



Topsoil pollution in highway medians in the State of São Paulo (Brazil): determination of potentially toxic elements using synchrotron radiation total reflection X-ray fluorescence

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Abstract

The presence of metals in vehicle emissions is due to several factors, such as the composition of fuels and lubricating oils, the wear of engine components, and their use in catalytic converters. It is known that the soil near highways is greatly affected by heavy vehicle traffic, since the use of highways is of fundamental importance for the flow of goods and public transport, especially in Brazil, street transport being the main form of transport in the country. Considering the scenario described, the main objective of this study was to monitor the concentration of potentially toxic elements in surface soils located on the medians of the main access highways in the city of Campinas (SP—Brazil) and classify the soils through geoaccumulation index. Using SR-TXRF it was possible to detect and determine the concentrations of 5 elements of toxic-environmental interest (Cr, Ni, Cu, Zn, and Pb) and 11 natural soil composition elements (Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, Rb, and Sr). To evaluate the influence of highway distance on elementary concentrations, ANOVA and Tukey statistical tests were applied. Nickel, Cu, and Zn showed a decrease in their concentrations moving away from the highway, indicating their relation with vehicular emissions. Applying principal components analysis (PCA), it was possible to identify four groups of the quantified elements: those mainly related to the soil itself, those produced by traffic of automotive vehicles, and those emitted by industrial activities.

Keywords Topsoil pollution · Highway · Synchrotron radiation · Total reflection X-ray fluorescence · Traffic-related metals · Potentially toxic elements · Possible sources of pollutants

Introduction

Automotive vehicles are largely responsible for emissions of air pollutants. These pollutants can contaminate the soil as

they are subject to dry or wet deposition. The presence of metals in vehicle emissions is due to several factors, from the composition and burning of fuels and lubricating oils, to the wear of the engine components, as well as their use in catalytic converters and to the surface wear of the tracks (Chen et al. 2010; Wang et al. 2017). The soils located nearest to roads and highways usually show high concentrations of elements related to vehicular traffic, such as Cr, Ni, Cu, Zn, Sb, Ba, and Pb, and their concentrations tend to decrease with the depth of the soil and distance from the road (Carrero et al. 2013; Werkenthin et al. 2014).

In gasoline combustion, beside CO₂, mainly sulfur and nitrogen oxides as well as traces of several elements such as Mn, Cr, Zn, Cu, Fe, B, Mg, and Pb can be emitted, most of which comes from crude oils before refining (Guiguer 1996). The exhaustion of diesel engines presents a high presence of elements such as Al, Ca, Fe, Mg, and Si, which represents about 80% of the metal(loid)s in the diesel fuel (Wang et al. 2003). The remaining 20% are Ag, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sb, Sr, Ti, V e Zn (Wang et al. 2003). The main

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source of contamination of ethanol fuel by metal species is the corrosive process suffered by the distillation columns, distillation tanks, and fuel stations (Bergamini et al. 2006). The main metals present in ethanol are therefore Zn, Cu, Pb, and Cd (de Oliveira et al. 2002; Bergamini et al. 2006). Among heavy metals, Zn certainly constitutes a strong contaminant in alcoholic matrices, since it is used in the biochemical processes of ethanol production (de Oliveira et al. 2002).

Another possible source of metals from vehicles is the abrasive wear of parts of the engine itself or other metallic parts. In diesel cycle, internal combustion engines, the first cylinder ring, usually receive an anti-wear coating consisting of a Mo-, Ni-, and Cr-based alloy; the piston is made by an alloy of Al; and the wall of the cylinder, in turn, is almost always made of gray cast iron, containing mainly Si, Mn, S, Cr, Ni, and Cu, among others (Tomanik 2000). Wear of tires and brake pads can still be an important source of elements such as Cr, Co, Ni, Cu, Zn, Cd, Sb and Ba (Thorpe and Harrison 2008; Winther and Slentø 2010; Földi et al. 2018). In addition to the pollutants emitted directly by the vehicle flow, some other factors that can release metals in the environment should be also considered, such as the presence of guardrails, traffic signals, and other galvanized steel structures, road age, traffic density in mining areas, and operation of industries near the studied sites (Carrero et al. 2012; Li et al. 2014; Werkenthin et al. 2014; De Silva et al. 2016; Suryawanshi et al. 2016).

Pollutants derived from vehicular traffic can compromise the soil use and can pose high risks to the health of the population (Li et al. 2014; Nikolaeva 2017). The highways are the main form of transportation in Brazil; however, there is a lack of studies on the elemental composition of soils near highways with intense vehicular traffic, whose knowledge is of fundamental importance from the environmental point of view.

The objectives of this study were (i) to evaluate the elemental composition of the surface soils of the main access roads to the city of Campinas (SP); (ii) to verify if they present potentially toxic elements in concentrations higher than the reference values for soils established by the legislation in force in the State of São Paulo, as defined by the Environmental Company of the State of São Paulo (CETESB—a monitoring and licensing agency for potentially polluting activities); (iii) to calculate the geoaccumulation index (*I_{geo}*) (Müller 1969) for the investigated soils, as recommended index (instead of local reference values) to assess the metal contamination in roadside soils (Carrero et al. 2012).

For this purpose, synchrotron radiation total reflection X-Ray fluorescence (SR-TXRF) was used, an analytical technique based on the measurement of the intensity of characteristic X-ray emission lines of the chemical elements present in a sample, when properly excited. In TXRF, absorption and reinforcement effects are strongly reduced, and consequently, matrix effect correction is not

required (La Calle et al. 2013; Dalipi et al. 2017). Owing to the low incidence angles used in TXRF, it is possible to reduce the scattering and the excitation of the elements present in the support material, thus resulting in background reduction and consequently allowing to obtain more accurate results with an extremely low detection limit (Klockenkamper and Von Bohlen 1996; Marguá et al. 2018). Due to the advantages described, the TXRF technique is competitive with other atomic analytical techniques, such as flame atomic absorption spectrometry (FAAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), or atomic absorption spectroscopy (AAS) (Riaño et al. 2016; Dalipi et al. 2017).

Materials and methods

Sampling sites

The city of Campinas is located in the southeast region of Brazil, in the State of São Paulo, at a distance of approximately 90 km from the state capital, São Paulo (S 22°53' 20" and W 47°04'40"). The city has a population of approximately 1,173,000 inhabitants, distributed across 795 km² of territorial area, and a fleet of 857 thousand vehicles (IBGE 2016). Because of its great importance in the State and National scenario, the city of Campinas was chosen to carry out this study.

