



Background levels of selenium in some selected Brazilian tropical soils



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ABSTRACT

Selenium is an essential trace element required in low amounts by humans and animals, but it can be toxic when ingested at high concentrations. Information regarding Se background levels in soils is important to prevent Se deficiency, to optimize human nutrition, and to prevent toxicological effects. Background Se levels in Brazilian soils were evaluated and correlated with other soil characteristics. Se concentrations were quantified in samples from the superficial layer (0–0.2 m) and from the subsurface layer (the highest portion of the B horizon) for 58 soils. Soils were selected across a wide range of soil types and parent materials. Se concentrations ranged from <0.08 to 1.61 mg kg⁻¹, with a mean of 0.19 mg kg⁻¹. Concentrations of Se in the samples collected in the superficial layer were positively correlated with cation exchange capacity, as well as with clay, organic matter, and oxide contents of the soils. In the subsurface samples, only pH and aluminum oxide content were correlated with Se concentrations.

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1. Introduction

Selenium is a trace element that is widespread in different biogeochemical environments. Low quantities of Se are essential for animal and human nutrition, and play a role in important processes like the antioxidant function in organisms. Studies have identified Se deficiency as a cause of cardiomyopathy in some areas of China where Keshan disease is endemic (Tan et al., 2002). The Institute of Medicine of the National Academy of Science of the United States recommends that adults ingest 55 µg of Se per day (Boyd, 2011). Above a very narrow content range, Se can be toxic for animals, and daily intake by humans should not exceed 400 µg (Fernández-Martínez and Charlet, 2009).

Because the difference between essential and toxic Se concentrations is very small, it is important to quantify background Se concentrations in soils and therefore the amount of Se that may enter the food chain. Worldwide, the total amount of Se in soils is typically between 0.1 and 2 mg kg⁻¹ (Pezzarossa and Petruzzelli, 2001). Researchers have observed Se deficiency in soils of various countries, including 0.03 to 1.42 mg kg⁻¹ in China (Zhang et al., 2008); 0.11 to 0.88 mg kg⁻¹ in Scotland (Fordyce et al., 2010); 0.05 to 2.80 mg kg⁻¹ in Japan (Yamada et al., 2009); and 0.01 to 2.7 mg kg⁻¹ in Spain (Pérez-Sirvent et al., 2010). Se concentration in other soils can be extremely toxic. For example, 11 samples collected in natural areas of China's Yutangba region had concentrations ranging from 346 to 2,018 mg kg⁻¹, which represent serious risks to local residents (Zhu

et al., 2008). The amount of Se in soils is closely correlated with soil mineralogical composition (Winkel et al., 2012). Se concentrations in soil reflect either the parent material or human activities, and some soil characteristics play an important role in maintaining Se in the soil phase.

The Se occurs in soils in a variety of organic and inorganic species, which show distinct behaviors. In the soil solution, the predominant inorganic Se species are selenite (SeO₃²⁻) and selenate (SeO₄²⁻). Selenite occurs under neutral and mildly oxidizing pH conditions, and selenate occurs under higher pH (Neal et al., 1987). Selenite is adsorbed to the surface of some soil components as strong inner-sphere complexes containing no water between the adsorbing Se(IV) ion and the surface functional groups (Barrow and Whelan, 1980; Goldberg et al., 2007).

Selenium adsorbs strongly to surfaces of colloids with net positive charge balance. It is well known that soils in the wet tropics contain a large amount of pH-dependent charges, such as Fe and Al oxides (Fontes and Alleoni, 2006; Goh and Lim, 2004). Organic matter is also an important component of selenite adsorption in soil (Weng et al., 2011). Selenate is weakly adsorbed on the surface of soil components (Neal and Sposito, 1989). For this reason, it is the most mobile and biologically active Se species, and can easily leached from soil to groundwater.

The amount of Se in food is usually a consequence of Se levels in the soils where the crops were grown. In Brazil there is evidence of high Se content in some soils from the Amazon region (Lemire et al., 2010). That large region, however, contains only 8 % of the Brazilian population (Brasil, 2010). Brazil nut (*Bertholletia excelsa* H.B.K.), an edible seeds of the Brazil nuts with high Se concentrations (Lemire et al., 2010; Parekh et al., 2008), has been reported as an important source of Se in Amazonian areas of northern Brazil.

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Brazil is an enormous country, however Brazil nut trees are not cultivated in the apparently Se-poor regions in São Paulo state, in the country's southeastern region. In Brazil's central-southern region some animals fed in natural pastures have shown symptoms of Se deficiency, soils there are assumed to be deficient in Se (Oliveira et al., 2007).

São Paulo has the largest population of all Brazilian states. With more than 40 million inhabitants living in an area of 250,000 km², the state accounts for 31 % of Brazil's gross national product. In 2005 the São Paulo Environmental Agency published Guideline Values for soils and groundwater, including the "Quality Reference Value" obtained from the background levels of Se in soils from the state (CETESB, 2005). For some elements, including Se, most samples presented values below the detection limit, and in such cases the background value was considered to be the detection limit (0.25 mg kg⁻¹ of Se). However, equipment with higher analytical precision and a larger number of soil samples that better reflects edaphic variation across the entire state should provide a more accurate determination of naturally occurring Se levels in soils there. This study was carried out to determine Se background levels in soils of the state of São Paulo and to evaluate the possible correlations between Se concentrations and some other soil characteristics.

2. Materials and methods

2.1. Soil selection

The experiment was carried out with samples of 58 soils from São Paulo state, collected separately in the topsoil (0–0.2 m) and subsoil (the highest portion of the B horizon) layers, under natural vegetation. Samples were chosen to reflect a broad range of different soil types and parent materials, and their representativeness in São Paulo state. Sampling locations are listed in Table 1.

