Barium and Cadmium in Tropical Soils Cropped and Under Native Forest

Iolanda Maria Soares Reis (iolanda.reis@ufopa.edu.br)
Federal University of West Pará, 68040-255
https://orcid.org/0000-0001-6619-0730

Wanderley José de Melo
Universidade Estadual Paulista Julio de Mesquita Filho

Erica Souto Abreu Lima
Universidade Federal Rural do Rio de Janeiro

Marcos Gervásio Pereira
Universidade Federal Rural do Rio de Janeiro

Ulisses Sidnei da Conceição Silva
Universidade Federal do Oeste do Para

Mateus Alves de Sousa
Universidade Federal do Oeste do Para

José Marques Júnior
Universidade Estadual Paulista Julio de Mesquita Filho

Lívia Arantes Camargo
Universidade Estadual Paulista Julio de Mesquita Filho

Gabriel Maurício Peruca de Melo
Universidade de Descalvado

Ademir Sergio Ferreira Araújo
Federal University of Piauí

Otávio Augusto Queiroz dos Santos
Universidade Federal Rural do Rio de Janeiro

Research Article

Keywords: soil pollution, logging, soil cultivation, trace elements, phytoavailability

Posted Date: August 23rd, 2021

DOI: https://doi.org/10.21203/rs.3.rs-813516/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
Abstract

Toxic elements pose a high environmental risk because of their long persistence in soil, water, and food chain. This study aimed to estimated potentially available and pseudototal contents of barium (Ba) and cadmium (Cd) in tropical soil under native forest vegetation, sugarcane and maize crops. Soil samples were collected at 0.00–0.20 m depth in different municipalities in São Paulo State, Brazil, and analyzed for fertility, texture, total iron, iron oxides, pseudototal and available Ba and Cd contents. Heavy metals were extracted using different extraction solutions (Mehlich-1, Mehlich-3, and DTPA). Data were subjected to descriptive and multivariate analyses. Correlations between soil clay content, mineralogy, and fertility were also investigated. Of the three extraction solutions tested, Mehlich-3 was the most effective to estimate the potential availability of Ba and Cd. Ba extracted by Mehlich-3 was negatively correlated with goethite, and pseudototal barium was positively correlated with pH CaCl$_2$. Cd extracted by Mehlich-3 was positively correlated with pH CaCl$_2$, and pseudototal cadmium was strongly correlated with iron oxide, clay, and organic matter contents.

Introduction

Heavy metals occur naturally in soil but their concentrations can be increased by anthropic activities. Such metals may remain in soil for extremely long periods like thousands of years. Heavy metals half-life varies according to the type of metal (Alloway and Jackson 1991; Brokes 1995). Some of them, such as Cu, Zn, Mo, Se, and Fe, are essential for plants and animals, while others do not have any known benefits, such as Cd and Ba (Cipollini and Pickering 1986). Any of these elements, however, can be toxic at high concentrations. Heavy metals are among the most studied elements because they pose environmental and health risks.

Contamination of soil, water, and crops with heavy metals may damage human health because they can accumulate in the trophic chain (Hooda and Alloway 1998; Chen et al. 2015).

Knowledge of the availability of heavy metals is essential to monitor the environmental impacts caused by these elements (Pascual et al. 2004; Liu et al. 2018). In soil, heavy metals can occur in bioavailable forms, being readily absorbed by plants. Phytoaccumulation is influenced by adsorption, leaching, and other soil properties (Qian et al. 1996; Hooda et al. 1997; Fontes and Alleoni 2006). The presence of heavy metals has increased in inadequately managed agricultural systems, especially with the indiscriminate use of agricultural inputs as phosphate fertilizers, and contaminated sewage sludge (Halim et al. 2003), possibly leading to reductions in crop yield and increased risks of biomagnification and bioaccumulation (Coscione et al. 2009).

It is common the use of chemical extraction methods to assess the availability of soil heavy metals to plants (Revoredo and Melo 2006). These techniques allow evaluating the dynamics of nutrients and heavy metals in soil–plant relationships and their mobility in the soil profile (Rauret 1998). However, one of the main problems encountered in the development of remediation programs for areas contaminated with heavy metals is the low reliability of methods for estimating total and available contents of these metals (Tavares and Oliveira 2017). A variety of extraction methods can be used for quantification available heavy metals, and values differ according to the chosen method. Such differences are attributed to the mode of action of extraction solutions and soil characteristics influencing metal availability (Nascimento et al. 2002).
This study aimed to evaluate the availability of Ba and Cd in *Latossolos* under native forest vegetation and sugarcane and maize crops using different extraction solutions and investigate associations between soil properties and pseudototal metal contents.

**Material And Methods**

Twelve samples of *Latossolos* under native forest or cropped were collected in five municipalities in São Paulo state, Brazil. These soils were previously characterized by Oliveira (1977) and Andrioli and Centurion (1999). The samples were taken from areas cropped with sugarcane (*Saccharum* spp.), maize (*Zea mays* L.) or under native forest or old reforestation. Sampling sites and sample codes are described in Table 1.