Two highways were chosen for the study, the Anhanguera Highway (SP-330) and the Bandeirantes Highway (SP-348). The Anhanguera Highway (SP-330) is the longest state highway in the country with approximately 450 km. It starts in the city of São Paulo and continues towards the northern region of the State of São Paulo, connecting 31 cities. Anhanguera is considered one of the most important highways in Brazil and one of the busiest, with the highest traffic segment between São Paulo and Campinas, with an average circulation of 64,000 vehicles per day in the section nearest to the city of Campinas (Departamento de Estradas de Rodagem 2015). The Bandeirantes Highway (SP-348) starts in the city of São Paulo and connects 15 cities to the interior of the state, with approximately 159 km of extension. The segment between São Paulo and Campinas is also the one with the highest traffic flow, with a daily average of 71,000 vehicles (Departamento de Estradas de Rodagem 2015). The highways make up the Anhanguera-Bandeirantes complex, which is considered the largest financial corridor in the country. Thus, its economic importance in the national scenario is undeniable, justifying the choice of these highways for the development of the study.

The sampling sites can be identified in Fig. 1. Three sampling sites were selected on each of the highways: km 98 (SS1), km 103 (SS2), and km 106 (SS3) on Anhanguera, and km 88 (SS4), 93 (SS5), and 100 (SS6) on Bandeirantes, all within the perimeter of the city of Campinas.

Soil sampling

Due to the great heterogeneity of the soil composition, samples were collected in order to guarantee the representativeness of the study sites. Thus, at each sampling site, 20 perforations were carried out in each sampling campaign, composing 4 samples at different distances from the highway, according to the procedure described in the Figure reported as Online Resource 1 (supporting material). Thus, 4 samples (P1, P2, P3, and P4) were collected, with P1 at 30 cm from the highway, P2 at 1.3 m, P3 at 2.3 m, and P4 at 3.3 m (each sample consists of 5 perforations at the same distance from the highway). This subdivision was done to try to evaluate the influence of the distance of the highway on the concentration of the elements analyzed. Five sampling campaigns were carried out in 2014 in order to increase the number of samples of the sites evaluated, and, therefore, a total of 20 samples were collected for each site (five P1, five P2, five P3, and five P4), totaling 60 samples for each highway. The sampling campaigns were carried out in March, May, August, September, and December, always according to the authorization and availability of the company that manages the highways. The full sampling scheme is summarized in Table ESM1 (Online Resource 2—supporting material).

The soil was collected with the aid of plastic shovels to a maximum depth of 5 cm, since the intention of the study was to analyze the top-soil. The choice of this soil layer was

justified since several works in the literature demonstrate that at a soil depth of 10–20 cm the concentrations of all heavy metals usually significantly decrease (Kluge and Wessolek 2012).

Sample preparation

The samples were oven dried at a temperature of 40 °C for 24 h. Coarse interfering materials (grass, cigarettes, papers, among others) were removed by manual separation and with the aid of a plastic sieve. The soil was then ground in a mortar grinder (Pulverisette 2—Fritsch) with an agate (SiO₂) grinding set for 20 min. The soil was passed through a plastic sieve with a mesh of 74 μm in diameter. The accomplishment of these procedures guaranteed uniformity and granulometric equivalence between the soil samples and the certified reference material, used in the calibration of the system and validation of methodology.

The samples were submitted to a very strong acid digestion process that dissolves the environmentally available elements in sediments, sludges, and soils samples, as described by the USEPA (method 3050B) (US EPA 1996). For the acid digestion, 10 mL of 1:1 (v/v) HNO₃ (65% PA) were added to 1 g of sample (in a glass test tube) and then heated to 95 °C in a block digester, refluxing for 15 min. After taking samples away of the heating, when they reached room temperature, 5 mL of concentrated HNO₃ were added. The samples were heated again at 95 °C, refluxing for 30 min. The last step (5 mL of HNO₃ + reflux) was repeated until the sample did not release further brown fumes. After the samples reached room temperature, 2-mL deionized water (Milli-Q), 10 mL H₂O₂ (30% volume) were added, and the samples were heated again at 95 °C, maintaining reflux for 2 h. Finally, 10 mL of H₂O₂ was

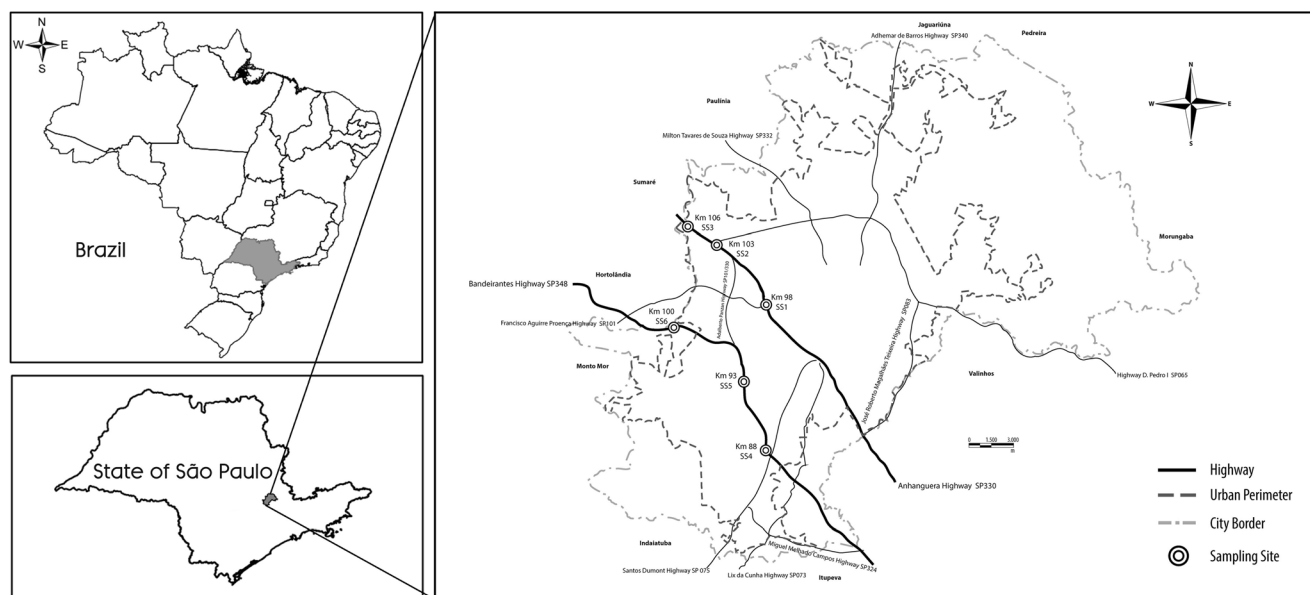


Fig. 1 Sampling sites localization

added until the samples showed no more effervescence, or their aspects remained unchanged. The resulting solution was transferred to a becker where it was added with deionized water to the final volume of 100 mL.

