



Research article

Background concentrations and quality reference values for some potentially toxic elements in soils of São Paulo State, Brazil



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ABSTRACT

Quality reference values (QRV) for potentially toxic elements (PTE) in soils are established as a tool for prevention and monitoring of soil pollution. These values should be periodically revised in order to ensure soil safety for agricultural purposes. Brazil is market leader for several commodities; therefore, the safety of Brazilian soils is of worldwide strategic importance. The objective of this study was to determine the natural background concentrations and the QRV for As, Ba, Cd, Cr, Ni, Pb, Se, and Zn by investigating 30 representative pedotypes in the São Paulo State, one of the most important agro-industry economy at worldwide level. Multivariate statistical analysis was applied to determine the sources of PTE and their variability. The mean natural background concentrations of PTE in the soils were generally lower to those reported in literature. QRV, calculated for each element as the 75th and 90th percentiles, were lower (75th for As, Cd, Pb, and Zn), similar (75th for Ba, Cr, and Se) or above (90th for Ba, Cr, and Se and 75–90th for Ni) those previously proposed by the Brazilian environmental protection agencies. The results indicate that 75th percentile may be too restrictive. The PTE in the investigated soils appear to have come mainly from two primary natural sources: a prevalent one of geogenic and a secondary of pedogenic origin. These results confirm the predominant natural source of selected PTE in the investigated soils, thus sustaining the possibility of using the data set to develop QRV for the State of São Paulo.

1. Introduction

The term potentially toxic elements (PTE, Alloway, 1995) is referred to a group of elements, such as As, Ba, Cd, Cr, Ni, Pb, Se, and Zn. This term is more inclusive and appropriate than toxic or heavy metals as it embraces metals, metalloids, nonmetals and other elements in soil-plant-animal systems (Coppola et al., 2010). PTE occurs naturally in soils and are influenced by both natural factors (parent materials and pedogenesis) and anthropogenic activities (Zhao et al., 2007).

Environmental monitoring of PTE is important for controlling their concentrations in the environment, particularly in agricultural soils (Chrzan, 2016). The natural background concentrations of PTE in soils

with no or minimal human influences, represent an important level used for establishing threshold values in order to differentiate contaminated from “clean” soils (Coppola et al., 2010). These values can serve as legislative tools for developing guideline values for soil pollution prevention, control and, remediation activities if necessary.

The Brazilian legislation has been characterized by a very innovative regulatory approach in the last decade and establishes the following three guiding values: 1) quality reference (QRV) representing the natural concentrations of chemical elements in soils without anthropic influence, i.e., soil background concentration; 2) a prevention value (PV) representing a sort of alert; and 3) an intervention value (IV) for agricultural, residential, and industrial areas (threshold value).

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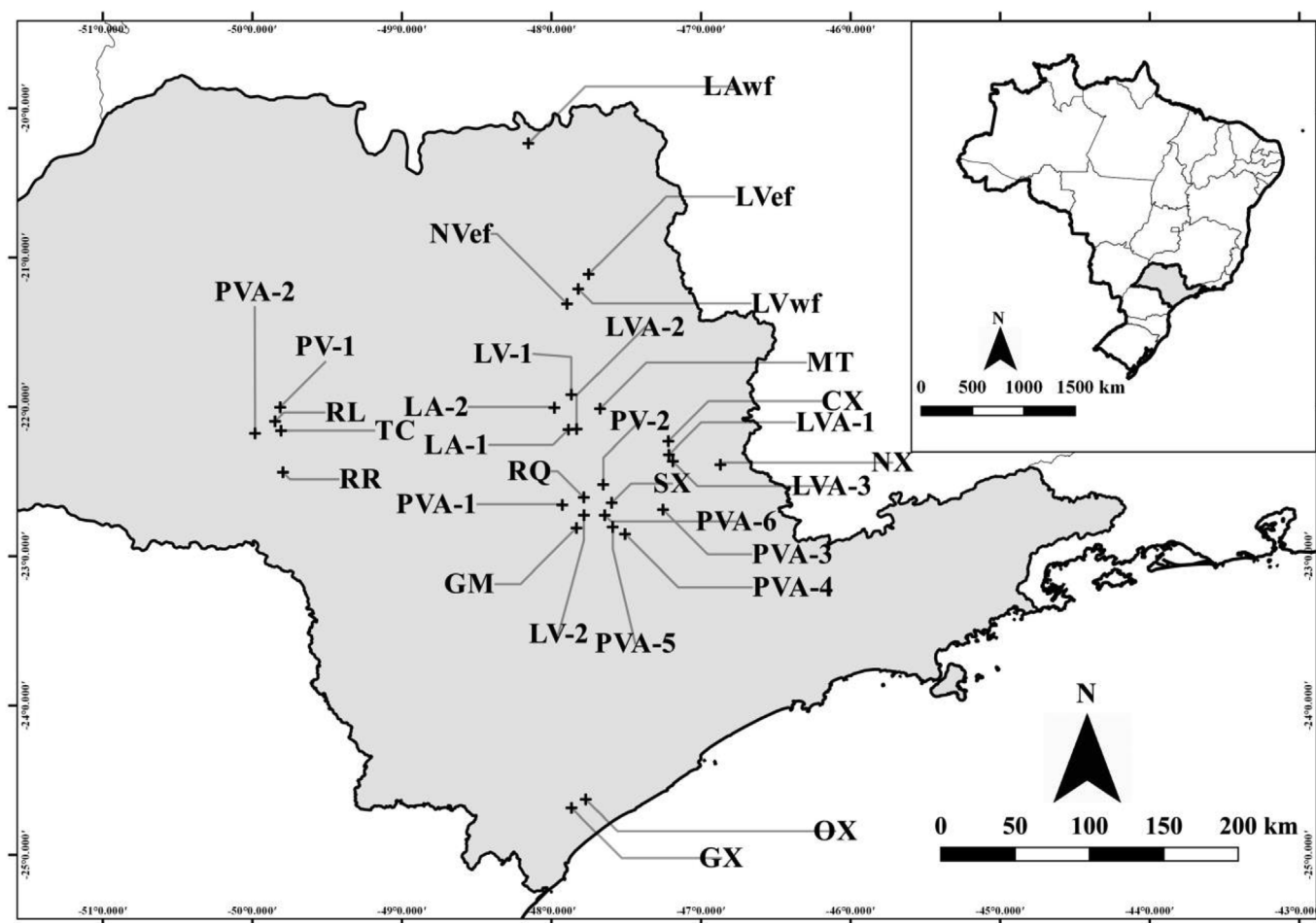


Fig. 1. Study area and sampling locations in São Paulo State, Brazil.