**Table 1** Soil sampling sites in different regions of São Paulo State, Brazil

| Soil                        | Code  | Municipality | Soil cover      | Latitude         | Longitude      |
|-----------------------------|-------|--------------|-----------------|------------------|----------------|
| Latossolo Vermelho Amarelo  | LVA<sub>IF</sub> | Itirapina     | Native forest   | 22°22’12.7” S  | 047°54’16.8” W |
| Latossolo Vermelho Amarelo  | LVA<sub>IC</sub> | Itirapina     | Maize           | 22°22’11.4” S  | 047°55’09.1” W |
| Latossolo Vermelho          | LV<sub>SF</sub> | São Carlos    | Native forest   | 22°15’12.0” S  | 047°50’38.5” W |
| Latossolo Vermelho          | LV<sub>SC</sub> | São Carlos    | Sugarcane       | 22°15’19.5” S  | 047°50’37.3” W |
| Latossolo Vermelho          | LV<sub_RF</sub> | Ribeirão Preto | Native forest   | 21°28’11.2” S  | 047°53’38.9” W |
| Latossolo Vermelho          | LV<sub_RC</sub> | Ribeirão Preto | Sugarcane       | 21°28’10.2” S  | 047°53’38.9” W |
| Latossolo Amarelo           | LA<sub>IF</sub>  | Itirapina     | Native forest   | 22°24’03.0” S  | 047°52’52.0” W |
| Latossolo Amarelo           | LA<sub_IC</sub> | Itirapina     | Sugarcane       | 22°24’12.5” S  | 047°52’51.8” W |
| Latossolo Amarelo           | LA<sub_MF</sub> | Miguelópolis  | Native forest   | 20°13’18.5” S  | 048°01’40.3” W |
| Latossolo Amarelo           | LA<sub_MC</sub> | Miguelópolis  | Sugarcane       | 20°13’18.8” S  | 048°01’39.5” W |
| Latossolo Vermelho          | LV<sub_JF</sub> | Jaboticabal   | Native forest   | 21°14’52.55” S | 048°16’10.1” W |
| Latossolo Vermelho          | LV<sub_JC</sub> | Jaboticabal   | Maize           | 21°14’54.04” S | 048°16’13.3” W |

Source: adapted from Reis et al. (2014).

Plots with 100 m² were demarcated at each native forest site. Soil samples were collected within the plots and in their vicinity with the same soil type but cultivated with sugarcane or maize. Twenty individual samples
were collected from each site at 0.00–0.20 m depth using a Dutch auger and combined to form a composite sample. All sampling points were georeferenced. Samples were air-dried, crushed, and sieved through a 2.00 mm mesh screen for analysis of fertility, texture, mineralogy, Cd and Ba availability, and pseudototal contents. Soil fertility (Table 2) was assessed according to the methods described by Raij et al. (2001).

For the determination of pseudototal metal contents, soil samples were digested with HNO$_3$ in a microwave oven, according to United States Environmental Protection Agency method 3051A (USEPA, 1996). Ba and Cd concentrations were determined in digestion extracts by atomic absorption spectrophotometry using acetylene/air flame. The results were validated by comparison with those of a certified soil sample contaminated with sewage sludge (RTC-CRM 005-050). Certified and analyzed Ba contents were respectively 852.9 and 1086.52 mg kg$^{-1}$ (127.4% recovery), and certified and analyzed Cd contents were respectively 13.7 and 13.76 mg kg$^{-1}$ (100.4% recovery).

**Table 2** Chemical properties of *Latossolos* samples collected at 0–0.20 m depth in different regions of São Paulo State, Brazil

| Sample$^a$ | Soil cover       | P resin (mg dm$^{-3}$) | OM (g dm$^{-3}$) | pH (CaCl$_2$) | K (mmol$_c$ dm$^{-3}$) | Ca | Mg | H + Al | SB | CEC | BS |
|------------|------------------|------------------------|------------------|---------------|------------------------|----|----|--------|----|-----|----|
| LVA$_{IF}$ | Native forest    | 7                      | 35               | 5.3           | 1.5                    | 36 | 4  | 20     | 42 | 62  | 67 |
| LVA$_{IC}$ | Maize            | 29                     | 17               | 4.6           | 0.5                    | 11 | 2  | 28     | 14 | 42  | 33 |
| LV$_{SF}$  | Native forest    | 14                     | 27               | 4.3           | 0.6                    | 12 | 3  | 52     | 16 | 68  | 23 |
| LV$_{SC}$  | Sugarcane        | 27                     | 15               | 4.5           | 0.6                    | 6  | 1  | 60     | 8  | 68  | 12 |
| LV$_{RF}$  | Native forest    | 19                     | 47               | 4.1           | 1.9                    | 9  | 4  | 72     | 15 | 87  | 17 |
| LV$_{RC}$  | Sugarcane        | 69                     | 36               | 5.5           | 2.4                    | 41 | 25 | 28     | 68 | 96  | 71 |
| LA$_{IF}$  | Native forest    | 15                     | 36               | 4.5           | 5.2                    | 14 | 9  | 47     | 28 | 75  | 38 |
| LA$_{IC}$  | Sugarcane        | 69                     | 36               | 5.5           | 2.4                    | 41 | 25 | 28     | 68 | 96  | 71 |
| LA$_{MF}$  | Native forest    | 37                     | 64               | 4.9           | 1.7                    | 41 | 11 | 58     | 54 | 112 | 48 |
| LA$_{MC}$  | Sugarcane        | 41                     | 40               | 5.3           | 4.7                    | 28 | 9  | 38     | 42 | 80  | 52 |
| LV$_{JF}$  | Native forest    | 22                     | 41               | 6.4           | 5.4                    | 97 | 28 | 15     | 13 | 145 | 90 |
| LV$_{JC}$  | Maize            | 25                     | 28               | 5.6           | 3.7                    | 31 | 17 | 25     | 52 | 77  | 67 |
Soil samples were coded according to Brazilian Soil Classification System (LVA, Latossolo Vermelho Amarelo; LV, Latossolo Vermelho; LA, Latossolo Amarelo) (Santos et al. 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland).

