



## Agricultural management of an Oxisol affects accumulation of heavy metals



Guilherme Deomedesse Minari<sup>a</sup>, David Luciano Rosalen<sup>b</sup>, Mara Cristina Pessôa da Cruz<sup>c</sup>, Wanderley José de Melo<sup>a, d</sup>, Lucia Maria Carareto Alves<sup>a</sup>, Luciana Maria Saran<sup>a, \*</sup>

<sup>a</sup> Technology Department, São Paulo State University (UNESP), School of Agricultural and Veterinarian Sciences, Acesso Prof. Paulo Donato Castellane, S/N, 14884-900, Jaboticabal, SP, Brazil

<sup>b</sup> Rural Engineering Department, São Paulo State University (UNESP), School of Agricultural and Veterinarian Sciences, Acesso Prof. Paulo Donato Castellane, S/N, 14884-900, Jaboticabal, SP, Brazil

<sup>c</sup> Soils and Fertilizers Department, São Paulo State University (UNESP), School of Agricultural and Veterinarian Sciences, Acesso Prof. Paulo Donato Castellane, S/N, 14884-900, Jaboticabal, SP, Brazil

<sup>d</sup> Universidade Brasil, Av. Hilario da Silva Passos, 950, 13690-000, Descalvado, SP, Brazil

### HIGHLIGHTS

- Cd, Cr and Ni levels in the native forest exceeded the reference quality values.
- 12% of the experimental area is contaminated with Cd, 16% with Cr and 0.3% with Ni.
- The management with sewage sludge increased the levels of Cd and Ni.
- The Cr content in soil was not affected by the type of management.

### ARTICLE INFO

#### Article history:

Received 20 December 2016

Received in revised form

26 May 2017

Accepted 2 July 2017

Available online 3 July 2017

Handling Editor: T. Cutright

#### Keywords:

Soil contamination

Cadmium

Chromium

Nickel

Spatial distribution

### ABSTRACT

Soil contamination may result from the inadequate disposal of substances with polluting potential or prolonged agricultural use. Therefore, cadmium (Cd), chromium (Cr) and nickel (Ni) concentrations were assessed in a Eutroferic Red Oxisol under a no-tillage farming system with mineral fertilizer applications, a conventional tillage system with mineral fertilizer application and a conventional tillage system with sewage sludge application in an area used for agriculture for more than 80 years. We evaluated the spatial distributions of these elements in the experimental area and the effect of the different management practices on the soil retention of these metals. The concentrations of metals extracted from 422 soil samples by open-system digestion with HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HCl were assessed by flame atomic absorption spectroscopy. The pH and soil organic matter were also assessed, and spatial distribution maps were designed. The mean concentrations of Cd, Cr and Ni (1.0, 50 and 14 mg kg<sup>-1</sup>, respectively) in the native forest were higher than the reference values (100, 25 and 8% greater, respectively) in Brazilian legislation, indicating that the source material was the determining factor of the high metal concentrations in the study soils. Soil management with sewage sludge was the major contributor to the accumulation of Cd and Ni, whereas Cr concentration did not vary with management type. Approximately 0.3, 12 and 16% of the experimental area is contaminated with Ni, Cd and Cr, respectively, because their concentrations exceeded the values for alertness or prevention in Brazilian legislation.

© 2017 Published by Elsevier Ltd.

### 1. Introduction

Heavy metals are naturally occurring components of soil

because they are present in the source material (the rocks). The natural concentrations of metals in the soil depend on the nature of the rocks and the addition and loss processes that occur during soil formation. Atmospheric deposition is the main addition process under natural conditions (Brandl, 2005). Leaching and erosion are the main loss processes and result in the transfer of metals from one point to another in the landscape. The source material is the

\* Corresponding author.

E-mail address: [imsaran@fcav.unesp.br](mailto:imsaran@fcav.unesp.br) (L.M. Saran).

main factor that determines the heavy metal levels of the soil, although vegetation and human activity also contribute (Zhang et al., 2002; Nagajyoti et al., 2010). Among human activities that input heavy metals into soils, agriculture is a major contributor through the application of acidity correctives, fertilizers and pesticides (Nicholson et al., 2003; Wei and Yang, 2010).