While the PV and IV are established by the CONAMA Resolution (human health-based risk), and valid for the whole country, whereas QRV must be determined by each state (CONAMA, 2009). Consequently, studies have been carried out to establish QRV for some Brazilian regions (Paye et al., 2010; Biondi et al., 2011; Santos and Alleoni, 2012; Gabos et al., 2014; Oliveira et al., 2014; Preston et al., 2014; Almeida Júnior et al., 2016; Silva et al., 2017). However, a lot of areas have been partially or totally neglected. This cannot be considered as a Brazilian concern only; Brazil is market leader for several commodities such as corn (*Zea mays* L.), sugarcane (*Saccharum officinarum* L.) for sugar and ethanol production, meat, coffee (*Coffea* sp.), soybean (*Glycine* sp.) and ethanol, which have been exported to worldwide (USDA, 2017), making Brazil the “breadbasket of the world” (Seibel, 2007). Therefore, the safety of Brazilian soils for agricultural production is of worldwide strategic importance for food safety.

QRV are established through statistical interpretation of natural concentrations in soil samples from a specific region, taking into account soil types and physical-chemical properties (Malkoc and Yazici, 2017). Since the Brazilian territory is extremely wide, being the 5th largest country in the world, with a consequent huge pedovariability, it is essential to assess the PTE natural background concentrations at a regional scale. This is crucial in order to establish reliable limits between natural and anthropogenic concentrations. In the absence of PTE background values, Brazilian environmental protection agencies still use international generic values (CETESB, 2014, 2016). This is a rather paradoxical situation since such values were often established for totally different conditions, in terms of both geological and pedological processes. Consequently, the use of these values may lead to incorrect risk estimation and subsequent socio-economic consequences.

Few studies have been carried out to validate the existing guiding values (CETESB, 2014, 2016). The aim of the present study was to determine the natural background concentrations and the QRV for As, Ba, Cd, Cr, Ni, Pb, Se, and Zn in representative pedotypes of São Paulo State, representing the most important area of Brazil in terms of economy and agricultural activities and one of the most important agro-industry economy at worldwide level (IBGE, 2014). Additionally, multivariate statistical analysis was applied to determine the origin of the observed variability and to distinguish the main sources of the investigated PTE.

2. Materials and methods

2.1. Study area

The study area is located in the São Paulo State, Brazil (Fig. 1). It is characterized by 44 million inhabitants living in an area of around 250,000 km² (Gabos et al., 2014), representing the Brazil's biggest consumer market and agro-industry economy, contributing 33% of the Brazilian Gross National Product (IBGE, 2014).

According to Köppen the climate is strongly influenced by relief variation: tropical wet and dry (Aw) in the shore coastline (mean T 20°–22 °C; mean P 4154 mm); humid subtropical (Cwa) in the plateau (20 °C; 1300 mm); tropical wet and dry (As) in the northwest region (24 °C; 1000–1250 mm); humid subtropical (Cfa) in the south region (18°–20 °C; 1500 mm). The natural vegetation is dominated by Atlantic forest along the shores and around the plateau. The remaining areas had fragments of semideciduous forest and a vegetation including formations of the Cerrado biome, such as clean grass fields, grassland with

Table 1Physical and chemical attributes of soil samples from São Paulo State, Brazil ($n = 30$).

	Min	Max	Mean	Median	SE
pH _(H2O)	4.0	7.3	5.2	5.3	0.1
pH _(KCl)	3.2	6.7	4.2	4.0	0.1
Clay (g kg ⁻¹)	40	716	305	245	35
Silt (g kg ⁻¹)	20	448	212	207	25
Sand (g kg ⁻¹)	75	880	482	530	45
OC (g kg ⁻¹)	6.7	213.4	45.3	33.3	9.0
P (mg kg ⁻¹)	1.1	76.3	11.6	5.2	3.0
CECt (mmol _c kg ⁻¹)	7.0	137.8	51.8	43.4	6.6
CECe (mmol _c kg ⁻¹)	4.9	105.5	33.2	23.8	4.4
K (mmol _c kg ⁻¹)	0.3	5.2	1.7	1.2	0.2
Ca (mmol _c kg ⁻¹)	1.3	82.1	17.8	12.2	3.5
Mg (mmol _c kg ⁻¹)	0.6	25.2	7.1	5.1	1.2
Al (mmol _c kg ⁻¹)	0.7	41.0	6.6	1.4	1.9
H + Al (mmol _c kg ⁻¹)	3.0	124.2	25.1	16.7	4.9
SB (mmol _c kg ⁻¹)	2.5	104.5	26.6	18.2	4.7
BS (%)	7	95	49	53	5
m (%)	1	81	28	16	5.4
SiO ₂ -AE (g kg ⁻¹)	13.5	236.8	99.9	93.5	12.0
Al ₂ O ₃ -SA (g kg ⁻¹)	9.8	247.9	96.0	69.0	13.6
Fe ₂ O ₃ -SA (g kg ⁻¹)	6.8	331.8	76.1	29.6	17.8
Mn ₂ O ₃ -SA (g kg ⁻¹)	0.10	3.80	0.82	0.40	0.18
TiO ₂ -SA (g kg ⁻¹)	1.5	45.1	12.7	6.6	2.6
Fe ₂ O ₃ -OXA (g kg ⁻¹)	0.2	19.3	3.9	1.7	0.9
Al ₂ O ₃ -OXA (g kg ⁻¹)	0.2	9.9	2.4	1.1	0.5
Mn ₂ O ₃ -OXA (g kg ⁻¹)	0.00	3.25	0.41	0.09	0.14
Fe ₂ O ₃ -CBD (g kg ⁻¹)	3.0	208.2	48.3	20.5	10.7
Ki	0.8	4.5	2.2	2.2	0.2
Kr	1.4	4.6	2.7	2.5	0.1

SA = sulfuric acid digestion; AE = alkaline extraction; OXA = ammonium oxalate; CBD = sodium dithionite-citrate-bicarbonate; SE = standard error.

shrubs, and the Cerrado *strictu sensu* (short savannah, mainly arbustive and herbaceous), and the forest formation of “cerradão” (closed savanna approaching a forest). The dominating soil types are Oxisols, Ultisols, Alfisols, Entisols, Inceptisols, Histosols, and Mollisols (Supplementary file 1).

2.2. Soil sampling and analysis

Surface soil samples (A horizon, 0–20 cm) from 30 representative soil profiles were collected in the areas of native vegetation and/or ancient reforestation (Fig. 1). These profiles were selected according to a preliminary GIS (by consulting and assessing soil, geological, and geomorphological maps) and field campaign (aiming to identify the more representative pedotypes). At the end, 30 locations were selected for soil profile sampling in order to ensure that the main geological, geomorphological and pedological conditions were represented (Supplementary file 1). This phase was crucial for investigating natural soils that are representative of the lithology, topography, and climate of the investigated state. Although the conditions of environments totally free from anthropic influence are rarely found, this is the first step to identify natural conditions.