OM, organic matter; SB, sum of bases; CEC, cation-exchange capacity; BS, base saturation.

Source: adapted from Reis et al. (2014).

Soil texture was analyzed by the pipette method using 0.1 mol L\(^{-1}\) NaOH solution as dispersant (Donagema et al., 2011).

Fe in the form of Fe\(_2\)O\(_3\) was obtained by sulfuric acid digestion, as proposed by Camargo (1986). For qualitative mineralogical analysis, samples of iron-free clay were used as proposed by Menhra and Jackson (1960) and clay with concentrated oxides was evaluated according to the method of Norrish and Taylor (1961) as modified by Kâmpf and Schwertmann (1982). Analyses were conducted using X-ray diffractometry.

Kaolinite/(kaolinite + gibbsite) and goethite/(goethite + hematite) ratios were calculated using the peak areas of kaolinite (001), gibbsite (002), hematite (012), and goethite (110).

Potentially available Ba and Cd contents were obtained by the following extraction methods: Mehlich-1 (De Filippo and Ribeiro 1997), Mehlich-3 (Mehlich 1984), and DTPA (Lindsay and Norvell 1978). For Mehlich-1 extraction, 2.5 g of soil were added to 25 mL of extraction solution (0.05 mol L\(^{-1}\) HCl + 0.0125 mol L\(^{-1}\) H\(_2\)SO\(_4\), pH 1.2). The mixture was stirred at 120 rpm for 5 min and filtered. For Mehlich-3 extraction, 2.5 g of soil were added to 25 mL of extraction solution (0.2 mol L\(^{-1}\) CH\(_3\)COOH + 0.25 mol L\(^{-1}\) NH\(_4\)NO\(_3\) + 0.015 mol L\(^{-1}\) NH\(_4\)F + 0.013 mol L\(^{-1}\) HNO\(_3\) + 0.001 mol L\(^{-1}\) EDTA, pH 2.5). The mixture was shaken at 120 rpm for 5 min, and filtered. DTPA extraction was performed by adding 10 cm\(^3\) of soil to 20 mL of extraction solution (0.005 mol L\(^{-1}\) DTPA + 0.1 mol L\(^{-1}\) TEA + 0.01 mol L\(^{-1}\) CaCl\(_2\), pH 7.3), stirring for 2 h, and filtering. Ba and Cd concentrations in the extracts were determined as above described.

Results were subjected to descriptive analysis. After standardization of variables to null mean and unit variance (\(\mu = 0, \sigma = 1\)), data were subjected to hierarchical cluster analysis using Euclidean distance as a measure of similarity between observations and Ward's method as a clustering strategy. Principal component analysis (PCA) was also performed. The criteria adopted for choosing the number of retained principal components (PCs) were those proposed by Kaiser (1958): eigenvalues greater than 1.00 and cumulative variance greater than 70%. For a better understanding of data behavior, we performed Pearson correlation analysis at the 5% significance level. All statistical analyses were carried out using RStudio version 4.0.

**Results And Discussion**

Two acid extraction solutions (Mehlich-1 and -3) and one chelating agent (DTPA) were used to extract available Ba and Cd contents from soil. Acid extractors are more suitable for tropical soils, promoting greater metal recovery because of their mode of action (acid dissolution of colloids). According to Santos et al. (2015), acid solutions can remove metals from soil solution, exchange sites, and complexes or adsorbed
materials. DTPA, on the other hand, extracts metals bound to organic fractions via complexation, according to complex stability (Iwegbue et al. 2000). Table 3 presents the available and pseudototal contents of Ba and Cd determined using Mehlich-1, Mehlich-3, and DTPA solutions.

