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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 comes 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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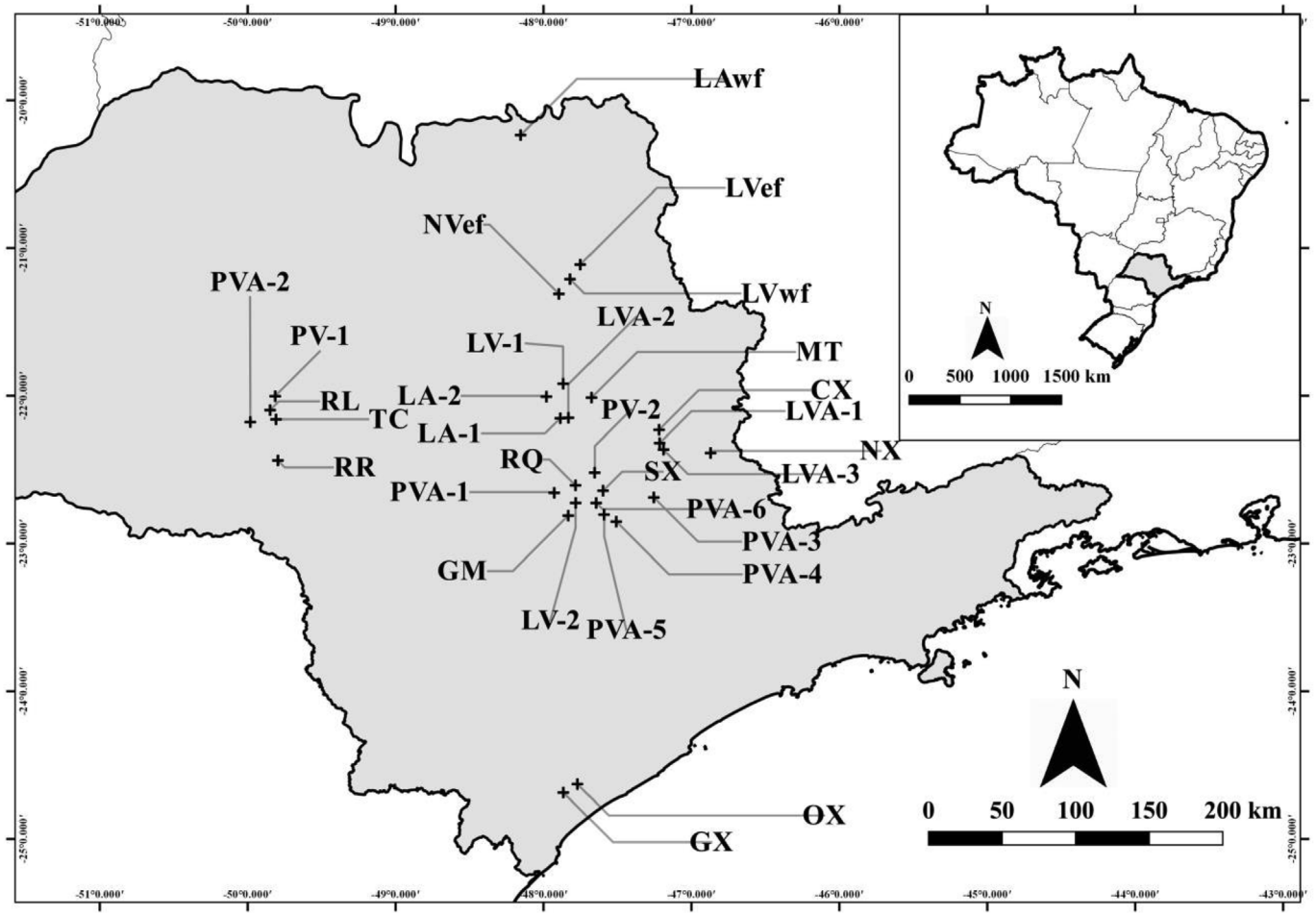

Fig. 1. Study area and sampling locations in São Paulo State, Brazil.

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 km^2 (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