The selected Pedons were described using standard soil survey methodology (Schoeneberger et al., 2012) and classified according to Soil Survey Staff (2014).

Soil physical-chemical analyses were performed on air-dried < 2 mm soil according to the official Brazilian procedures (Raij et al., 2001) in compliance with international standards. The densimeter method was used for particle-size analysis. Soil pH was measured potentiometrically in a soil/solution mixture of 1:2.5 H₂O, 1:2.5 1 M KCl. Organic carbon (OC) content in soil was estimated by the Walkley-Black method. Available amounts of P, Ca²⁺, K⁺ and Mg²⁺ in soils were estimated by an ion-exchange resin procedure. Phosphorous concentration in soil extracts was quantified by colorimetric method; Ca and Mg were determined by atomic absorption spectrophotometer

(AAS) (VARIAN SpectrAA 220FS), while K in a flame-photometer (METEOR NAK-II). Exchangeable Al was extracted and determined with 1 M KCl and 0.025 M NaOH solutions, respectively. Total acidity (H + Al) was extracted with buffer solution of calcium acetate pH 7.0 and determined by titration with ammonium hydroxide (0.025 M). From these values, the sum of exchangeable cations (SB = Ca²⁺ + Mg²⁺ + K⁺), the total cation exchange capacity (CEC) at pH 7.0 [CEC_T = SB + (H + Al)], saturation of exchangeable cations [BS% = (SB x 100)/CEC_T] and aluminum saturation [$m\% = (Al^{3+} \times 100)/(SB + Al^{3+})$] were obtained.

Iron, Al, Mn, and Ti contents in soil, expressed as oxides (Al₂O₃, Fe₂O₃, TiO₂, and MnO), were extracted using 9 M H₂SO₄. Silicon was determined with 1 M NaOH and expressed as SiO₂. Fe, Mn, and Al concentration in the extracts were determined using AAS, Ti by colorimetry and Si by gravimetry. Ki (SiO₂%x1.7/Al₂O₃%) and Kr (SiO₂%x1.7/[Al₂O₃% + (Fe₂O₃%x0.64)]) indexes were used to indicate the degree of weathering of the soils and the degree of alteration of minerals in soils, respectively.

Sodium dithionite–citrate–bicarbonate solution was used to extract the well crystalline contents of iron from iron oxides; the concentration of poorly crystalline oxides of Fe, Al, and Mn was extracted by oxalate extraction at pH 3.

2.3. PTE extraction method and quality control

All investigated PTE (As, Ba, Cd, Cr, Ni, Pb, Se, and Zn) were extracted according to USEPA-3051A (USEPA, 2007), which is the official method for determining QRVs for Brazilian soils. In brief, 0.5 g of sieved samples ($\phi < 0.2$ mm) was transferred into Teflon digestion vessels, and 10 mL of concentrated HNO₃ (ICP-MS grade) was added and left to react for 15 min. Next, the tubes were sealed and placed in a microwave oven (TC plus labstation, Milestone, Sorisole, Italy) set at 260 W and 415 kPa for 10 min at 175 °C. The extracts were cooled to room temperature and then filtered and diluted with type 1 water (resistivity at 25 °C ≥ 18.2 M Ω cm, TOC ≤ 5 μ g L⁻¹, prepared using a Milli-Q purification system – Millipore, Bedford, MA, USA) in 50 mL round-bottomed flasks. PTE in the digests were determined by inductively coupled plasma mass spectrometry (ICP-MS) (Model Agilent 7500ce).

All analyses were carried out in triplicates and blank samples were analyzed simultaneously. In order to ensure very low limits of detection all acids, reagents and water were ICP-MS compatible grade. The detection limit (DL) was calculated according to INMETRO (2003). Standard reference materials (SRM 2709a – San Joaquim and SRM 2710 – Montana Soil) were used to assure the accuracy and precision of the analytical methods. The recovery of metals in SRM was within 89–124%, representing the recommended range for the investigated elements (USEPA, 1996).

2.4. Statistical analysis

Univariate and multivariate statistical analysis were performed using the version 9.2. of SAS (SAS Institute, 2010) and 4.0 of CANOCO software programs (Ter Braak and Smilauer, 1998).

As recommended by CONAMA (2009), the following procedure was adopted to establish QRV: i) anomalous values (outliers) were removed, before any further elaboration, by identifying them through a boxplot analysis; ii) QRV were established based on 75th and 90th percentile (sample universe).

Correlation matrix (CM) was elaborated to understand the PTE-soil properties relationships. Pearson's product moment correlation coefficient was used for Box-Cox transformed data with statistical significance determined with the Student's *t*-test (Capra et al., 2014).

A principal component analysis (PCA) was performed to select the (group of) soil attributes that affect PTE natural concentrations in the soil in terms of both variability and main sources. PCA is a technique that indicates associations between variables by reducing the size of the