Table 3 Potentially available and pseudototal ($T_P$) contents of barium and cadmium determined by Mehlich-1, Mehlich-3, and DTPA extraction from *Latossolos* in São Paulo State, Brazil

| Sample $^a$ | Soil cover | Barium (mg kg$^{-1}$) | Cadmium (mg kg$^{-1}$) |
|-------------|------------|------------------------|------------------------|
| LVA$_{IF}$  | Native forest | 3.87 13.94 4.14 20.07 | 0.03 0.19 0.01 0.69 |
| LVA$_{IC}$  | Maize      | 1.91 15.68 4.54 17.27 | 0.03 0.12 0.01 0.54 |
| LV$_{SF}$   | Native forest | 2.47 17.87 6.06 26.67 | 0.02 0.12 0.01 1.11 |
| LV$_{SC}$   | Sugarcane  | 2.24 58.14 6.14 62.07 | 0.05 0.07 0.01 1.19 |
| LV$_{RF}$   | Native forest | 2.29 8.36 4.86 20.89 | 0.05 0.07 0.01 3.05 |
| LV$_{RC}$   | Sugarcane  | 4.60 16.18 3.98 26.36 | 0.06 0.17 0.01 3.10 |
| LA$_{IF}$   | Native forest | 3.45 12.23 4.67 13.10 | 0.04 0.09 0.01 1.01 |
| LA$_{IC}$   | Sugarcane  | 3.59 9.32 5.92 10.10 | 0.04 0.06 0.01 1.07 |
| LA$_{MF}$   | Native forest | 3.59 16.82 5.01 35.65 | 0.05 0.08 0.01 2.72 |
| LA$_{MC}$   | Sugarcane  | 2.87 19.75 5.62 26.24 | 0.06 0.15 0.01 3.14 |
| LV$_{JF}$   | Native forest | 6.97 53.30 13.33 171.69 | 0.09 0.18 0.02 2.21 |
| LV$_{JC}$   | Maize      | 4.76 75.71 30.62 222.08 | 0.05 0.16 0.01 2.19 |

$^a$ Soil samples were coded according to Brazilian Soil Classification System (LVA, *Latossolo Vermelho Amarelo*; LV, *Latossolo Vermelho*; LA, *Latossolo Amarelo*) (Santos et al., 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland).

Mehlich-3 was found to be the best extraction solution for Ba, followed by DTPA and Mehlich-1. Mehlich-3 was able to extract potentially available Ba from all samples. For Cd, Mehlich-3 also provided the best results, followed by Mehlich-1. DTPA did not extract relevant amounts of Cd.
According to Tavares and Oliveira (2017), environmental agencies that monitor metal-contaminated areas usually opt for extraction methods that afford the highest contents. The authors found that Mehlich-3 was the most appropriate extraction solution for determining metal contents in the exchangeable (bioavailable) fraction of soil, as it detected higher levels of virtually all metals of interest. Oliveira et al. (2008), in evaluating Cd availability in different soils, found that Mehlich-1, Mehlich-3, DTPA-TEA, and CaCl\textsubscript{2} had the following descending order of recovery efficiency: Mehlich-1 > Mehlich-3 > DTPA-TEA > CaCl\textsubscript{2}.

The recovery rates of Ba and Cd obtained by each extraction solution as percentage of pseudototal extraction are depicted in Fig. 1.

The potentially available contents of Ba and Cd extracted by Mehlich-1 were 1.91–6.97 mg kg\textsuperscript{-1} and 0.02–0.09 mg kg\textsuperscript{-1}, respectively. Mehlich-1 solution has been widely to assess the potential availability of heavy metals (Revoredo and Melo 2006; Oliveira et al. 2008; Cunha et al. 2008).

Mehlich-3 solution afforded available Ba contents of 8.36 to 75.71 mg kg\textsuperscript{-1} and available Cd contents of 0.06 to 0.9 mg kg\textsuperscript{-1}. Mantovani et al. (2004) reported that Mehlich-3 showed good extraction capacity for Ni, Pb, Cu, and Mn. The highest available Ba and Cd contents were obtained by extraction with Mehlich-3, attributed to EDTA complexation and solution acidity, which increases extraction efficiency. Acids partially dissolve structures containing metals, whereas EDTA preferably extracts metals complexed to organic matter (Tavares and Oliveira 2017).

DTPA extracted 3.98–30.62 mg kg\textsuperscript{-1} of Ba and only 0.01–0.02 mg kg\textsuperscript{-1} of Cd, not being an efficient extraction solution for Cd. It was necessary to adopt the detection limit of the apparatus to facilitate statistical analysis. Similar results for DTPA were obtained by previous studies using the extraction solution to determine the potential availability of heavy metals (Borges and Coutinho 2004; Oliveira et al. 2008).

In general, native forest soils had lower available Ba and higher available Cd contents by Mehlich-3 extraction. These results might be associated with soil genesis or, more remotely, to phosphate fertilizers blown by the wind (due to the proximity of the areas), since such fertilizers normally contain Cd. Freitas et al. (2009) evaluated the availability of Cd and Pb in soil under maize crop fertilized with phosphate fertilizers. The authors found that simple superphosphate and natural phosphate from Gafsa had the highest contents of Cd and Pb and that Gafsa phosphate was responsible for the high Cd and Pb contents in maize plants.