After the acid digestion, 1 ml was transferred to an Eppendorf tube, and 100 μl of gallium solution (100 mg L^{-1}) were added as internal standard, used to eliminate the non-uniformity of the aliquot in the carrier, since the thin film formed on the reflector does not have regular geometry (Espinoza-Quiñones et al. 2018). In fact, the intensity of the emitted X-rays obtained during the irradiation of the sample depends on the position in which it is placed in the reflector. The addition of the internal standard helps to compensate for eventual inhomogeneities in sample irradiation due to the position of the sample. The addition of the internal standard at known concentration allows the calculation of the concentration of other elements by using the Ga signal intensity to correct possible matrix effects.

After this procedure, the final solution was stirred for homogenization, and 5 μL were pipetted into perspex support (acrylic) and dried with an infrared lamp under a laminar flow fume hood. After drying, the samples were stored in petri dishes to avoid contact with the external environment and possible contamination.

All samples were prepared in triplicate, minimizing errors deriving from contamination of sample supports and pipetting errors. In addition, several analytical blanks were prepared, which were submitted to the same digestion process used in the samples.

Instrumentation

Sample analyses by SR-TXRF were performed at the Brazilian Synchrotron Light Laboratory (located in the city of Campinas), which is the only source of synchrotron light in Latin America and currently has 15 beamlines in operation. The standards and soil samples were measured for 100 s each using a polychromatic (white) beam of 5 mm width and 0.1 mm height, for excitation in the energy range of 2–20 keV. X-rays were detected with a hyperpure germanium detector with 150 eV resolution at 5.9 keV. The distance sample-detector was 12 mm and the incidence angle was 1 mrad, that provided total reflection conditions. The spectra obtained were analyzed using the Quantitative X-ray Analysis System for Windows (WinQxas) software package provided at no charge by the International Atomic Energy Agency (IAEA). After the analysis of spectra, the fluorescence intensity was obtained, allowing to calculate the concentrations for each element present in the samples.

In order to obtain the relative sensitivities, multielement standard solutions were prepared containing Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Se, Sr, and Mo for the K-line-emission series (K-series) and containing Mo, Ba, Sm, Lu, Pt, and Pb

for the L-line-emission series (L-series), all at known concentrations. As in the samples, Ga was added as an internal standard. Standard solutions were prepared in triplicate, as well as blank, and measured for 100 s at line D09B-XRF from the Brazilian Synchrotron Light Source Laboratory. To ensure the validity of SR-TXRF technique two standard reference materials were measured by SR-TXRF. The reference materials used were: (i) drinking water pollutants (DWP), provided by Sigma Aldrich (catalog number 413933) and (ii) San Joaquin Soil, provided by the National Institute of Standards and Technology (NIST 2709).

Soil guiding values

The guiding values are chemical boundary concentrations that provide guidance to assess the soil quality conditions. They are an important tool of soil quality control, being used as instruments for prevention and control of contamination and for the management of contaminated areas (São Paulo 2009; São Paulo 2013).

The quality reference values (QRV) define the maximum concentrations for each element/substance analyzed for a soil to be considered clean. The prevention values (PV) define the concentrations above which detrimental changes to soil quality may occur. Thus, the limits established by the PV are indicative of alert for the quality of the soil. These values indicate the quality of a soil capable of sustaining its primary functions, protecting the ecological receptors and groundwater quality (São Paulo 2009). The intervention values (IV) are concentrations above which there are direct or indirect potential risks to human health, thus being considered indicative concentrations of contaminated areas (São Paulo 2009). The subdivision between the agricultural, residential, and industrial areas depends on the increasing risk that pollutants could come into direct contact with humans and thus cause direct damage to health.

The Brazilian guiding values also include the elements Sb, As, Ba, Cd, Co, Hg, Mo, Ag, and Se, which were not detected in the analyzed samples, and therefore, their limits are not presented in Table 1. The Brazilian legislation (Table 1) and the screening values for warning risk for metals and metalloids in European countries, presented in Table 2, were used to compare the data obtained in this study and served as a basis for the discussion of the results obtained.

Geoaccumulation index

The levels of heavy metal contamination on surface soils can be evaluated using the geoaccumulation index (*I_{geo}*) (Müller 1969). The calculation of the *I_{geo}* allows the evaluation of the heavy metal contamination based on

Table 1 Guidance values of inorganic elements for soils of the State of São Paulo (mg kg⁻¹ d.w.) (CETESB 2014)

	Quality reference	Prevention values	Intervention values		
			Agricultural	Residential	Industrial
Cr	40	75	150	300	400
Ni	13	30	190	480	3800
Cu	35	60	760	2100	10,000
Zn	60	86	1900	7000	10,000
Pb	17	72	150	240	4400

the comparison of the current concentrations of these elements in horizons O and A with geochemical background, considering pre-industrial concentrations (Nowrouzi and Pourkhabbaz 2014). The geoaccumulation index is calculated using Eq. 1:

$$I_{geo} = \log_2 (C_n/1.5B_n) \tag{1}$$

where C_n is the measured concentration of the element in the environment; B_n is the geochemical background value in soil of the same element; the constant 1.5 is used to represent natural fluctuations in the content of a given substance in the environment and limited anthropogenic influence (Barbieri 2016; Wei and Yang 2010). In this study, the quality reference values (QRV) (São Paulo 2009; São Paulo 2013) were used as the background values for calculating the I_{geo} values. The interpretation of I_{geo} results is done through the classification of the values obtained: uncontaminated ($I_{geo} \leq 0$); uncontaminated to moderately contaminated ($0 < I_{geo} \leq 1$); moderately contaminated ($1 < I_{geo} \leq 2$); moderately to heavily contaminated ($2 < I_{geo} \leq 3$); heavily contaminated ($3 < I_{geo} \leq 4$); heavily to extremely contaminated ($4 < I_{geo} \leq 5$); extremely contaminated ($I_{geo} \geq 5$).