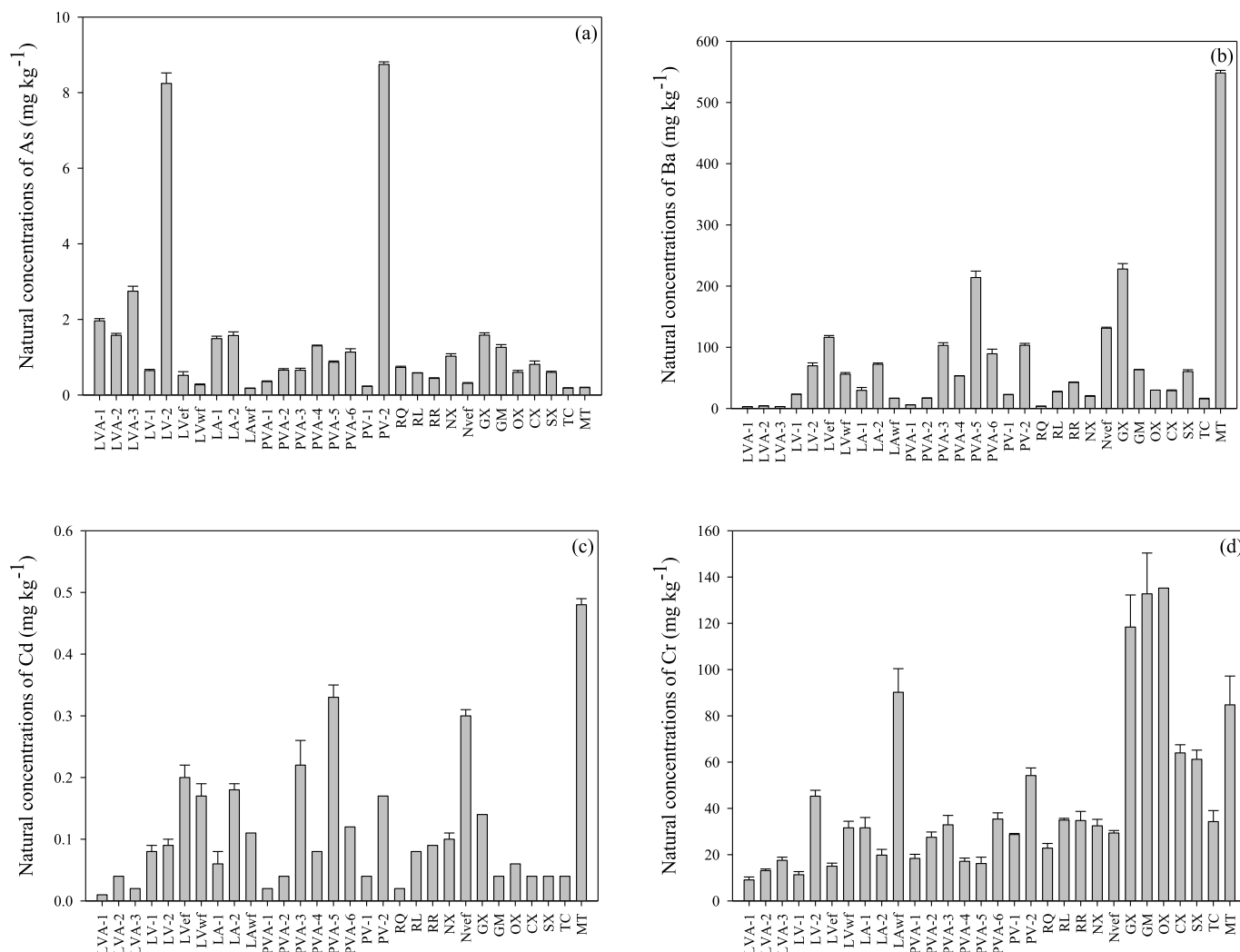


Fig. 2. Concentrations of As (a), Ba (b), Cd (c) and Cr (d) in natural soils from São Paulo State, Brazil.

number of data, conserving most of the useful statistical information present in the original data, and grouping them with greater similarity (Capra et al., 2014). Biplots were applied to establish crucial variables. The PTE were used as response variables while physical-chemical soil parameters used as explanatory variables. In the biplots both PTE and soil physical-chemical parameters are represented by arrows, indicating the direction of the maximum gradient in which the length of the arrow is proportional to the correlation of the characteristic with the axes and their importance in explaining the variance projected on each axis.

Values in the text indicate the mean $\pm$ standard error of the mean.

3. Results and discussion

3.1. Soil physical-chemical properties

According to the huge pedovariability of selected representative soils (Supplementary file 1), a great variability was recorded in terms of physical-chemical and mineralogical properties (Table 1). The pH-H₂O ranged from 4.0 to 7.3, with a mean of 5.2 ± 0.1 , indicating the prevalence of acidic soils. The delta pH values (pH_{KCl}-pH_{H2O}) were negative for all the investigated pedotypes, showing that these soils were dominated by negative surface charges.

Data on particle size distribution (Table 1) shows a clay content ranging 40–716 g kg⁻¹ (mean 305 ± 35 g kg⁻¹), a silt content ranging 20–448 g kg⁻¹ (212 ± 25 g kg⁻¹) and a sand content ranging

75–880 g kg⁻¹ (482 ± 45 g kg⁻¹); consequently, soil texture varied considerably among the pedons with a mean prevalence of the loam one. Both OC and P contents were generally low, averaging 45.3 ± 9.0 g kg⁻¹ and 11.6 ± 3.0 mg kg⁻¹, respectively. Values for total CEC ranged from very low to very high with mean of 51.7 ± 6.6 mmol_c kg⁻¹; however, the effective CEC, expressing the soil's expressing the soil's ability to retain cations when near the value of its natural pH, was generally low (Table 1). In agreement with values observed for CEC and exchangeable cations, even base saturation (BS) greatly varied from very low (7%) to high (95%) values, averaging $49 \pm 5\%$. According to mean values of the investigated oxides, they were representative of well developed and weathered soils of the tropical areas, as evidenced by their high weathering indexes (Ki and Kr of 2.2 ± 0.2 and 2.7 ± 0.2 ; respectively).

3.2. Natural concentrations of PTE

The mean natural background contents for selected PTE varied considerably among the investigated pedotypes (Figs. 2–3), with the following range of variation, in mg kg⁻¹: As = 0.2–8.8, Ba = 2.9–548.3, Cd = 0.01–0.48, Cr = 9.1–135.2, Ni = 6.3–177.5, Pb = 2.0–50.6, Se = 0.01–0.70, and Zn = 4.0–68.5.

The lowest PTE contents were observed in Oxisols and Entisols. They were in agreement with the main pedological and mineralogical properties since these soils are usually sandy. Soils developed on