According to Nogueiro and Alleoni (2013), pseudototal Ba concentrations above 150 mg kg\textsuperscript{-1} (prevention value) can seriously compromise soil quality. The São Paulo State Environmental Company (CETESB 2016) established that the prevention value for nonagricultural soils is 120 mg kg\textsuperscript{-1} Ba and the intervention value is 500 mg kg\textsuperscript{-1} Ba. In the present study, the pseudototal content of Ba was 171.69 mg kg\textsuperscript{-1} in native forest soil and 222.08 mg kg\textsuperscript{-1} in cropped soil. In evaluating the available Ba contents of these sites, we found that the recovery rate was lower than 50% (Fig. 1). Biondi et al. (2011) argued that in-depth analyses are needed to understand metal mobility and availability in undisturbed soils with high heavy metal contents.

We used multivariate exploratory analysis to better characterize soils with regard to data variability. Fig. 2 shows the dendrogram and phylogenetic tree of pseudototal Ba content and Ba contents obtained using
Mehlich-1, Mehlich-3, and DTPA solutions. Three distinct groups were formed by using a Euclidean distance close to 4. Group 1 was formed by LV_JC and LV_JF; group 2 by LV_RC, LA_IF, LA_IC, LVA_IF, and LA_MF, and group 3 by LV_SC, LV_SF, LA_MC, LVA_IC, and LV_RF. Group 1 soils had higher pseudototal Ba contents, standing out from the other groups.

Principal component analysis revealed only one factor with an eigenvalue greater than one. However, for biplot construction, we used PC1 and PC2 (Fig. 3), which together explained 94.97 % of the total variance contained in the original data. The position of variables on the biplot confirmed the results of cluster analysis. PC1 explained 78.65 % of the variance in data, correlating positively with contents extracted by the USEPA method (pseudototal contents), DTPA, and Mehlich-3, in descending order. PC2 accounted for 16.32 % of the original variance, positively correlating with Mehlich-1 extraction results.

Fig. 4 shows the dendrogram and phylogenetic tree of pseudototal and available Cd contents. Three groups were formed using a Euclidean distance of about 4.5. However, a Euclidean distance of about 6.5 would generate only two large groups. Group 1 comprised LA_IF, LV_SC, LA_IC, LVA_IF, and LV_SF, group 2 contained only LV_JF, and group 3 was composed of LV_RF, LA_MF, LV_JC, LV_RC, and LA_MC. LV_JF differed from other samples possibly for having a higher Cd content by DTPA extraction.

PCA afforded two PCs with eigenvalues greater than 1. Variables had a strong correlation (>0.7) with PC1 and PC2, as shown by the biplot in Fig. 5. Both PCs explained 80.61% of the total variance in data, 55.50% of which was explained by PC2 and 25.11% by PC1. PC1 was more strongly correlated with Mehlich-1, DTPA, and pseudototal content, in descending order, whereas PC2 was correlated with Mehlich-1 only.

The results of Pearson correlation analysis (Fig. 6) demonstrated that available Ba determined by Mehlich-3 extraction had a negative correlation with goethite/(goethite + hematite) ratio, suggesting that soils with minor goethite contents have higher Ba availability. Available Ba correlated positively with pseudototal Ba. Pseudototal Ba showed a positive correlation with pH CaCl$_2$, indicating that soils with higher pH had higher pseudototal Ba contents.

Cd extracted by Mehlich-3 showed a positive correlation with pH CaCl$_2$ and pseudototal content. Pseudototal Cd, in turn, was highly correlated with total iron, clay, and organic matter contents. According to Pichtel et al. (2000), Cd availability is influenced by total Cd concentration, medium pH, and oxyreduction potential.

Harter and Naidu (2001) reported that the soil attributes that most affect metal availability are pH, solution composition and ionic strength, element species and concentration, and presence of ligands and competing ions. In particular, pH is positively correlated with adsorption of metals in soil; the availability and mobility of heavy metals decrease as the pH increases in soils with variable loads (Sposito, 2008). It is noteworthy that the pH of the study soils ranged from 4.1 to 5.6 (acidic soils), except for LV_JF, which had a pH of 6.4 (Table 2). According to Rieuwerts et al. (2006), under low pH conditions, metal cations (Cu$^{2+}$, Zn$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Fe$^{2+}$, Cr$^{2+}$, Co$^{2+}$, Pb$^{2+}$, and Cd$^{2+}$) become more mobile, especially in very weathered soils. This is because functional groups such as iron and aluminum oxyhydroxides are pH-dependent. Gray and Mclaren (2006) evaluated the solubility of heavy metals in soils and observed that Cd availability is related to pH, organic matter content, and iron oxide content.
Although vegetation is crucial for soil protection, in the present study, it was not possible to observe any effect of native forest or crop cover on Ba or Cd availability.