The most commonly used soil acidity correctives in agriculture are ground limestone rocks, which are mixtures of minerals, including calcite and dolomite (Weirich-Neto et al., 2000). The metal concentration in the limestone rocks sold in Brazil is low and, in most cases, is below the legal limits for cadmium (Cd), chromium (Cr) and nickel (Ni) (Amaral Sobrinho et al., 1992; Soares et al., 2015). However, the high acidity of tropical soils leads to the addition of large quantities of correctives and, consequently, of the micronutrients, such as copper (Cu), zinc (Zn), iron (Fe), manganese (Mn) and Ni, present in the compositions of these correctives that are thus indirectly added to soils (Carvalho et al., 2012). Among fertilizers, phosphates have received the most attention due to the high Cd concentrations in phosphate rocks, which are considered the main route of Cd input into agricultural soils (Jiao et al., 2012). However, the Cd concentration depends on the nature of the rock from which the fertilizer is produced. The Cd levels of Brazilian phosphate fertilizers are lower than the levels reported in other countries because the former are primarily produced from igneous rocks (Lavres Jr et al., 2011), whereas the latter are produced from sedimentary rocks. The Cd levels in Brazilian phosphate fertilizers are much lower than the levels in imported fertilizers (Gabe and Rodella, 1999; Campos et al., 2005).

In addition to industrial fertilizers, organic fertilizers are also sources of heavy metals. Although the agricultural use of manure, compost and sewage sludge is a key method for nutrient recycling, the presence of heavy metals, including Cd, Cr and Ni, in their compositions is an environmental concern (McBride, 2003; Nogueira et al., 2008).

The presence of these metals requires monitoring the use of correctives and fertilizers without overlooking the following key issues: limestone and fertilizers (industrial and organic) are essential to maintaining or increasing food production; the quantities of metals reaching the soil with a single application of both is very small, and therefore, changes in natural levels resulting from their application are only observable after decades of use (Jiao et al., 2012). Furthermore, most metals in limestone rocks and fertilizers react with the soil matrix (particularly Fe and aluminum (Al) oxides and organic matter) when solubilized and are converted into their non-bioavailable forms because metals have low soil mobility and tend to accumulate (Ali and Malik, 2011). The latter issue particularly justifies the monitoring of changes in metal levels in fertilized soils to ensure soil quality, especially for food production. Several studies have reported the presence of high metal concentrations in agricultural and urban soils that compromise soil quality (Micó et al., 2006; Fagbote and Olanipekun, 2010; Zheng et al., 2010; Ali and Malik, 2011; Ghrefat et al., 2011; Harmanescu et al., 2011; Chandrasekaran et al., 2015). However, to date, no studies have been published on the Cd, Cr and Ni pollution levels and sources in agricultural soils under different management strategies in Brazil.

The objective of this study was to assess the Cd, Cr and Ni concentrations in Eutroferric Red Oxisol cropped mainly with maize and soybean under no-till farming with mineral fertilizer, conventional tillage with mineral fertilizer application and conventional tillage with sewage sludge application in an area that had been farmed for more than 80 years, to evaluate the spatial distribution of these elements in 422 soil samples from the experimental area, and to assess the effect of the different agricultural management practices on the retention of these metals in soil. These experiments were based on the hypothesis that the

application of acidity corrective and fertilizer increases the heavy metal levels in agricultural soils and that the degree of interference is greater in management systems using sewage sludge as a nutrient supplier.

## 2. Materials and methods

### 2.1. Description of the study area, soil sampling and analyses

Soil collection was performed in a 34.7 ha area of the Teaching, Research and Extension Farm (Fazenda de Ensino, Pesquisa e Extensão - FEPE) of the School of Agricultural and Veterinarian Sciences of São Paulo State University (Universidade Estadual Paulista - UNESP), Jaboticabal Campus, São Paulo (SP), at a total of 422 collection points. The sampling area is located at approximately 21°14'54" South latitude and 48°16'54" West longitude, with an average altitude and slope of 560 m and 6 to 12%, respectively. The regional climate is tropical, with a 5-year average temperature and rainfall of 22.6 °C and 1258 mm yr<sup>-1</sup>, respectively. The soil of the sampled area is clayey Oxisol derived from basalt that has been cultivated for over 80 years and has been partially reserved for agricultural research for the last 50 years. Sampling was performed from February 19 to 21, 2014, using a Dutch auger the top 0.20 m of soil. The adopted sampling grid featured 30 m × 30 m spacing. The location of the grid in the field was determined with a Global Navigation Satellite System (GNSS) Trimble R6 receiver using the Real-Time Kinematic (RTK) relative positioning method by adopting a geodetic frame with the Brazilian Geodetic System (Sistema Geodésico Brasileiro – SGB) as the base station.