Statistical tests

Analysis of variance (ANOVA) and Tukey test

In order to confirm that the elemental concentrations decreased as the distance from the highway increased,

Analysis of variance (ANOVA test) was used, which is a dispersion analysis in relation to the mean, which uses the variance within each of the analyzed groups and the variance among all these groups analyzed together. In this case, the ANOVA test could relate the variance within each of the distances P1, P2, P3, and P4 for each element, with the variance between these groups.

Since the evaluation of only one factor that can influence the elementary concentration change was made, which in this case is the distance from the highway, the ANOVA one-way test has been used. This test gives information whether a factor gives a statistically significant contribution to the change in concentration of an element as compared with other factors that could lead to the change in concentration.

For the elements that displayed significant changes of concentration with the distance from the highway, the Tukey test was also performed. Tukey test compares each of the groups in pairs, showing whether or not there is a significant difference between them, indicating with greater clarity the main distances that most influenced the concentration of each of the elements (Barbetta et al. 2000).

Principal component analysis (PCA)

Using a multivariate analysis method, principal component analysis (PCA), the data were grouped in order to determine the possible sources of the elements detected in the soil samples. Using the XLSTAT software (free trial version), PCA was performed on the original data matrix containing 16 variables, i.e. the concentrations of the elements detected by SR-TXRF (Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr,

Table 2 Screening values for warning risk for metals and metalloids in soil (residential use) (mg kg⁻¹ d.w.) (adapted from Carlon 2007)

	Austria	Belgium	Czech Rep.	Finland	Germany	Slovakia	Denmark	Sweden
Cr	50	125	450	100	400	250	500	250
Ni	70	150	180	50	140	100	30	150
Cu	100	110	500	100	–	100	500	–
Zn	–	230	1500	200	–	500	500	700
Pb	100	195	250	60	400	150	40	300

and Pb) in all the sampling points around the Anhanguera and Bandeirantes highways.

Results and discussion

Relative sensitivity

Relative sensitivities (Fig. 2) were calculated through Eqs. 4 and 5, where $S_{i(K)}$ is the relative sensitivity for the *K*-series elements, $S_{i(L)}$ is the relative sensitivity for the *L*-series elements and *Z* is the atomic number of the elements.

$$S_{i(K)} = \exp(-0.0001 Z^3 - 0.0107 Z^2 + 0.9960 Z - 16.8591) = 0.9978 \tag{4}$$

$$S_{i(L)} = \exp(-0.0048 Z^2 + 0.6703 Z - 24.0247) = 0.9983 \tag{5}$$

The use of multielemental standard solutions is a common procedure for TXRF analysis, as reported by Chimidza et al. (2001), Towett et al. (2013), Rodrigues dos Santos et al. (2017) and Marguí et al. (2018). The sensitivity is an instrumental parameter, and the calculation depends on the atomic number, as can be observed in Eqs. 4 and 5. It is believed that the matrix has no influence on the sensitivity calculation in TXRF, since thin samples are analyzed and matrix effects does not apply (Towett et al. 2013). In any case, the sensitivity was used to calibrate the instrumentation and, to ensure the validity of the technique, the NIST 2709 certified standard was

also evaluated, with the same matrix of the studied samples.

Limit of detection (LOD)

The detection limits for soil samples were calculated through Eq. 6 (Ladisich et al. 1993) for 100 s measuring time (Table 3) where I_i is the signal intensity of element *i* in the sample; I_y is the signal intensity of the internal standard (*y*) in the sample; C_y is the concentration of the internal standard (*y*) in the sample; S_i is the relative sensitivity for element *i*; BG corresponds to the background signal intensity (counts per second) and *t* is the measuring time in seconds. For the LOD determination, 360 measurements (triplicate of all 120 samples collected, 60 per highway) were used.

$$LOD_i = 3 \cdot \sqrt{\frac{I_i(BG)}{t} \cdot \frac{C_y}{I_y S_i}} \tag{6}$$

SR-TXRF validation procedure

In order to validate the methodology used, the analysis of two different standard reference materials were carried out. Drinking water pollutants (DWP) and a San Joaquin Soil standard reference material, provided by the National Institute of Standards and Technology (NIST 2709) were used. Fifteen measurements were made, over 100 s, and the comparison between the measured and certified values is shown in Table 4. The confidence interval was calculated for a value of $\alpha = 0.05$ (95% confidence level) representing the level of significance.

Fig. 2 Relative sensitivity, experimental, and fitted, for *K* and *L* series using SR-TXRF

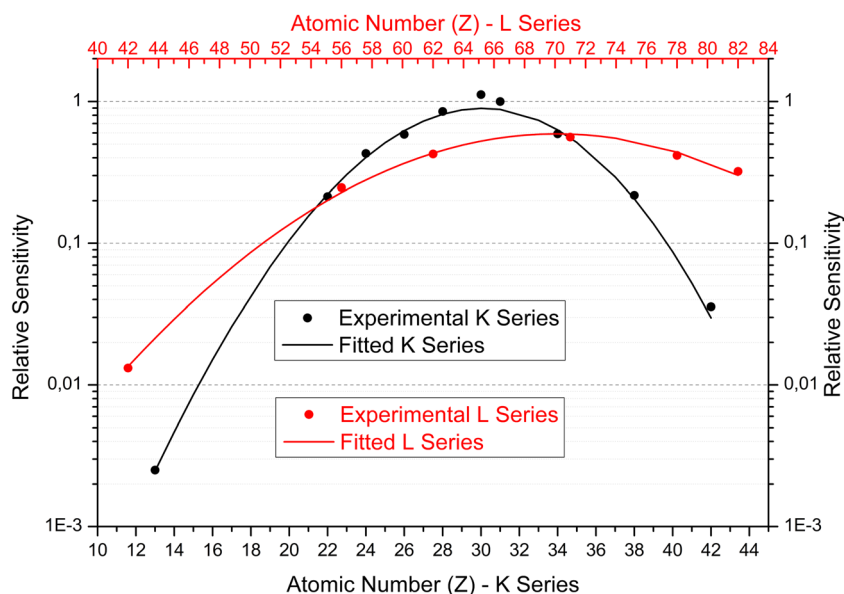


Table 3 Limits of detection for soil samples determined by SR-TXRF

Element	Atomic number (Z)	LOD \pm SD (mg kg ⁻¹)
Al	13	71 \pm 3
Si	14	39 \pm 3
S	16	13.4 \pm 0.6
Cl	17	8.2 \pm 0.4
K	19	3.5 \pm 0.1
Ca	20	2.38 \pm 0.01
Ti	22	1.25 \pm 0.09
Cr	24	0.76 \pm 0.05
Mn	25	0.62 \pm 0.04
Fe	26	0.53 \pm 0.03
Ni	28	0.43 \pm 0.02
Cu	29	0.41 \pm 0.02
Zn	30	0.40 \pm 0.03
As	33	0.48 \pm 0.02
Br	35	0.65 \pm 0.03
Rb	37	1.01 \pm 0.06
Sr	38	1.32 \pm 0.08
Pt	78	3.25 \pm 0.09
Pb	82	1.5 \pm 0.1

After the data evaluation of the two multi-element standard reference materials, there were deviations of less than 10% for all elements when certified and measured values were compared, showing a good accuracy. According to Towett et al. (2013) deviations of $\pm 10\%$ are acceptable, and in the case of a deviation of more than 10% an error analysis must be performed, which is not the case.