Conclusions

1. Mehlich-3 extractor provided the best results for both Ba and Cd, followed by Mehlich-1. DTPA solution was not effective in extracting Cd.
2. Vegetation cover had no influence on Cd or Ba availability.
3. The soil properties that most influenced Ba and Cd availability were goethite/(goethite + hematite) ratio, pH CaCl$_2$, clay, and organic matter.

Declarations

Acknowledgements The authors thank the Brazilian Federal Agency for Support and Evaluation of Graduate Education (CAPES) for awarding a scholarship to the first author. We are also grateful to the Brazilian National Council for Scientific and Technological Development (CNPq) for the financial support and the research productivity grant awarded to the second author.

Conflict of interest The authors declare that they have no conflict of interest related to this study.

References

1. ANDRIOLI I, CENTURION JF (1999) Levantamento detalhado dos solos da Faculdade de Ciências Agrárias e Veterinárias de Jaboticabal. Congresso Brasileiro de Ciência do Solo, 27, Brasília, 1999. Anais Brasília, Sociedade Brasileira de Ciência do Solo, 32p
2. ALLOWAY BJ, JACKSON AP (1991) The behaviour of heavy metals in sewage sludge amended soils. Science of the Total Environment 100:151–176. https://doi.org/10.1016/0048-9697(91)90377-Q
3. BIONDI CM, NASCIMENTO CWA, NETA ABF (2011) Teores naturais de bário em solos de referência do estado de Pernambuco. Revista Brasileira de Ciência do Solo 35:1819-1826. https://doi.org/10.1590/S0100-06832011000500036
4. BORGES MR, COUTINHO ELM (2004) Metais pesados do solo após aplicação de biossólido: II - Disponibilidade. Revista Brasileira de Ciência do Solo 28:557-568. https://doi.org/10.1590/S0100-06832004000300016
5. BROKES PC (1995) The use of microbial parameters in monitoring soil pollution by heavy metals. Biol Fertil Soils 19:269-279.
6. CAMARGO OA, MONIZ AC, JORGE JA, VALADARES JMAS (1986) Métodos de análise química, mineralógica e física de solos do Instituto Agronômico de Campinas – Boletim técnico106. Campinas: IAC, 94p.
7. CETESB (2016) Companhia Ambiental do Estado de São Paulo. Valores Orientadores para Solos e Águas Subterrâneasno Estado de São Paulo. DECISÃO DE DIRETORIA Nº 256/2016/E, DE 22 DE NOVEMBRO DE 2016.
8. CHEN H, TENG Y, LU S, WANG Y, WANG J (2015) Contamination features and health risk of soil heavy metals in China. Science of the Total Environment 512–513:143–153, 2015. https://doi.org/10.1016/j.scitotenv.2015.01.025
9. CIPOLLINI ML, PICKERING JL (1986) Determination of the phytotoxicity of barium in leach-field disposal of gas well brines. Plant and Soil 92:159-169.
10. COSCIONE AR, BERTON RS (2009) Barium extraction potential by mustard, sunflower and castor bean. Scientia Agricola 66:59-63. https://doi.org/10.1590/S0103-90162009000100008
11. CUNHA KPV, NASCIMENTO CWA, PIMENTEL RM, ACCIOLY AMA, SILVA AJ (2008) Disponibilidade, acúmulo e toxidez de cádimo e zinco em milho cultivado em solo contaminado. Revista Brasileira de Ciência do Solo 32;1319-1328. https://doi.org/10.1590/0100-06832008000300039
12. DE FILIPPO BV, RIBEIRO AC (1997) Análise Química do Solo (metodologia – 2ª edição). Universidade Federal de Viçosa. Viçosa, 26p.
13. DONAGEMA KD, CAMPOS DVB, CALDERANO SB, TEIXEIRA WG, VIANA JHM (2011) Manual de métodos de análise de solo. 2.ed. Rio de Janeiro, RJ: Embrapa Solos.
14. FONTES MPF, ALLEONI LRF (2006) Electrochemical attributes and availability of nutrients, toxic elements, and heavy metals in tropical soils. Scientia Agricola 63:589-608. https://doi.org/10.1590/S0103-90162006000600014
15. FREITAS EVS, NASCIMENTO CWA, GOURLART DF, SILVA JPS (2009) Disponibilidade de cádimo e chumbo para milho em solo adubado com fertilizantes fosfatados. Revista Brasileira de Ciência do Solo 33:1899-1907. https://doi.org/10.1590/S0100-06832009000600039
16. GRAY CW, MCLAREN RG (2006) Soil factors affecting heavy metal solubility in some new zealand soils. Water, Air, & Soil Pollution 175:3–14.
17. HALIM M, CONTE P, PICCOLO A (2003) Potential availability of heavy metals to phytoextraction from contaminated soils induced by exogenous humic substances. Chemosphere 52:265-275. https://doi.org/10.1016/S0045-6535(03)00185-1