At the time of sampling, the area was cropped with maize for animal feed. The area was divided into three subareas subjected to different management styles, identified in the text by the acronyms NT (no-tillage), CT (conventional tillage) and ST (sludge tillage). Subarea NT has been maintained for 25 years under a no-tillage farming system with the application of mineral fertilizers. Conventional tillage with mineral fertilizer application has been practiced in subarea CT for over 50 years, and subarea ST has been under minimal tillage with sewage sludge application for 17 years. Native forest (NF) soil collections were also performed in an area located nearby as a reference non-cultivated soil without direct anthropogenic interference.

The sewage sludge was from the Basic Sanitation Company of the State of São Paulo (Companhia de Saneamento Básico do Estado de São Paulo – SABESP) from the municipalities of Barueri, Monte Alto, and Franca, all in the State of São Paulo, and was applied annually at doses of 0 (control with mineral fertilization based on soil chemical analysis), 5, 10 and 20 Mg dry mass (DM) ha<sup>-1</sup>. The sewage sludge used in the seventeenth year of application came from the municipal sewage treatment plant of Monte Alto and had the following chemical attributes (expressed in DM): 45 g N kg<sup>-1</sup>; 20 g P kg<sup>-1</sup>; 2.5 g K kg<sup>-1</sup>; 0.19 g Cu kg<sup>-1</sup>; 0.07 mg Mn kg<sup>-1</sup>; 0.5 mg Zn kg<sup>-1</sup>; 0.05 mg Cr kg<sup>-1</sup>; 1.66 mg Cd kg<sup>-1</sup>; 0.02 mg Ni kg<sup>-1</sup> and 0.10 mg Pb kg<sup>-1</sup>. The moisture content of the sewage sludge was 62.15%, i.e., every 100 kg of sludge applied had 62.15 kg of water. Soil samples were air-dried in the shade, clod-broken and sieved through a 2-mm mesh. The pH in CaCl<sub>2</sub> and the soil organic matter (SOM) content were assessed according to Rajj et al. (2001).

The United States Environmental Protection Agency (USEPA) method 3050B, which involves sample heating and open-system digestion with HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub> and HCl, was used for Cd, Cr and Ni extraction (USEPA, 1996). The metals in the extracts were quantified by air-acetylene flame (Cd and Ni) or acetylene-nitrous oxide (Cr) atomic absorption spectroscopy in a GBC Avanta spectrophotometer.

## 2.2. Data analysis and surface map creation

A digital surface model was generated from the sample data values for each element. The inverse distance square interpolation method was used to generate surface maps (INPE, 2014). The classification of the study areas as a function of their SOM and metal levels was performed using digital surface models. The SOM levels were classified as low ( $<24 \text{ g C kg}^{-1}$ ), medium ( $24\text{--}30 \text{ g C kg}^{-1}$ ), suitable ( $31\text{--}45 \text{ g C kg}^{-1}$ ) and high ( $>45 \text{ g C kg}^{-1}$ ) according to Sousa and Lobato (2004).

The concentrations of metals were used to classify the soil by quality reference values (QRV), prevention values (PVs) and agricultural interdiction values (AIV) according to CETESB (2014) and CONAMA (Brasil, 2009), as shown in Table 1. Furthermore, the mean Cd, Cr and Ni concentrations of the 422 soil samples were compared with the concentrations of these metals in NF soils, with the PVs and AIV established in resolution 420/2009 of CONAMA (Brasil, 2009) and with QRV for Cd, Cr and Ni stipulated by CETESB (2014).