Quantitative analysis—elemental composition, concentrations and contamination levels

From the analysis by SR-TXRF, 16 elements were detected: Al, Si, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Pb. Only those of toxicological interest were selected to discuss their results: Cr, Ni, Cu, Zn, and Pb (Agomuo and Amadi 2017). Several studies have shown that Cu, Zn, As, Cd, and Pb are indicators of soils contaminated by heavy metals near highways (Chen et al. 2010; Werkenthin et al. 2014; Zhang et al. 2015). The descriptive statistics of potentially toxic elements concentrations in the soils of the evaluated highways are summarized in Fig. 3, that present the minimum, average, and maximum concentrations, as well as 25%, 50%, and 75% percentiles in the concentration distribution, considering the 20 samples collected at each sampling site. The box plot charts show the distribution of concentrations obtained by sampling sites. The box plot charts did not consider the distance from the samplings to the highway.

The accumulation of Pb in soils near to highways may be related to the use of the element as additive in gasoline for many years (Zhang et al. 2015; Yan et al. 2018; De Silva et al. 2016; Nannoni and Protano 2016; Gilbert and Weiss 2006). In addition, the yellow paint, used to demarcate the highways, is composed of high levels of PbCrO₄, which can also contribute to lead concentrations (Yan et al. 2018). However, in the evaluation of the Anhanguera highway, according to the results obtained in the analysis of surface soils, it is possible to affirm that most of the samples displayed concentrations of Cr and Pb below the quality reference values (Table 5). The reduction of Pb levels in gasoline over the years has implied a significant decrease of this metal in the environment (Bellés et al. 1995) which may explain the low concentration detected in the analyzed highways. With the removal of Pb from gasoline, average childhood blood Pb levels in the USA plummeted from approximately 16 mg/dL in 1976 to 3.2 mg/dL in 1994, thus its removal was properly viewed as a public health triumph (Gilbert and Weiss 2006).

Although some authors report the presence of Cr in automotive sources, such as fuels, oils, and wear of tires and brake systems (Hjortenkrans et al. 2006; Li et al. 2001; Winther and Slentø 2010; De Silva et al. 2016; Zhang et al. 2015), only a few samples had Cr concentrations higher than the prevention values and none exceeded the intervention value in the studied highways. Similar results were obtained in Shanghai (Yan et al. 2018), where detected concentrations of Cr were below the background. The presence of Cr may also be associated with building materials and cement industries, and may be indicative of reforms and constructions (Mokrzycki et al. 2003; Yongming et al. 2006; Shi et al. 2010). Some studies associate the presence of some metals, among them Cr, to natural sources because they are constituent of different soil minerals or are adsorbed to them (Yan et al. 2018; Cannon and Horton 2009), these being the most probable source of Cr in this study. However, Cr and Pb sources are not an immediate concern in this region according to the concentrations obtained.

Nickel concentrations in most of the results were higher than the quality reference values and lower than the prevention values, for SS1 and SS2. At km 106 (SS3), the majority of the samples had concentrations lower than the quality reference values, indicating a better soil condition compared with the other two evaluated locations. This small difference can be due to the fact that km 106 has a lower circulation of vehicles than the other two points evaluated, since the volume of traffic may reflect the concentrations of metals detected (Yan et al. 2018; De Silva et al. 2016; Nannoni and Protano 2016). In all three sites at the Bandeirantes Highway, only one sample presented Ni concentration higher than the prevention values, but it may be a sign of increased concentration over time.

Copper and Zn are elements found in the environment that may be related to vehicle traffic (Zhang et al. 2015; Yan et al.

Table 4 Comparison of measured and certified values for Drinking Water Pollutants and San Joaquin Soil standard reference materials measured by SR-TXRF

	Element	Certified value	Average measured value ± SD	Recovery (%)
DWP	Cr	10 ± 0.05 µg L ⁻¹	9.9 ± 0.7 µg L ⁻¹	99
	As	10 ± 0.05 µg L ⁻¹	10.6 ± 0.4 µg L ⁻¹	106
	Se	5 ± 0.025 µg L ⁻¹	4.75 ± 0.06 µg L ⁻¹	95
	Ba	101 ± 0.505 µg L ⁻¹	102 ± 5 µg L ⁻¹	101
	Pb	10 ± 0.05 µg L ⁻¹	9.4 ± 0.6 µg L ⁻¹	94
San Joaquin Soil (NIST 2709)	Ca	1.89 ± 0.05%	1.82 ± 0.04%	96
	Fe	3.5 ± 0.11%	3.5 ± 0.4%	100
	Cr	130 ± 4 mg kg ⁻¹	129 ± 20 mg kg ⁻¹	99
	Mn	538 ± 17 mg kg ⁻¹	478 ± 25 mg kg ⁻¹	88
	Ni	88 ± 5 mg kg ⁻¹	80 ± 4 mg kg ⁻¹	91
	Cu	34.6 ± 0.7 mg kg ⁻¹	36 ± 2 mg kg ⁻¹	104
	Zn	106 ± 3 mg kg ⁻¹	111 ± 18 mg kg ⁻¹	105

2018) and/or industrial contributions (Yu et al. 2016). In areas close to highways, their sources may be tire wear, lubricating oil, guardrails, brake linings, or galvanized barriers (Cuncell et al. 2004; Kluge and Wessolek 2012; Carrero et al. 2013; De Silva et al. 2016; Yan et al. 2018). Copper and zinc displayed to be the major problems detected on the Anhanguera highway, since all the samples had concentrations above the prevention values and some samples above the intervention values, indicating the possibility of harmful alterations to the soil and environment. It is worth noting that the Brazilian

legislation during its last revision in 2014 (CETESB 2014) lowered the intervention values. According to the previous legislation, the intervention limits in agricultural areas were 200 and 450 mg kg⁻¹, for Cu and Zn, respectively. Thus, the mean Zn concentrations found would be higher than the intervention values at all points, and the mean concentrations of Cu would also be higher than the intervention values at km 98. These facts highlight the need to control the possible sources emitting these elements, as well as continuous monitoring of the region.