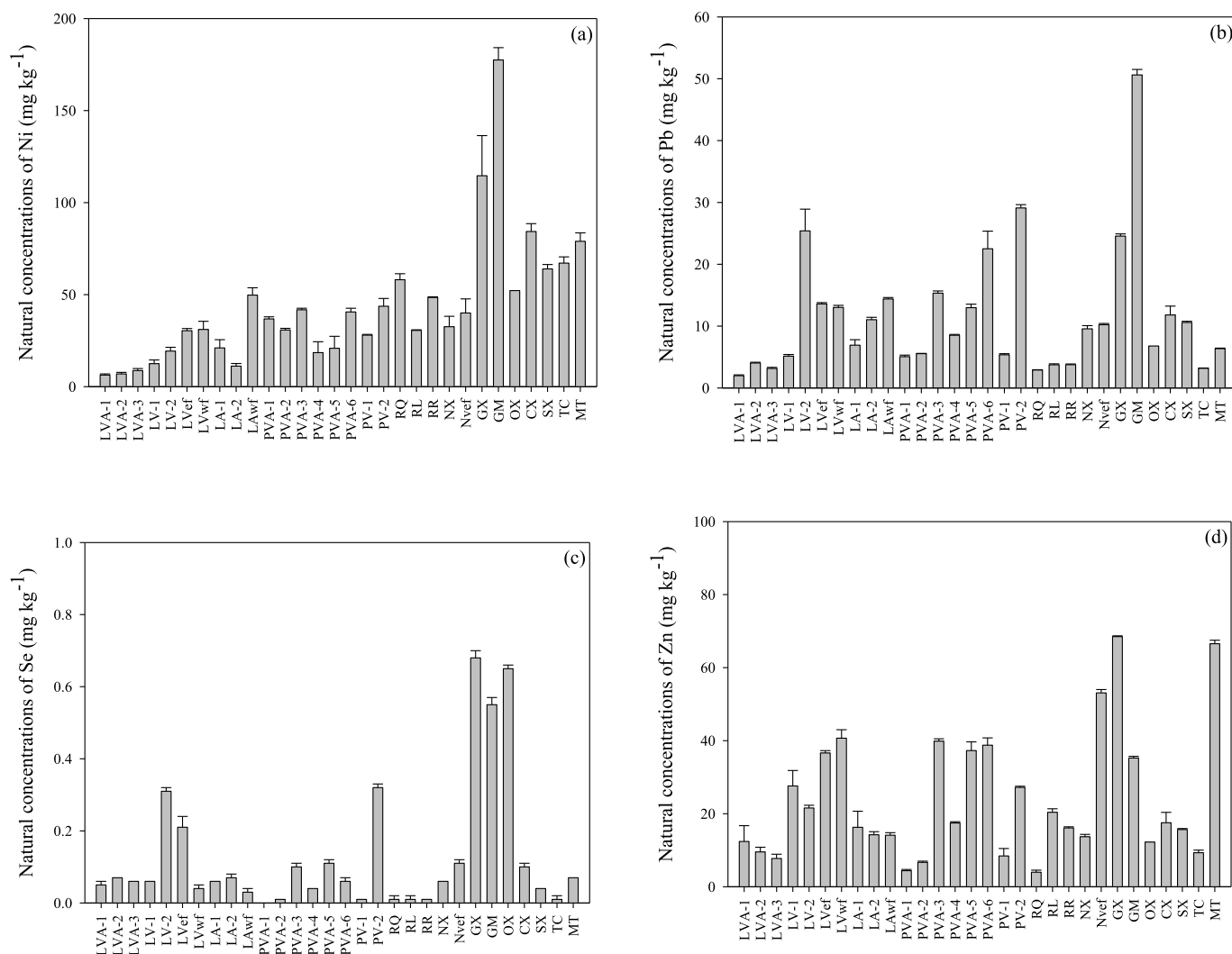


Fig. 3. Concentrations of Ni (a), Pb (b), Se (c) and Zn (d) in natural soils from São Paulo State, Brazil.

sedimentary and crystalline acid igneous rocks usually contain lower contents of PTE, as compared with those derived from basic rock, particularly those naturally enriched in metals (such as mafic rocks; [Paye et al., 2010](#)). The highest levels of PTE were generally observed in Mollisols, Histosols, Entisols, Inceptisols, Alfisols and Ultisols, all developed on basic igneous rocks such as basalt and diabase, richer in metals ([Brazil Geological Service, 2004](#)). These results are consistent with those obtained by [Lopes \(2009\)](#) and [Biondi et al. \(2011\)](#), showing that even under severe climatic conditions such as in the humid tropics, parent materials still play an important role in determining the content of most heavy metals in soils. On the other hand, the influence of pedogenesis cannot be neglected or underestimated, considering that the mean contents of PTE widely varied between samples of different Orders and within the same Order (Figs. 2–3). As a matter of fact, the increase in PTE concentration in the investigated soils is not only influenced by parent material, but also by the complexation of these metals with soil organic matter and adsorption onto silicate minerals/oxides in oxidic soils ([Kabata-Pendias and Mukherjee, 2007](#)). In addition, the high contribution of soil texture to the natural metal content was evident ([Supplementary file 1](#)). As a matter of fact, soils of loamy (Oxisols) and sandy (Entisols) texture generally had the lowest PTEs concentration relative to clayey soils (Alfisols and Ultisols).

The mean natural background contents of PTE in the soils were in the following order, in mg kg^{-1} : 54 (Ba) > 36 (Cr) = 36 (Ni) > 22 (Zn) > 10 (Pb) > 1.4 (As) $\gg$ 0.1 (Cd) = 0.1 (Se). These values are

usually lower or close to those reported for soils of other countries and/or other Brazilian states ([Table 2](#)). This demonstrates that the selected pedotypes belong to natural areas where the human impact was low and consequently, they can be considered as adequate benchmarks for PTE natural background values in the State of São Paulo. From a pedo-geochemical point of view, these values reflect the low content of these metals in the parent materials of the State of São Paulo, mainly composed of metamorphic and sedimentary rocks ([Oliveira et al., 2014](#)).

3.3. Soil quality reference values

Since the natural background concentration of PTE had been quantified, the next step was to establish their normal distribution by using a box-plot analysis. This must be done (*vide supra*) in order to satisfy the following criteria ruled by Brazilian law: 1) removal of anomalous values, i.e., outliers, and 2) individuation of the 75th and the 90th percentile. The Brazilian legislation ([CETESB, 2014](#)) suggested that each state can select one of the two percentiles; however, the 75th is generally preferred by local governments and environmental agencies, because with the exclusion of 25% of the highest values it is considered more conservative and environmental-friendly; whereas, the 90th percentile is usually preferred by private companies and some scholars ([Santos and Alleoni, 2013](#)). Indeed, data used to obtain QRVs comes from soils that are broadly representative of a region;

Table 2Mean concentrations of PTE (mg kg⁻¹) in natural soils from São Paulo State, as compared to the data compiled from the literature.

Soils	As	Ba	Cd	Cr	Ni	Pb	Se	Zn
<i>International</i>								
Australia ^a	NA	NA	1.0	100.0	60.0	150.0	NA	1400.0
China ^a	9.2	450.0	0.07	53.9	23.4	23.6	NA	67.7
USA ^a	5.2	440.0	1.6	37.0	12.4	16.0	NA	48.0
Cuba ^b	10.8	128.7	1.2	463.2	294.2	34.6	NA	90.7
Spain ^c	13.0	277.3	NA	38.1	36.2	46.9	NA	69.1
World soils ^d	0.5–80.0	84–960	0.01–2.0	5–1500	2–750	2–750	0.05–0.50	1–900
<i>Brazilian</i>								
Minas Gerais ^e	17.8	190.9	0.5	100.1	30.1	3.9	NA	13.1
Paraná ^f	7.2	NA	0.18	105.0	34.1	23.2	NA	75.2
Espírito Santo ^g	6.8	NA	BDL	41.1	6.6	8.8	NA	22.6
Mato Grosso e Rondônia ^h	NA	NA	BDL	39.4	1.3	8.1	NA	6.8
Rio Grande do Norte ⁱ	NA	43.9	0.07	23.0	14.0	10.9	NA	17.9
São Paulo ^j	1.34	NA	0.2–1.5	NA	NA	NA	0.19	NA
<i>This study</i>								
São Paulo	1.38	54.1	0.1	36.6	36.0	10.1	0.12	21.8

NA = not available; BDL = below the detection limit.

^a Chen et al. (1991).^b Alfaro et al. (2015).^c Tume et al. (2006) and Díez et al. (2009).^d Alloway (1995) and Kabata-Pendias and Mukherjee (2007).^e Caires (2009).^f MINEROPAR (2005).^g Paye et al. (2010).^h Santos and Alleoni (2012).ⁱ Preston et al. (2014).^j Gabos et al. (2014) and Oliveira et al. (2014).**Table 3**Soil quality reference values (QRVs) for some PTE in São Paulo State, Brazil ($n = 30$).