2.2. Sample characterization

Samples were air dried, crushed, and passed through a 0.150 mm (100 mesh) sieve. The pH values were potentiometrically determined in water (pH_{water}), with a 1:2.5 soil/water ratio, and in a 0.01 M CaCl₂ suspension, with a 1:2.5 soil/solution ratio. Total soil organic carbon (OC) content was obtained with the Walkley–Black method (Nelson and Sommer, 1982). Phosphorus, K, Ca, and Mg contents were extracted by an ion exchange resin and determined by colorimetry (P), flame emission photometry (K), and atomic absorption spectrometry (AAS) (Ca and Mg) (van Raij et al., 1986). Exchangeable aluminum was extracted by a 1 M KCl solution and determined by titration with 0.025 M ammonium hydroxide. Potential acidity (H + Al) was extracted by a 1 M calcium acetate solution and determined by titration with 0.025 M ammonium hydroxide. The following parameters were calculated: total cation exchange capacity at pH 7.0 (CEC_T = SB + (H + Al)) and saturation of the exchange complex (V% = (SB × 100)/CEC_T), where SB is the sum of exchangeable cations – Ca + Mg + K. The densimeter method was used for particle-size analysis (Gee and Or, 2002).

Sodium citrate-bicarbonate-dithionite (CBD) solution was used to extract the iron from the iron oxides (Mehra and Jackson, 1960). Iron and aluminum in non-crystalline iron oxides (Ox-Al and Ox-Fe) were extracted by oxalate solution (Loeppert and Inskeep, 1996). A 9 M H₂SO₄ solution was employed to solubilize secondary minerals containing Fe and Al, such as hematite, goethite and gibbsite. The same process was performed for Si, which was extracted with a 30 % NaOH solution (Camargo et al., 1986). Concentrations of Fe and Al in the abovementioned solutions were determined by AAS, and Si was quantified by gravimetry (Camargo et al., 1986).

2.3. Selenium contents

The "Total" (pseudo total) contents of Se in soil samples were extracted with aqua regia (ISO, 11466:1995, 1995). Pseudo total concentrations of Se in soils are commonly measured by researchers for two reasons: (i) the difficulty of determining very low concentrations of available Se in solution (Shand et al., 2010); and (ii) the lack of an aqueous solution to extract the available fraction for all different soils (Keskinen et al., 2009). For this reason, Se contents extracted by aqua regia have been considered a good indicator of total Se in soils (Shand et al., 2010).

In a Teflon vessel 0.5 g of soil was weighed, mixed with 3 mL of HNO₃ (65 %) and 9 ml of HCl (37 %), and allowed to digest overnight at room temperature. Vessels were then sealed and placed in a microwave oven. After digestion the extracts were filtered and the volume filled up to 25 mL with ultrapure water. For Se determination, the element in the extracts was reduced to Se (IV) using 5 ml of the digests, 2.5 ml of hydrochloric acid, and 2.5 ml of ultrapure water, heated in a water bath for 1 h at 70° C, and the volume completed to 25 mL in volumetric flasks (ISO, 20280:2007, 2007). The amount of Se was determined by hydride generation in a flow injection analysis system coupled to an atomic absorption spectrometer (HG-AAS) using 0.2 % borohydride and 10 % hydrochloric acid (USEPA - United States Environmental Protection Agency, 2007).

A certified soil sample of SRM soil 2709a (San Joaquin Soil) from the National Institute of Standards and Technology (NIST) with 1.5 mg kg⁻¹ of Se was included in each digestion series to ensure a quality analysis control (recovery rate between 76 and 82 %; LOQ 0.089 mg kg⁻¹ – calculated by the average of ten results of blank samples, plus five times the standard deviation of these blank results). Data were obtained in triplicate, and means subjected to a Pearson covariance analysis using Statistical Analysis System software (SAS Institute, 1993).

3. Results and discussion

3.1. Selenium in soil

Levels of Se in the soils under study varied from <0.089 to 1.612 mg kg⁻¹ (Table 1), with a mean of 0.191 mg kg⁻¹ and a median of 0.111 mg kg⁻¹. Half of the soils had less Se than the quantification limit (0.089 mg kg⁻¹), and 75 % of the soil samples had less than 0.223 mg kg⁻¹. In China, Tan et al. (2002) studied the relationships between soil Se and endemic human diseases, and they considered 0.123–0.175 mg kg⁻¹ as reference threshold values for assessing the risk from potential selenium deficiency in soils.

Concerns regarding Se in tropical soils of São Paulo state were initially motivated by an interest in establishing reference levels for soil quality. Background levels are required to prevent environmental damage, and São Paulo's status as the most populated and industrialized state in Brazil makes it vulnerable to pollution risks. However, the results of this study make it clear that studies of Se in soil should not restrict their focus to environmental safety. Selenium deficient soils are a health concern, and especially so for people whose diet is based on food produced from such areas, since people with a more diversified diet have greater chances of obtaining Se from other sources. São Paulo state contains 22 % of the Brazilian population (Brasil, 2010), and has 20 million hectares of productive agricultural lands (CATI, 2008).

The Brazilian regulatory agency has defined the 75th percentile as the standard concentration for soil quality (CONAMA, 2009). In our experiment, the value representing the 75th percentile was 0.22 mg Se kg⁻¹. This result is very similar to the preliminary value established by the Environmental Agency of São Paulo State (0.25 mg kg⁻¹, CETESB, 2005).

The range of Se concentrations observed in the soils of São Paulo state was similar to those observed in other parts of the world where

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