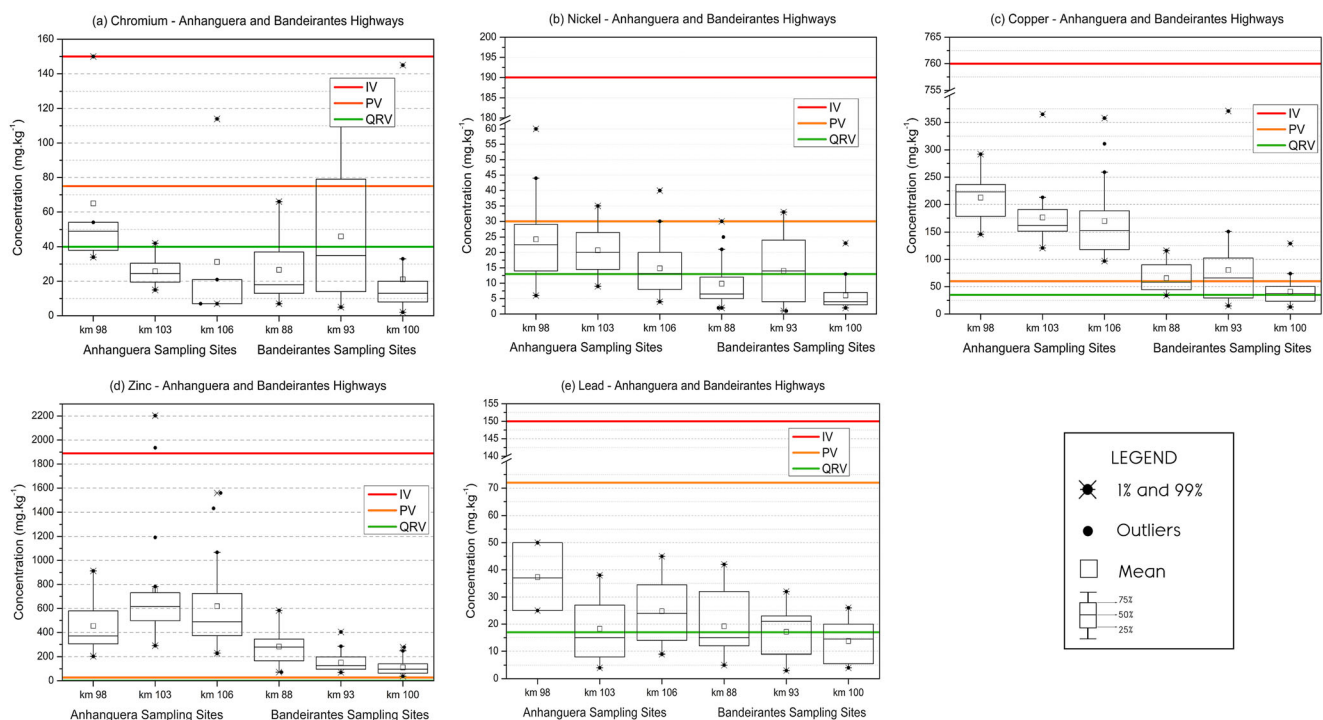


Fig. 3 Summarized descriptive statistics of toxicological interest elements concentrations (mg kg⁻¹) detected by SR-TXRF on Anhanguera and Bandeirantes highways

Table 5 Number of samples and CETESB reference values, according to potentially toxic elements concentrations determined by SR-TXRF

Highways		Number of samples				
		Cr	Ni	Cu	Zn	Pb
Anhanguera	N < QRV	55	22	0	0	44
	QRV < N < PV	3	31	0	0	16
	PV < N < IV	2	7	60	58	0
	N > IV	0	0	0	2	0
Bandeirantes	N < QRV	47	45	17	5	44
	QRV < N < PV	7	14	20	7	16
	PV < N < IV	6	1	23	48	0
	N > IV	0	0	0	0	0

N Number of samples (frequency of samples); QRV Quality Reference Value; PV Prevention Value; IV Intervention Value

Very similar behavior was observed on the Bandeirantes highway, where high concentrations of Cu and Zn were detected, mostly above the values of prevention, indicating the need for continuous monitoring of the site. It is important to note that the average concentrations for Cu and Zn on the Bandeirantes highway were lower than those found on the Anhanguera highway which can be explained by the age of this highway and its more intense traffic (De Silva et al. 2016).

In general, Cr, Ni, and Pb displayed low concentrations and are not of immediate environmental concern in the evaluated locations of the Bandeirantes highway, except at km 93, where some samples presented concentrations of Cr and Ni above the prevention values, indicating the possibility of point sources of these elements in that region.

The mean concentrations of Cu detected at all points on the Anhanguera highway are still higher than the guideline values for Austria, Belgium, Finland, and Slovakia, and the mean concentrations of Zn are higher than the guideline values for Austria, Belgium, Finland, Slovakia, Denmark, and Sweden, as shown in Table 2 (Carlon 2007). On the Bandeirantes highway, Cu concentration was below European values, and Zn, only at km 88, had higher concentrations than those established by Belgium and Finland (Carlon 2007).

The concentrations obtained in each of the 60 collected samples were compared with the Brazilian guiding values and, in Table 5 the frequency of samples (N) are presented in comparison with the CETESB guiding values, that is, the number of samples that had concentrations below QRV (N < QRV), the number of samples that had concentrations higher than the QRV and lower than the PV (QRV < N < PV), the number of samples that presented concentrations higher than the PV and lower than the IV (PV < N < IV) and, finally, the number of samples that had concentrations above IV (N > IV).

In addition to the comparisons with the local guiding values, the I_{geo} values were also calculated for both highways and are presented in Table 6.

Table 6 Geoaccumulation index of potentially toxic elements in Anhanguera and Bandeirantes sampling sites

Location	Cr	Ni	Cu	Zn	Pb
SS1	0.12	0.32	2.01	2.34	0.55
SS2	-1.21	0.09	1.75	3.06	-0.48
SS3	-0.94	-0.40	1.69	2.78	-0.04
SS4	-1.17	-0.99	0.32	1.65	-0.40
SS5	-0.39	-0.48	0.62	0.76	-0.57
SS6	-1.52	-1.67	-0.36	0.31	-0.90

The calculation of the geoaccumulation index confirms the conclusion that the elements Cu and Zn are the main problems encountered on the analyzed highways, especially on the Anhanguera highway, since all evaluated points can be classified as moderately to heavily contaminated due to Zn concentrations and moderately contaminated due to Cu. The results obtained by I_{geo} confirm the comparison with the guiding values of CETESB, which presented Cu and Zn as the elements with the largest number of samples above the prevention value, although just a few have exceeded the intervention values. These results are also consistent with the results found by Zanello et al. (2018) that detected significant contaminations by Zn along a highway in the city of Curitiba, in southern Brazil.