The QRV is the concentration of a given substance or element that defines the natural soil quality, and both CONAMA and CETESB define the PV as the maximum concentration of a given substance or element above which changes detrimental to the quality of soil and groundwater may occur. The AIV corresponds to the soil concentration of a given substance or element that poses a potential direct or indirect risk to human health when exceeded, considering a standardized exposure scenario. In the present study, metal concentrations greater than the PV and less than or equal to the AIV were termed the monitoring values (MVs) because the prevention values should be used to regulate inputs of substances and elements into soils, and the continuity of the activity should be subjected to reassessment when the prevention values are exceeded. Thus, according to CETESB (2014), the individuals who are legally accountable for inputs of pollutant loads must perform the monitoring of the resulting impacts.

The content of SOM, Cd, Cr and Ni for each grid point was entered into Spring version 5.3 to evaluate the spatial distribution within the experimental area (Camara et al., 1996). All spatial distribution maps were designed using the Universal Transverse Mercator (UTM) projection system (Zone 22, Southern Hemisphere) and the SIRGAS2000 geodetic reference system.

## 2.3. Statistical analysis

The results were submitted to analysis of variance, with a level of significance of 5%, with four groups (CT, NT, ST and NF), and the samples in each group as replicates. Tukey's test ( $\alpha = 0.05$ ) was used in the multiple comparisons of the means, using the General Linear Models (GLM) procedure in SAS (SAS 9.1, SAS Institute, Cary,

NC, USA).

The data obtained for pH, SOM, Cd, Cr and Ni were subjected to exploratory data analysis using multivariate statistical methods, and the values were standardized using Statistica (Statsoft, 2004). Principal component analysis (PCA) was performed to interpret and identify the relationships among the variables. Only components related to eigenvalues  $\lambda_i \geq 1$  (Kaiser criterion) were retained in the system (Kaiser, 1958).

## 3. Results

### 3.1. Soil metal levels

In the reference forest soil, NF, the mean Cd, Cr and Ni levels resulting from the arithmetic means of the concentrations of each metal at the sampling points were higher than the QRVs (100, 25 and 8% higher, respectively).

For all metals, the highest concentration was observed in ST, which was amended with sewage sludge (Table 2). The Cd content of all the subareas was higher than the reference value for Brazilian Oxisols ( $0.66 \pm 0.19 \text{ mg kg}^{-1}$ ) assessed using the 3051A method in a set of 19 samples from ten Brazilian states (Campos et al., 2003). No significant difference was observed among the Cd contents from NF, CT and NT, i.e., the mean Cd contents of CT and NT, subjected to mineral fertilization, showed virtually no difference from NF. Cd contents from NT and ST also did not differ statistically (Table 2). The Cr content was lowest in NF, with no differences among the other subareas, CT, NT and ST (Table 2). The Ni content from CT did not differ statistically from those of NF and NT, which were all lower than ST, where sewage sludge was applied.

The SOM contents of CT, NT and ST were low (Sousa and Lobato, 2004) and did not differ statistically from each other. NF presented desirable content of SOM that was much greater than in the other subareas. The pH values of NF, CT, NT and ST were all in the range 5.3–5.9 and did not differ statistically.

The coefficient of variation (CV) values for the three metals ranged from 19 to 29%. The CV of Cd was the highest (29%), suggesting greater variation among soil samples and a higher likelihood of an anthropogenic effect (Chen et al., 2008; Cai et al., 2015). Cr (19%) had the lowest CV, as was also found by Cai et al. (2015) in 238 samples of agricultural soils in China.

The presence of Cd, Cr and Ni was detected throughout the experimental area, as presented in Table 3. Most of the study area, i.e., more than 80% of the experimental area, had Cd, Cr and Ni contents within the range of PVs, which represent alert values, as discussed above. Approximately 12% of the experimental area is considered contaminated with Cd, 16% with Cr and 0.3% with Ni because the contents of these metals exceeded the values for alertness or prevention.

**Table 1**

Soil metal concentration ranges adopted to classify the Cd, Cr and Ni risks to the environment according to CETESB (2014) and CONAMA (Brasil, 2009) in the study area.

Quality Index	Metal Concentration ( $\text{mg kg}^{-1}$ )		
	Cd	Cr	Ni
Quality Reference Value (QRV) <sup>a</sup>	<0.5	$\leq 40$	$\leq 13$
Prevention Value (PV) <sup>b</sup>	0.5 to 1.3	$\leq 75$	$\leq 30$
Monitoring Value (MV)	1.3 to 3.0	75 to 150	30 to 70
Agricultural Investigation Value (AIV) <sup>b</sup>	>3.0	>150	>70

<sup>a</sup> CETESB (2014) - Technology and Environmental Sanitation Company.