Variable	As	Ba	Cd	Cr	Ni	Pb	Se	Zn
	mg kg ⁻¹							
Mean	1.38	54.15	0.10	36.66	36.05	10.11	0.12	21.84
Maximum	8.75	131.23	0.22	90.16	67.11	22.51	0.70	40.68
Minimum	0.18	15.72	0.04	15.02	11.16	4.04	0.01	8.43
QRV/P 75 ^a	1.4	72	0.1	38	46	13	0.11	31
QRV/P 90 ^a	2.0	103	0.2	63	57	15	0.32	38
State of São Paulo, Brazil ^b	3.5	75	< 0.5	40	13	17	0.25	60

 n = number of analyzed samples.^a QRVs proposed in this research obtained by the USEPA 3051A method, which is the official method for determining QRVs for Brazilian soils.^b QRVs established by CETESB (2014) for managing contaminated areas.

consequently, “anomalous” values could simply represent the natural pedovariability.

Considering both quartiles (Table 3), the QRVs for As (75th = 1.4 mg kg⁻¹; 90th = 2.0 mg kg⁻¹), Cd (0.1 mg kg⁻¹; 0.2 mg kg⁻¹), Pb (13 mg kg⁻¹; 15 mg kg⁻¹), and Zn (31 mg kg⁻¹; 38 mg kg⁻¹) are lower than that adopted by CETESB (2014). Values reported in this study come from really representative pedotypes under natural conditions. So, the current limits established by CETESB (2014) for these elements are extremely consistent. A different situation can be observed for Ba (72 mg kg⁻¹; 103 mg kg⁻¹), Cr (38 mg kg⁻¹; 63 mg kg⁻¹), and Se (0.11 mg kg⁻¹; 0.32 mg kg⁻¹). The 75th percentile was similar to QRV proposed by CETESB (São Paulo State; CETESB, 2014), but higher if the QRV is ruled in agreements with the 90th percentile. The situation for Ni is even more different, since both percentiles (46 mg kg⁻¹; 57 mg kg⁻¹) were higher than QRVs adopted by CETESB (2014). For all these elements, but with particular reference for Ni, the QRV established by CETESB seems too restrictive and a little bit far from the real pedogeochemical conditions of the natural pedotypes

characterizing the area. As a matter of fact, in most of the investigated pedons (Fig. 3a) the Ni concentration show a natural tendency towards high values, with the highest reached in clayey (such as Alfisols) and organic enriched (such as Mollisols and Alfisols) soils. Just in very few cases (Fig. 3a) Ni natural concentration was lower than 30 mg kg⁻¹, and all these pedons were highly alternated, poor in organic matter content, and sandy-loam in texture (Oxisols). Previous studies have observed a close natural relationship between increments of Ni in soils according to clay, organic matter and, consequently, CEC content (Kabata-Pendias and Mukherjee, 2007). Such high values were mainly attributed to natural origins, as demonstrated by the correlation matrix (Table 4) where a significant relationship ($p < 0.01$) was observed between Ni vs. total CEC ($r = 0.52$) and OC ($r = 0.60$).

The QRVs determined in this study can be different from those of other states with different pedogeochemical, climatic, and land use conditions that affect natural background PTE concentration in soil. For instance, the QRV established by the State of Paraná (southern Brazil) is similar to that of this study for As (1.4 mg kg⁻¹) (Alleoni et al., 2013); however, the corresponding QRV in the State of Minas Gerais (central-eastern Brazil; 8.0 mg kg⁻¹) is 471% higher and Pernambuco (north-eastern Brazil; 0.6 mg kg⁻¹) 57% lower (CPRH, 2014), as compared to this study (considering the 75th percentile). For soils of the State of Espírito Santo (south-eastern Brazil), Paye et al. (2010) suggested QRV for Cd (< 0.13 mg kg⁻¹) and Zn (30 mg kg⁻¹), which are close to those observed in the present study; on the other hand, the QRVs for Ni (9.17 mg kg⁻¹) and Pb (< 4.54 mg kg⁻¹) were respectively 402% and 186% lower. In soils of Mato Grosso and Rondônia (southwestern Amazonian Brazil), Santos and Alleoni (2012) established QRVs for Ni (2.1 mg kg⁻¹), Pb (9.0 mg kg⁻¹), and Zn (3.0 mg kg⁻¹), which are below those obtained in this study. In soils of Rio Grande do Norte (north-eastern Brazil; Preston et al., 2014), the QRVs are lower for Ba (59 mg kg⁻¹), Cr (31 mg kg⁻¹), Ni (20 mg kg⁻¹), and Zn (24 mg kg⁻¹), but similar for Cd (0.1 mg kg⁻¹), as compared to this study. In Pernambuco, the QRVs established for Cr (35 mg kg⁻¹), Pb (13 mg kg⁻¹), and Zn (35 mg kg⁻¹) are similar or close to those reported in the present study (CPRH, 2014).

Table 4Pearson correlation matrix between soil attributes and concentrations of PTE in the natural soils of São Paulo State, Brazil ($n = 30$).