18. HARTER RD, NAIDU R (2001) An assessment of environmental and solution parameter impact on trace-metal sorption by soils. Soil Science Society of American Journal 65:597-612. https://doi.org/10.2136/sssaj2001.653597x
19. HOODA PD, MCNULTY D, ALLOWAY BJ, AITKEN MN (1997) Plant availability of heavy metals in soils previously amended with heavy applications of sewage sludge. Journal of the Science of Food and Agriculture 73:446-454 https://doi.org/10.1002/(SICI)1097-0010(199704)73:4<446::AID-JSFA749>3.0.CO;2-2
20. HOODA PS, ALLOWAY BJ (1998) Cadmium and lead sorption behaviour of selected English and Indian soils. Geoderma 84:121-134. https://doi.org/10.1016/S0016-7061(97)00124-9
21. IWEGBUE CMA, EMUH FN, ISIRIMAH NO, EGUN AC (2007) Fractionation, characterization and speciation of heavy metals in composts and compost-amended soils. African Journal of Biotechnology 6:67-78.
22. Kaiser, H.F. (1958) The varimax criterion for analytic rotation in factor analysis. Psychometrika 23:187-2000.
23. KÄMPF N, SCHWERTMANN U (1982) Relações entre óxidos de ferro e cor em solos cauliníticos do Rio Grande do Sul. Revista Brasileira de Ciência do Solo 07:27-31.
24. LINDSAY WL, NORVELL WA (1978) Development of a DTPA test for zinc, iron, manganese and copper. Soil Science Society America Journal 42:421–428. https://doi.org/10.2136/sssaj1978.0361599500420000009x
25. LIU H, XU F, XIE Y, WANG C, ZHANG A, LI L, XU H (2018) Effect of modified coconut shell biochar on availability of heavy metals and biochemical characteristics of soil in multiple heavy metals contaminated soil. Science of the Total Environment 645:702-709. https://doi.org/10.1016/j.scitotenv.2018.07.115
26. MANTOVANI JR, CRUZ MCP, FERREIRA ME, ALVES WL (2004) Extratores para avaliação da disponibilidade de metais pesados em solos adubados com vermicomposto de lixo urbano. Pesquisa Agropecuária Brasileira 39:371-378. https://doi.org/10.1590/S0100-204X2004000110
27. MEHLICH A (1984) Mehlich – 3 soil test extractant: a modification of Mehlich – 2 extractant. Communications Soil Science Plant Analisys 15:1409–1416. https://doi.org/10.1080/00103628409367568
28. MENHRA OP, JACKSON ML (1960) Iron oxide from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. Clays Mineralogy 07:317-327. https://doi.org/10.1016/B978-0-08-009235-5.50026-7
29. NASCIMENTO CWA, FONTES RLF, NEVES JCL (2002) Dessorção, extração e fracionamento de manganês em Latossolos. Revista Brasileira de Ciência do Solo 26: 589-597. https://doi.org/10.1590/S0100-06832002000300003
30. NOGUEIROL RC, ALLEONI LRF (2013) Sequential extraction and speciation of Ba, Cu, Ni, Pb and Zn in soil contaminated with automotive industry waste. Chemical Speciation & Bioavailability 25:34-42. https://doi.org/10.3184/095422913X13584417355199
31. NORRISH K, TAYLOR RM (1961) The isomorphous replacement of iron by aluminium in soil goethites. The European Journal of Soil Science 12:294-306. https://doi.org/10.1111/j.1365-2389.1961.tb00919.x
32. OLIVEIRA JB, MENK JRF, ROTTA CL (1977) Levantamento semidetalhado dos solos do estado de São Paulo. Mapa escala 1:100.000. Campinas, Instituto Agronômico.
33. OLIVEIRA TMM, MENDES AMS, MORAES MJ A, DUDA GP (2008) Disponibilidade de cádmio em diferentes solos do Rio Grande do Norte. Revista Caatinga 21:57-63.
34. PASCUAL I, ANTO LIN MC, GARCIA C, POLO A, DIAZ, MS (2004) Plant availability of heavy metals in a soil amended with a high dose of sewage sludge under drought conditions. Biology and Fertility of Soils 40:291–299. 10.1007/s00374-004-0763-1
35. PICHTEL J, KUROIWA K, SAWYERR HT (2000) Distribution of Pb, Cd and Ba in soils and plants of two contaminated sites. Environmental Pollution 110:171-178. https://doi.org/10.1016/S0269-7491(99)00272-9
36. QIAN J, SHAN X, WANG Z, Tu Q (1996) Distribution and plant availability of heavy metals in different particle-size fractions of soil. The Science of the Total Environment 187:131-141. https://doi.org/10.1016/0048-9697(96)05134-0
37. RAIJ BV, ANDRADE JC, CANTARELLA H, QUAGGIO JA (2001) Análises químicas para avaliação da fertilidade de solos tropicais. Campinas: Instituto Agronômico.