<sup>b</sup> CONAMA (Brasil, 2009) - National Environment Council; QRV - value considered normal; PV - alert value; MV - value requiring environmental monitoring the concentration is greater than the PV value; AIV - interdiction value.

**Table 2**

Mean concentrations, standard deviations and coefficients of variation for Cd, Cr, Ni, soil organic matter (SOM) and pH in  $\text{CaCl}_2$  in the subareas of the experimental area.

Subarea	Metal Concentration ( $\text{mg kg}^{-1}$ )			SOM $\text{g C kg}^{-1}$	pH $\text{CaCl}_2$
	Cd	Cr	Ni		
NF	$1.0 \pm 0.2 \text{ b}$	$50 \pm 19 \text{ b}$	$14 \pm 2 \text{ c}$	$36 \pm 9 \text{ a}$	$5.9 \pm 0.8 \text{ a}$
CT	$1.0 \pm 0.3 \text{ b}$	$64 \pm 12 \text{ a}$	$18 \pm 5 \text{ bc}$	$21 \pm 3 \text{ b}$	$5.6 \pm 0.5 \text{ a}$
NT	$1.2 \pm 0.3 \text{ ab}$	$69 \pm 8 \text{ a}$	$21 \pm 3 \text{ b}$	$19 \pm 2 \text{ b}$	$5.3 \pm 0.4 \text{ a}$
ST	$1.3 \pm 0.2 \text{ a}$	$70 \pm 9 \text{ a}$	$26 \pm 2 \text{ a}$	$22 \pm 4 \text{ b}$	$5.4 \pm 0.3 \text{ a}$
CV	29	19	26	17	9

NF: native forest; CT: conventional tillage + mineral fertilizers; NT: no-till farming + mineral fertilizers; ST: minimal tillage + sewage sludge; CV: coefficient of variation. Means followed by the same letter in columns do not differ statistically by Tukey's test ( $\alpha = 0.05$ ).

**Table 3**

Total experimental area (in ha and in percentage) occupied by the quality index classes established for Cd, Cr and Ni based on the maximum concentration values of these metals in soil stipulated by CONAMA (2009) and CETESB (2014).

Soil Quality Classification	Cd, Cr and Ni Distribution in the Subareas					
	Cd		Cr		Ni	
	ha	%	ha	%	ha	%
Quality reference value	0.7	2.0	0.3	0.9	4.5	12.9
Prevention value	29.9	86.4	28.9	83.0	30.2	86.8
Monitoring value	4.0	11.6	5.6	16.1	0.1	0.3
Investigation value	0	0	0	0	0	0
Total area	34.7	100	34.7	100	34.7	100

### 3.2. Identification of pollution sources using PCA and spatial distribution maps

PCA was used to assess whether the different agricultural management practices similarly affected the retention of heavy metals. This analysis created a new set of variables (Table 4) with three eigenvectors (PC1, PC2 and PC3, accounting for 77.5% of the total data variance). However, only PC1 and PC2 are shown in Fig. 1 because they contain the highest percentage of the total variance. Eigenvectors with discriminatory value had coefficients greater than 0.5 or less than -0.5 (greater linear importance) and are highlighted in all eigenvectors.

The grouping resulting from PC1 (Table 4) involving the variables Ni and Cr was also found by Lado et al. (2008) in a study of European soils, wherein seismic activities and mineralization processes were associated with the increase of these metals in soils. The correlation observed in PC2 involved the variables SOM and Cd, which had the highest negative weights. The variable pH (PC3) showed discriminatory importance; however, it was not correlated with the other evaluated variables.

The statistical dispersion of points (Fig. 1) showed a heterogeneous distribution of metals in the areas under different management practices (CT, ST and NT).

The results showed that 15.2% of the area had medium SOM content and that 84.8% of the area had low SOM content (Fig. 2).

The spatial distributions of Cd and Cr (Fig. 3) indicate that the study area has undergone environmental pollution. The Ni concentrations of the study area were generally within the PV range or lower, albeit with outliers in the MV range.

