campus are also surrounded by trees, which may promote a higher accumulation of litter on topsoil that may also accumulate more traffic related dusts. Finally, the main entrances are in a topographically lower area and consequently accumulate more soil and other particles by runoff during high rainy events.

CONCLUSIONS

The study showed that concentrations of metals are generally lower than the reference value established by CETESB and other studies carried out in the São Paulo urban area, except for Cd, Ni, Pb, Cr and Zn. PMF analysis allowed to identifying the vehicular sources for trace metals and PAHs. Traffic sources are related to both exhaust and non-exhaust emissions such as abrasion of brakes, tires, car components (Cu, Zn, Ba, Sb, Pt, Pd, Cr) and dust re-suspension with soil contribution. We also identified traffic intensity, predominant wind direction, vegetation cover and road slope as driver of spatial distribution of concentrations. Potential carcinogenic risk calculated for PAHs showed low and very low risk for human health neither for inhalation, ingestion or dermal contact routes.

ACKNOWLEDGMENTS

AUTHOR CONTRIBUTIONS

Christine Laure Marie Bourotte contributed to the sampling, and physical and chemical characterization of the samples and all results discussion. Lucy Elaine Sagauara and Mary Rosa Rodrigues de Marchi constributed to the quantification of PAHs in samples and results discussion.Carlos Eduardo Souto-Oliveira contributed to the statistical analysis by PMF and results discussion.

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