Variable	As	Ba	Cd	Cr	Ni	Pb	Se	Zn
As	1.00							
Ba	ns	1.00						
Cd	ns	0.87**	1.00					
Cr	ns	ns	ns	1.00				
Ni	ns	ns	ns	0.78**	1.00			
Pb	0.42*	ns	ns	0.55**	0.64**	1.00		
Se	ns	ns	ns	0.77**	0.56**	0.63**	1.00	
Zn	ns	0.79**	0.77**	ns	0.39*	0.43*	0.39*	1.00
OC	ns	ns	ns	0.75**	0.60**	0.59**	0.80**	ns
pH _(H2O)	ns	ns	ns	ns	ns	Ns	ns	ns
P	ns	ns	ns	0.51**	ns	Ns	0.69**	0.36*
K	ns	0.45*	0.66**	ns	ns	Ns	ns	0.70**
Ca	ns	0.83**	0.86**	ns	ns	Ns	ns	0.72**
Mg	ns	0.62*	0.70**	ns	ns	Ns	ns	0.67**
Al	ns	ns	ns	0.70**	0.51*	0.46*	0.72**	ns
H + Al	ns	ns	ns	0.81**	0.62**	0.61**	0.75**	ns
SB	ns	0.79**	0.85**	ns	ns	Ns	ns	0.74**
CEC _t	ns	0.63**	0.60**	0.66**	0.52**	0.55**	0.63*	0.69**
CEC _e	ns	0.68**	0.65**	ns	ns	0.49**	0.55*	0.67**
BS	ns	0.37*	0.47**	ns	ns	Ns	ns	0.36*
<i>m</i>	ns	ns	−0.46**	ns	ns	Ns	ns	−0.39*
Variable	As	Ba	Cd	Cr	Ni	Pb	Se	Zn
SiO ₂ (AE)	ns	0.62**	0.55**	0.71**	0.55**	0.58**	0.70**	0.77**
Al ₂ O ₃ (SA)	ns	ns	0.41*	0.47**	ns	0.52**	0.47*	0.55**
Fe ₂ O ₃ (SA)	ns	0.43*	0.63**	ns	ns	Ns	ns	0.58**
Mn ₂ O ₃ (SA)	ns	0.79**	0.92**	ns	ns	Ns	ns	0.77**
TiO ₂ (SA)	ns	0.50**	0.69**	ns	ns	Ns	ns	0.62**
Ki	ns	ns	ns	ns	ns	Ns	ns	ns
Kr	ns	0.46*	0.42*	ns	ns	Ns	ns	ns
Fe ₂ O ₃ (CBD)	ns	ns	0.59**	ns	ns	Ns	ns	0.51**
Fe ₂ O ₃ (OXA)	ns	ns	0.53**	ns	ns	Ns	ns	0.47**
Al ₂ O ₃ (OXA)	ns	ns	0.55**	ns	ns	Ns	ns	0.47**
Mn ₂ O ₃ (OXA)	ns	ns	0.63**	ns	ns	Ns	ns	0.46**
Clay	ns	0.49**	0.61**	ns	ns	0.51**	0.41*	0.71**
Silt	ns	ns	ns	0.39*	ns	Ns	ns	ns
Sand	ns	−0.54**	−0.62**	−0.46**	ns	−0.56**	−0.53**	−0.70**

*Significant at $p < 0.05$; **Significant at $p < 0.01$; ns = not significant; n = number of analyzed samples; SA = sulfuric acid digestion; AE = alkaline extraction; OXA = ammonium oxalate; CBD = sodium citrate–bicarbonate–dithionite.

The differences in the QRVs proposed for the soils between the State of São Paulo and other Brazilian states can be attributed to the huge diversity of physical-chemical and mineralogical composition of the soils, parent materials, climatic conditions and pedogenetic processes (Preston et al., 2014).

The adoption of QRVs for PTE in soils is a first step in environmental quality monitoring actions (Paye et al., 2010). These values should be applied in areas with similar pedogeochemical conditions. It is essential to obtain QRVs for each region of the country, especially with huge geological, geomorphological, climatic, and pedological differences, like Brazil (Santos and Alleoni, 2012).

3.4. Multivariate statistic

Some differences were observed in PTEs baseline values, and relative QRVs, in this study and those reported by CETESB (2014) for the State of São Paulo or even with those established by other studies for different States. It is important to understand if such differences may well be the product of naturally enhanced concentrations and/or anthropogenic contamination. Additionally, it is also necessary to investigate which were the main variables (or group of) responsible for the observed variability inside the investigated pedosystem. From this point of view, comparing distributions of elements with pedological information can be a great help in identifying and distinguishing sources of PTE in soil. Indeed, correlation matrix (CM) and multivariate analysis, through principal component analysis (PCA), can help distinguish between natural geogenic, pedogenic, and, or anthropogenic sources (Capra et al., 2014).

3.4.1. Correlation matrix

Correlation matrix (CM) on Box-Cox transformed data was used to identify the relationship between PTE content and soil properties in the investigated soils (Table 4).

Correlations exist among all the PTEs couples, according to their pedogeochemical affinity (such as Ba–Cd, Ba–Zn, Cd–Zn, Cr–Ni, Cr–Pb, Cr–Se). Primary factors such as geogenic and pedogenic nature influence the concentration and distribution of elements in the investigated soils. The “geogenic” factor includes a part of “pedogenic” processes. The geogenic influence can be explained by the similarity of the investigated PTE in terms of their physical-chemical properties (atomic mass, ionic radius, and oxidation state) and the coexistence during the formation of the minerals (Kabata-Pendias and Mukherjee, 2007). The “pedogenic” component, is clearly related to several soil physical-chemical properties. For instance, organic carbon (OC) had a positive linear relationship with Cr ($r = 0.75$, $p < 0.01$), Ni ($r = 0.60$, $p < 0.01$), Pb ($r = 0.59$, $p < 0.01$), and Se ($r = 0.80$, $p < 0.01$) (Table 4); a correlation that was also reported by other authors and explained in terms of binding power of soil organic matter (Kabata-Pendias and Mukherjee, 2007; Coppola et al., 2010; Capra et al., 2014).

Cadmium, Zn, or Ba was positively correlated with Ca, Mg, SB, CEC, BS, oxides of Si, Fe, Mn and Ti, Kr and clay, whereas there was a negative correlation between each of these elements and sand contents (Table 4). The silicate minerals of clay fraction and oxides have been reported as the main attributes that correlated with the natural contents of Cd and other metals in soil (Alleoni et al., 2005). Biondi et al. (2011) also reported that clay content was best correlated with these metals. Positive correlations between clay vs. oxides and heavy metal content