## 4. Discussion

### 4.1. Soil metal levels

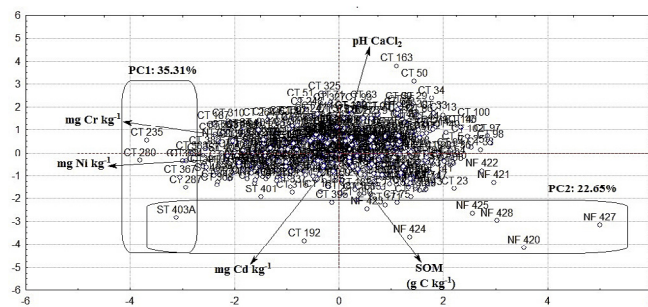
Heavy metals reach the soil from many sources: parent rock, rain, wind, natural phenomena such as volcanic eruption, earthquakes and anthropic actions. Soil management is an important

**Table 4**

Principal Components (PCs) found in the analysis involving pH, SOM, Cd, Cr and Ni in the study area.

Variables	PC1	PC2	PC3
SOM (g C kg <sup>-1</sup> )	0.3481	-0.6713*	0.3643
pH CaCl <sub>2</sub>	0.1024	0.4291	0.8871*
Cd (mg Cd kg <sup>-1</sup> )	-0.4377	-0.6707*	0.1942
Cr (mg Cr kg <sup>-1</sup> )	-0.8293*	0.2055	0.0208
Ni (mg Ni kg <sup>-1</sup> )	-0.8686*	-0.0766	0.1329

PC1 – principal component 1; PC2 – principal component 2; PC3 – principal component 3; SOM – soil organic matter; \*discriminatory values.



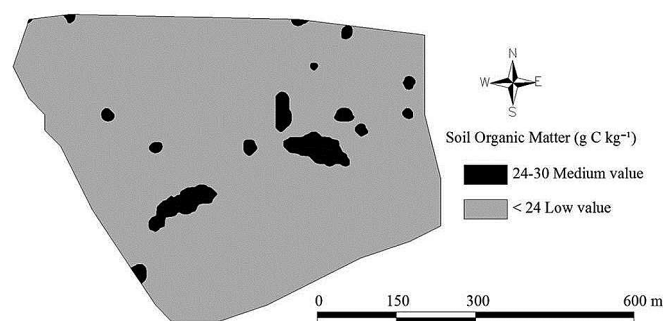
**Fig. 1.** Spatial projection and biplot of the principal components (PCs) found in the analysis of pH, SOM, Cd, Cr and Ni in the studied Oxisol. Ratio: variables/samples.

method of heavy metal addition to soil through organic or inorganic fertilizers, organic residues and other chemical products. Phosphate fertilizers are a source of Cd. Sewage sludge is a source of Ni and other heavy metals.

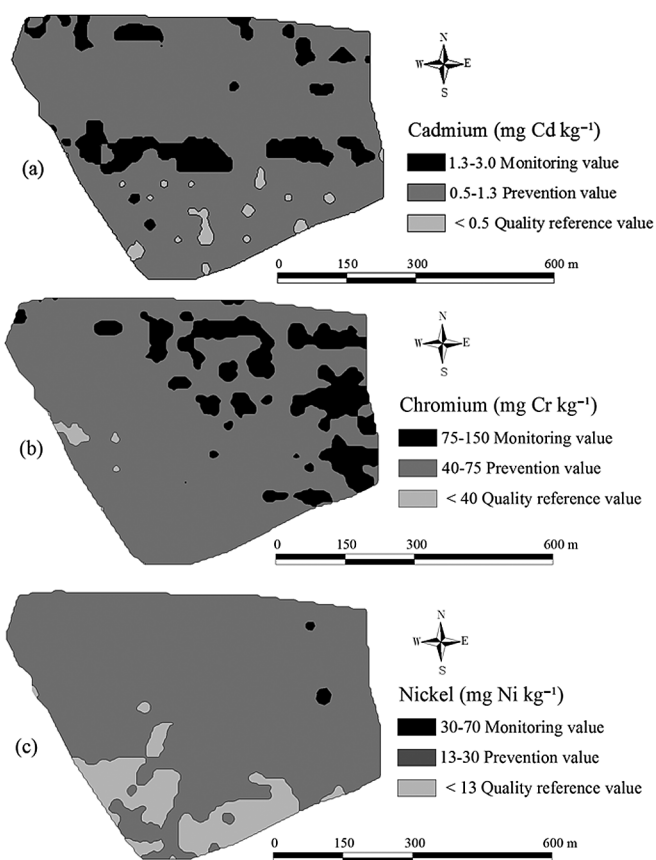
In this study, basalt should be the primary determining factor of the levels of the three metals in the forest area. This rock has higher mean Cd levels (0.21 mg Cd kg<sup>-1</sup>) than ultramafic rocks (0.05 mg Cd kg<sup>-1</sup>) and granite (0.13 mg Cd kg<sup>-1</sup>) (Alleoni et al., 2005).