38. RAURET G (1998) Extraction procedures for the determination of heavy metals in contaminated soil and sediment. Talanta 46:449-45. https://doi.org/10.1016/S0039-9140(97)00406-2

39. REIS IMS, MELO WJ, JÚNIOR JM, FERRAUDO AS, MELO GMP (2014) Adsorção de cádmio em Latossolos sob vegetação de mata nativa e cultivados. Revista Brasileira de Ciência do Solo 38:1960-1969. https://doi.org/10.1590/S0100-06832014000600030.

40. REVOREDO MD, MELO WJ (2006) Disponibilidade de níquel em solo tratado com lodo de esgoto e cultivado com sorgo. Bragantia 65:679-685. https://doi.org/10.1590/S0006-87052006000400019

41. RIEUWERTS JS, ASHMORE MR, FARAGO ME, THORNTON I (2006) The influence of soil characteristics on the extractability of Cd, Pb and Zn in upland and moorland soils. Science of the total Environment 366:864-875. https://doi.org/10.1016/j.scitotenv.2005.08.023

42. SANTOS NM, ACCIOLY AMA, NASCIMENTO CWA, SILVA IR, SANTOS JAG (2015) Biodisponibilidade de chumbo por extratores químicos em solo tratado com ácidos húmicos e carvão ativado. Revista Ciência Agronômica 46:663-668.

43. SANTOS, H. G.; JACOMINE, P. K. T.; ANJOS, L. H. C.; OLIVEIRA, V. A.; LUMBRERAS, J. F.; COELHO, M. R.; ALMEIDA, J. A.; ARAÚJO FILHO, J. C.; OLIVEIRA, J. B.; CUNHA, T. J. F. Sistema Brasileiro de Classificação de Solos. 5. ed. Brasília: Embrapa, 2018. 356 p.

44. SPOSITO G (2008) The Chemistry of Soils. 2nd Ed. Oxford University Press, New York.

45. TAVARES SRL, OLIVEIRA SA (2017) Avaliação de diferentes métodos de extração de metais pesados em solos contaminados provenientes de atividades de galvanoplastia. Dados eletrônicos – Rio de Janeiro: Embrapa Solos, 38 p.

46. USEPA - UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. METHOD 3051A (1996). Microwave assisted acid digestion of sediments, sludges, soils, and oils. Available from <http://www.epa.gov/storet/archive/modern/doc/FieldLabAnltPrcdAndEqpDetail.pdf>. Accessed 30 Jun 2015.

**Figures**

Figure 1
Recovery rate of (a) barium and (b) cadmium extracted using Mehlich-1, Mehlich-3, and DTPA, as calculated in relation to pseudototal contents. Soil samples are coded according to Brazilian Soil Classification System (LVA, Latossolo Vermelho Amarelo; LV, Latossolo Vermelho; LA, Latossolo Amarelo) (Santos et al. 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland)

Figure 2

(a) Dendrogram and (b) phylogenetic tree for barium availability determined by Mehlich-1, Mehlich-3, and DTPA extraction and barium pseudototal contents in Latossolos in São Paulo State, Brazil. Soil samples are coded according to soil (LVA, Latossolo Vermelho Amarelo; LV, Latossolo Vermelho; LA, Latossolo Amarelo) (Santos et al., 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland)
Figure 3

(a) Principal component analysis biplot and (b) correlation matrix for barium availability determined by Mehlich-1, Mehlich-3, and DTPA extraction and barium pseudototal contents in Latossolos in São Paulo State, Brazil. Soil samples are coded according to Brazilian Soil Classification System (LVA, Latossolo Vermelho Amarelo; LV, Latossolo Vermelho; LA, Latossolo Amarelo) (Santos et al. 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland)
Figure 4

(a) Dendrogram and (b) phylogenetic tree for cadmium availability determined by Mehlich-1, Mehlich-3, and DTPA extraction and cadmium pseudototal contents in Latossolos in São Paulo State, Brazil. Soil samples are coded according to Brazilian Soil Classification System (LVA, Latossolo Vermelho Amarelo; LV, Latossolo Vermelho; LA, Latossolo Amarelo) (Santos et al. 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland)
Figure 5

(a) Principal component analysis biplot and (b) correlation matrix for cadmium availability determined by Mehlich-1, Mehlich-3, and DTPA extraction and cadmium pseudototal contents in Latossolos in São Paulo State, Brazil. Soil samples are coded according to Brazilian Soil Classification System (LVA, Latossolo Vermelho Amarelo; LV, Latossolo Vermelho; LA, Latossolo Amarelo) (Santos et al. 2018), followed by subscript letters indicating the sampling location (I, Itirapina; S, São Carlos; R, Ribeirão Preto; M, Miguelópolis; J, Jaboticabal) and type of soil cover (F, native forest; C, cropland)
Figure 6

Pearson correlation matrix for Fe2O3, clay, kaolinite/(kaolinite + gibbsite) [kt/(kt + gb)] ratio, goethite/(goethite + hematite) [gt/(gt + hm)] ratio, P resin, organic matter (OM), pH in CaCl2, cation-exchange capacity (CEC), cadmium, and barium in Latossolos in São Paulo State, Brazil. Nonsignificant correlations (p > 0.05) are marked with an "X"