It is important to point out that several studies have used the geoaccumulation index as a way to classify roadside soils. Carrero et al. (2013) were able to determine pollution in surface soils caused by Cd, Cu, Pb, Zn, and Sb in soils close to highways in Spain. In this region, Pb presented $I_{geo} > 4$, due to its use as an additive in gasoline, being the main one responsible for the classification of the soil as heavily to extremely contaminated. In addition to Pb, at some sampling sites, Cu and Zn classified the soils as moderately to heavily contaminated, results similar to those presented in this study (Carrero et al. 2013).

In Eskisehir, Turkey, based on I_{geo} , the soils near the highways were classified as heavily polluted by Cr, Cu, Fe, Mn, Ni, Zn, and Pb. Among all I_{geo} values measured, only values for Cd varied from non-polluted to moderately polluted (Malkoc et al. 2010). There are also studies in which I_{geo} was used to classify roadside soils as uncontaminated, such as the Egyptian soils evaluated by Elnazer et al. (2015).

Table 7 shows average concentrations of the main elements found in surface soils of roads in studies developed throughout the world and the comparison with the concentrations obtained in this study. The mean concentrations obtained in all the samples of this study (60 samples per highway) were calculated, for comparison purposes with the other sites. Online Resource 3 shows the distribution of the elemental concentrations considering the 60 samples in each highway, demonstrating the mean concentrations presented in Table 7.

Table 7 Comparison of mean concentrations of heavy metals (mg.kg⁻¹) on roadside soils in Campinas and other cities

Location	Cr	Ni	Cu	Zn	Pb	Reference
Galway, Ireland	–	22.1	16.6	81.8	40.8	(Dao et al. 2010)
Jeddah, Saudi Arabia	53.3	46.7	–	222.2	47.5	(Kadi 2009)
Ibadan, Nigeria	51.6	38.9	31.4	86.1	307	(Olajire and Ayodele 1997)
Kampala, Uganda	–	–	–	140.9	45.3	(Nabulo et al. 2006)
Beijing, China	61.9	26.7	29.7	92.1	35.4	(Chen et al. 2010)
Tibetan Plateau, China	36.6	35.0	25.1	106.8	24.1	(Wang et al. 2017)
Tibetan Plateau, China	155.5	55.9	24.3	75.6	32.2	(Sheng et al. 2012)
Kavala, Greece	232.4	67.9	172.4	354.8	386.9	(Christoforidis and Stamatis 2009)
Trondheim, Norway	58	43	32	80	32	(Andersson et al. 2010)
Melbourne, Australia	18–29	7–20	–	11–89	16–144	(De Silva et al. 2016)
Shanghai, China	56.1	34.7	41.6	274.6	44.2	(Yan et al. 2018)
Berlin, Germany	–	–	55	172	177	(Kluge and Wessolek 2012)
Chhattisgarh region, India	88	38	31	54	12	(Bilo et al. 2014)
Campinas, Brazil, Anhanguera Highway	38	20	186	608	23	This study
Campinas, Brazil, Bandeirantes Highway	32	10	62	182	17	This study

The comparison with other studies shows very high concentrations of Cu and Zn on Anhanguera highway, which display the highest mean concentrations among all the studies evaluated. The values concentrations obtained for Pb in Anhanguera and Bandeirantes were superior only to those found by Bilo et al. (2014) and similar to those found by Wang et al. (2017). The other elements display average concentrations similar to the other countries already evaluated, and Cr and Ni displayed on Bandeirantes highway the lowest concentrations observed in comparison with the evaluated studies.

Due to the bioaccumulation characteristics, trace metals may remain in the environment and the food chain for a long period of time and, depending on blood levels, may cause adverse health effects. Thus, considering the preservation of the environment and the health of the population, a combination of scientific information and political initiatives is necessary to control the emission within safe and reliable limits.

Relation between elemental concentration and distance from the highway

The soil sampling grid (supporting material—Online Resource 1), with the samples P1, P2, P3, and P4, was developed taking into account the possibility of evaluating the effect that the change of distance from the highway would have on the elementary concentrations. Changes induced by anthropogenic sources decrease with increasing distance from the roadside. At a distance of about 10 m from the highway, there are almost original soil profiles (Kluge and Wessolek 2012), and in some cases, soils are classified as nonpolluted at 3 m of distance of the highway (Carrero et al. 2013). So, it was

initially believed that elemental concentrations would tend to decrease as the distance from the highway increased.

In the Anhanguera samples, the ANOVA test results showed *p* value < 0.05 for Ni, Cu, and Zn, indicating significant differences between the concentrations determined by SR-TXRF, indicating influence of the distance from the highway in the concentrations. The mean concentrations of the elements, as well as the standard error of the mean, are presented in Table 8, with the ANOVA and Tukey tests results. It is important to note that the values of the standard error of the means are not indicative of imprecision in the analytical measurements (which are below 10%), but rather an indication of the high variability of the concentrations obtained. The standard error of the means is a measure of variation of a sample mean relative to the population mean. Thus, it is a measure that helps to verify the reliability of the calculated sample mean. To calculate the standard error of the means, the sample standard deviation was simply divided by the square root of the sample size.

Table 8 ANOVA and Tukey test results for samples collected at different distances (P1 at 30 cm from the highway, P2 at 1.3 m, P3 at 2.3 m, and P4 at 3.3 m)

	P1	P2	P3	P4
Ni Mean concentration (mg kg ⁻¹)	28 ^a	16 ^b	21 ^{ab}	16 ^b
Standard error of the means (mg kg ⁻¹)	4	2	2	2
Cu Mean concentration (mg kg ⁻¹)	229 ^a	182 ^{ab}	162 ^b	172 ^b
Standard error of the means (mg kg ⁻¹)	18	14	9	10
Zn Mean concentration (mg kg ⁻¹)	955 ^a	558 ^b	478 ^b	440 ^b
Standard error of the means (mg kg ⁻¹)	144	76	44	45

Different letters indicate statistical differences between groups (*p* < 0.05)

As already explained, the samples P1, P2, P3, and P4 were collected at different distances, with P1 at 30 cm from the highway, P2 at 1.3 m, P3 at 2.3 m, and P4 at 3.3 m (each sample consists of 5 perforations at the same distance from the highway). The sampling procedure is described in the Figure reported as Online Resource 1 (supporting material).