The results of this study reinforce the claim that Brazilian Oxisols have higher heavy metal levels than the global average (Buol and Eswaran, 2000). Although this conclusion was based on a limited dataset, it indicates that QRVs should be detailed by soil order in future research studies. Furthermore, the results suggest that the Cd input into the system through industrial fertilizer application remains similar to the output through harvested crops, leaching and erosion.

Metals absorbed by plants at different depths are found in the plant debris deposited onto NT soils. The SOM produced tends to accumulate in the first centimeters of the soil because the residues are deposited and transformed on the soil surface in this system (Bayer et al., 2006; Calegari et al., 2008), and these metals may remain complexed to the organic molecules formed. Thus, enrichment of the soil surface layer with heavy metals occurs through metal removal from deeper layers and deposition on the surface, similar to the remobilization of plant nutrients. In tropical and subtropical regions, SOM content tends to be low because the microbial activity is high due to the high soil moisture and temperature. In these situations, oxides and hydroxides seem to have relevant importance in the control of the availability of heavy metals to plants and their movement into deeper layers. The association of metals with organic matter was generally lowest for Cd and Ni. Herbert (1997) found that Ni was bound primarily to cation exchange sites and organic matter in the reference soil, whereas in



**Fig. 2.** Map of the spatial distribution of soil organic matter (SOM) in the studied Oxisol using the Universal Transverse Mercator (UTM) projection system (Zone 22, Southern Hemisphere) and the SIRGAS2000 geodetic reference system.



**Fig. 3.** Maps of the spatial distribution of (a) Cd, (b) Cr and (c) Ni in the studied Oxisol using the Universal Transverse Mercator (UTM) projection system (Zone 22, Southern Hemisphere) and the SIRGAS2000 geodetic reference system.

polluted soils, metal partitioning was dominated by Fe oxide fractions, despite the high organic matter content.

The concentrations of Cd, Cr and Ni did not differ between CT and NT, likely because they received the same mineral fertilizers. ST tended to present the highest concentrations of the three metals but differed from CT only in Cd and Ni concentrations and from NT only in Ni. The absence of differences in Cd and Cr concentrations may be attributed to the amounts added by the mineral fertilizers and sewage sludge and likely to the formation of recalcitrant complexes not solubilized by the USEPA 3050B method. The difference between ST and NT in Ni concentration may be attributed to the high concentration of this metal in the sewage sludge taken from Barueri, which was used in 11 of the 17 years of application. This difference could have been greater considering that this metal produces recalcitrant complexes, and thus, the USEPA method evaluated only 20% of the total Ni present in this soil (Melo et al., 2007). The excess Cd content in ST compared with NT and CT may have resulted from the annual application of sewage sludge for 17 years (Bai et al., 2010; Merlino et al., 2010; Coscione et al., 2014).

Although the release of heavy metals associated with sewage sludge is strongly influenced by soil pH, cation exchange capacity, SOM, and mobility and speciation of specific metals, the bioavailability of sludge-borne heavy metals increases with the long-term application of sewage sludge (Singh and Agrawal, 2008).

The increase of Cr in CT, NT and ST is likely related to the use of limestone and industrial fertilizers, particularly phosphate fertilizers. Excluding thermophosphates, which have high Cr and Ni concentrations (Gabe and Rodella, 1999) and were not applied in the study areas, the phosphate fertilizers used in Brazil have low Cd,

Cr and Ni concentrations, ranging from 3 to 4 mg kg<sup>-1</sup> for Cd, from 14 to 26 mg kg<sup>-1</sup> for Cr and from 3 to 45 mg kg<sup>-1</sup> for Ni (Gabe and Rodella, 1999). However, metal accumulation is expected to occur over time because fertilizer application is annual and has been conducted for at least 50 years. The input of metals into the environment resulting from the use of limestone and fertilizers is the simplest explanation for the increase in the metal levels, although transformation processes must also be considered because the total levels are not assessed with the extractor used (Campos et al., 2003; Santos and Alleoni, 2013).