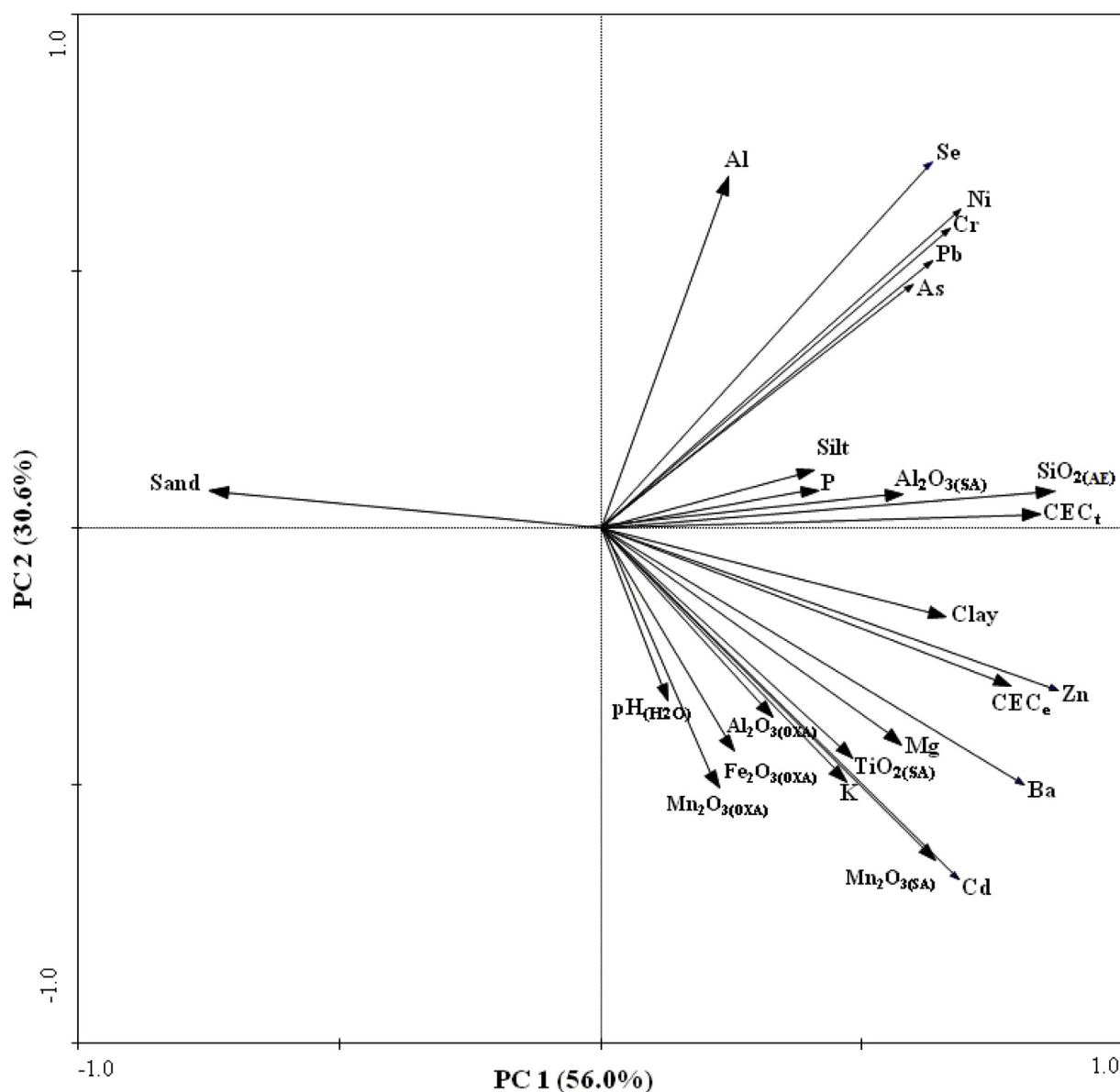


Fig. 4. Principal components analysis of variables related to physical and chemical attributes of soils from São Paulo State, Brazil. SA = sulfuric acid digestion; AE = alkaline extraction; OXA = ammonium oxalate.

were reported by other studies (Oliveira et al., 2014; Gabos et al., 2014) in natural soils. The natural concentration of Cr in the investigated soils was positively correlated with P, Al, H + Al, CEC_t, Si and Al oxides, and silt contents. Negative correlation was noted between Cr content and sand content. As with Cr, Ni content showed a positive relation with OC, Al, H + Al, CEC_t and Si oxide. The natural concentration of Pb was positively correlated with Al, H + Al, CEC_t, CEC_e, and Si and Al oxides; had a positive correlation with clay content but a negative relation with sand. These results corroborate those reported by Santos and Alleoni (2013), especially regarding the influence of soil texture. It is well known that clay fraction has higher affinity for heavy metals, such as Pb, and thus limits their mobility through adsorption processes (Biondi et al., 2011). The natural concentration of Se showed an high positive correlation with OC, SiO₂, Al₂O₃, P, CEC, Al, H + Al, or clay (Table 4). These correlations explained the lower Se concentration in the soils with lower CEC, OC, and clay contents. SOM and Fe and Al oxides were attributes strongly related to the natural levels of Se in Brazilian soils (Gabos et al., 2014). The significant correlations of Se-Al₂O₃, Se-clay and Se-P confirm the claims of Alleoni et al. (2009) that higher

concentrations of Se, and other PTE in Oxisols and Ultisols (Fig. 3c) were usually associated with the richness of parent materials and adsorption reactions. It is interesting to note the positive relationship of Se concentration with Si, Fe, Al, Mn and Ti oxides, and a negative correlation between clay and sand fraction (Table 4). pH, CEC, OC, clay content and type (silica clays and oxides) and ionic competition seem to have most influence on the retention and mobility of Zn and other heavy metals in the investigated soil, as reported in previous reports (Qian et al., 1996; Fontes et al., 2000). Fe, Al, Si, Mn and Ti were the attributes that were most correlated with Ba, Cd, and Zn concentrations in soils under a humid tropical climate; in such conditions soils are characterized by a high degree of weathering with Fe and Al oxides playing an important role in the behavior of heavy metals (Alleoni et al., 2005).

3.4.2. Principal components analysis

As a final step, the PCA has been elaborated in order to understand most important variables for the variability in the investigated soils. PC1 and PC2 explained 56.0% and 30.6% of the total variability,

respectively (Fig. 4). Together they accounted for 87% of the total variability. The PCA results strongly support previous observations reported through the analysis of matrix correlation. The PCA revealed two main distinct clusters of statistical significance (Fig. 4); the first is of mainly geogenic origin, and the second more related to enhanced pedogenic influence. In the first (geogenic) cluster, major relationships were noted between As, Pb, Cr, Ni, and Se, evidencing a strong geochemical affinity among these metals. Previous studies already reported a close relationship between As and Pb (Zhang et al., 2002), Cr and Ni (Zhang et al., 2002; Tume et al., 2006; Santos and Alleoni, 2013), Ba and Zn (Tume et al., 2006), Cd and Pb (Anju and Banerjee, 2011), and Cd and Zn (Aravind and Prasad, 2005) in natural soils. The second cluster showed that several soil physical-chemical parameters (such as CEC, clay, and pH) had a great influence on the variation of the components that are associated with metals such as Zn, Ba, Cd. Oxides of Al, Fe, Mn, Si, clay and CEC were already proved to be the attributes that have a close association with content of Cd and other PTE in natural soils of the State of São Paulo (Oliveira et al., 2014).

On the whole, the PCA corroborates the hypothesis about the (co) existence of two main groups of primary factors responsible for PTE source: geogenic origin being a prevalent one, and pedogenic processes as secondary, in terms of their influence in the PTE source and variability.

4. Conclusions

The mean values of natural PTE background content in the soils of the State of São Paulo are generally lower than those reported in other countries and/or other Brazilian states. The less restrictive 90th percentile, as upper limit for QRV, appears to be adequate.

Multivariate statistical analysis showed that the investigated PTE in the soils were mainly originated from the two natural sources: 1) geogenic, that is prevalent in terms of underlying processes and variability; and 2) pedogenic, that is fundamental in several observed processes, with anthropogenic influence being marginal.

Studies at regional scale are necessary to determine the natural background levels of PTEs into the soils, and this is important to avoid the use of data based on regions with different pedogeochemical conditions, that could bring to either over or under estimates in soil contamination.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jenvman.2018.05.048>.

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