According to the Tukey test results, Ni, Cu, and Zn showed similar behavior, presenting significant statistical differences between the samples of group P1, located 30 cm from the highway, with the samples of the other groups, which are more distant from the highway, indicating the tendency of decreasing concentration of these metals as the sampling is done at a longer distance from the Anhanguera highway.

The concentration decreasing tendency of the three elements is a strong indication that they are directly related to vehicular traffic, thus presenting higher concentrations when closer to the highways and, consequently, to their probable sources.

For the Bandeirantes highway, no *p* value calculated by ANOVA displayed a significant difference. This can occur due to a lower vehicular influence on the soil quality of the evaluated sites. It is noteworthy that similar behaviors were expected for the other elements in both highways. It is possible that the distance evaluated was very small to detect changes in the concentrations, being important the evaluation of soils of the lateral medians to the highways, where the samplings can be more distant to allow the assessment of the variations of concentrations of the other elements as the collections further away from the highways.

Principal component analysis (PCA)

Applying principal component analysis, four factors with eigenvalues greater than 1.0 were retained, explaining 71.36% and 73.13% of the data variability, respectively, as shown in the supporting material of the manuscript (Online Resource 2) with the factor loadings matrix. The communality values are also presented in the supporting material, that is the proportion of the variance of each variable (in this case the chemical elements) which is related to the common factors in the PCA. The values of commonality demonstrate how well each variable is explained by the factors and the closer the commonality is to 1, the better the variable is explained by the factors. The commonality is calculated by the sum of the squares of the values of each variable (elements) in each of the factors considered in the analysis (Johnson et al. 2002).

On the Anhanguera highway, the first factor associates mainly elements characteristic of the soil constitution, such as Al, Si, S, Fe, and Rb, being possibly the main source of these elements (Alloway 2012). In factor 2, the association of Mn, Cu, and Zn indicates a possible contribution of vehicle emissions associated elements, mainly from the burning of ethanol and gasoline (de Oliveira et al. 2002; Bergamini

et al. 2006). Another possible source of Zn are the guardrails and traffic signals (Thorpe and Harrison 2008; Carrero et al. 2012, 2013). It is worth mentioning that the presence of K, Ca, Ti, and Sr can also be related to the natural soil composition. In factor 3, the association of Cr, Ni, and Pb also shows a probable contribution from sources related to vehicular traffic, mainly to the burning of diesel oil and parts abrasion (Tomanik 2000; Wang et al. 2003; Winther and Slentø 2010; Carrero et al. 2013), or even industrial emissions. It is worth noting that in Brazil, the addition of Pb to gasoline has no longer been allowed since 1992, but the element is still related to vehicular emissions mainly due to the burning of oils and wear of parts. Factor 4 presents only the Cl element, which may be associated to a point source, more likely to come from industrial emissions (Ma et al. 2016; Xu et al. 2016).

On the Bandeirantes highway, as well as on Anhanguera highway, the first factor associates mainly elements characteristic of the soil constitution, such as Al, Si, S, K, Ti, Fe, and Rb. In addition to these elements, elements like Cr, Ni, and Cu appear, which are elements that may be naturally present in soils, but in very low concentrations, being more commonly related to vehicular emissions, mainly with gasoline burning and wear of automotive parts (de Oliveira et al. 2002; Bergamini et al. 2006). The fact that these elements appear grouped may suggest that the concentrations of Cr, Ni, and Cu may be natural, having a lower vehicular influence on this highway. This is the main difference between the PCA results of the studied roads, since in Anhanguera Highway, factor 1 presented exclusively elements characteristic of the soil constitution, maintaining Cu, Cr, and Ni in factors 2 and 3, more related to vehicle emissions, although with the presence of soil related elements, as previously discussed. The second factor on Bandeirantes analysis groups Ca and Zn, which can be an indication of the influence of the burning of gasoline and mainly of ethanol, since Zn is one of the main pollutants of this fuel (de Oliveira et al. 2002), or also the influence of guardrails and traffic signals (Thorpe and Harrison 2008; Carrero et al. 2012, 2013). In the third factor, the association of elements such as Mn and Pb can be indicative of burning diesel oil and gasoline (Tomanik 2000; Wang et al. 2003; Winther and Slentø 2010). Finally, factor four presents only the elements Cl and Sr, which, as evaluated on the Anhanguera Highway, may originate from some point source, and may be related to industrial emissions (Sillassen et al. 2014; Chen et al. 2015; Ma et al. 2016; Xu et al. 2016).

Conclusions

The SR-TXRF technique allowed the evaluation of the composition of the topsoil of the medians of the main access roads to Campinas City. Sixteen elements were detected, out of which five are considered potentially toxic elements of

environmental interest (Cr, Ni, Cu, Zn, and Pb). The concentrations of Cr, Ni, Cu, Zn, and Pb exceeded the quality values established by CETESB in at least one sample. However, the Igeo results show no problems related to Cr, Ni, and Pb, since the results for these elements classify the analyzed soils as uncontaminated. On the other hand, Cu and Zn are the most worrying elements from the environmental point of view, since they displayed concentrations higher than the prevention values established by the CETESB, in the majority of the analyzed samples of the two highways. This statement is further confirmed by the results of the I-geo index, which classify the soils analyzed on Anhanguera as moderately contaminated by Cu and moderately to heavily contaminated by Zn.

All the results for the elements Ni, Cu, and Zn obtained on Anhanguera demonstrated a decrease in the concentrations of these elements as the sampling sites move away from the highway, thus indicating that their emission sources are related to vehicular traffic of the highways. On the Bandeirantes highway, there was no influence of the distance of the highway in the elementary concentrations, thus demonstrating a lower correlation between the concentrations detected and the vehicle flow.

In comparison with other studies, it is possible to verify that the concentrations of Cu and Zn found on the Anhanguera highway are very high, being the one with the highest values in all the studies compared and also higher than the guiding values established in several European countries. The concentrations of these elements on the Bandeirantes highway samples are similar to the values found in the other studies.

It was possible to identify the main sources of pollutant emissions, being related mainly to the traffic of automotive vehicles, with characteristic elements of the burning of ethanol, gasoline, diesel oil, and even the wear of parts, as well as industrial emissions.

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