In the cultivated areas, the measured metal contents represent the balance among inputs, outputs and biochemical/chemical transformations. Inputs occurred through atmospheric deposition and by the application of limestone and fertilizers, particularly phosphates, and of sewage sludge where it was applied (Gonçalves Junior et al., 1999; Jiao et al., 2012). Although the limestone and phosphate fertilizers marketed in Brazil are not among the richest in heavy metals, the cumulative effect of annual applications for at least 50 years may result in increased soil concentrations of heavy metals (Amaral Sobrinho et al., 1992; Carvalho et al., 2012; Soares et al., 2015).

Outputs occur by 1) leaching, which should not be quantitatively important because the soil of the study area is clayey and rich in oxides and kaolinite, which are adsorbents with high metal retention power; 2) harvest, which despite the small quantities, occurs annually; and 3) erosion, which can be quantitatively important because the slope of the area is 11.48% and because of the many years when it was farmed with only one crop cycle per year, with plowing and harvesting leaving exposed soil for several months each year. Erosion may have transferred soil from higher parts to lower parts of the terrain, in the process transporting soil from the superficial layer, richer in SOM. However, in the last 50 years, the experimental area has been terraced to restrict surface erosion to some extent.

If the metal content in cultivated areas is increased relative to the natural condition (NF), a positive balance has occurred, i.e., the inputs were greater, or the crop resulted in changes in the chemical forms of the metals in the soil. Any conversion that occurred may have transformed unextractable forms of SOM into extractable forms. The main change in the soil when forested area is converted to cultivated area is a decrease in the SOM content, as observed in our results. In our study, forest areas were converted to cultivated areas, generally into conventional cultivation, upturning the soil (plowing and harvesting) in all areas. Later (in the last 10–20 years), the no-tillage system was used in a portion of the study area.

When SOM mineralizes, the adsorbed or complexed metals are solubilized, with only an extremely small fraction remaining in solution and most reacting rapidly with the solid phase adsorbents (the SOM itself, the oxides and kaolinite). Because SOM is decreasing, after the mineralization, readsorption to the oxides and kaolinite can be assumed to occur preferentially, and assuming an 80-year time interval, a significant portion of the metals associated with SOM may have become bound to oxides and silicate minerals. Depending on the chemical form of the metal in the soil, it may be unextractable or only partially extractable.

In our study, the metal extraction method favored the extraction of organic forms, and it did not clearly completely extract the metals associated with the SOM in the forest area because the amount of oxidant is limited by the procedure itself (effervescence remained when applying hydrogen peroxide to the forest samples when the procedure was interrupted). Therefore, with the USEPA 3050B method, it is not clear that the fraction of metals bound to the oxides for the cultivated areas or the forest was completely extracted because complete extraction is only obtained by solubilizing the oxides using a reducing agent not used in the USEPA

3050B method. The fraction bound to silicates is not extracted using this method. However, regardless of methodological difficulties, at some points in the experimental area, the Cd, Cr and Ni concentrations observed suggest contamination under Brazilian law.

Another consideration is that no-tillage leads to stratification; thus, if contamination occurs in no-tillage areas, the plants absorb metals from deeper layers and translocate them aboveground, the post-harvest residue decomposes and the metals are retained in the surface layer. This effect only occurs over many years.

#### 4.2. Identification of pollution sources by PCA and spatial distribution maps

In the present study, the direct relationship between higher levels and PC1 (−0.8686 and −0.8293 for Ni and Cr, respectively) showed that mineral fertilization and sewage sludge fertilization contributed similarly to increased soil Ni and Cr accumulation.

The correlation observed with PC2 and the variables SOM and Cd shows that the increase in SOM levels is accompanied by increases in Cd concentration; this interaction is explained by the adsorptive and complexing capacities of SOM, which may affect the solubility, bioavailability and mobility of metals, thereby retaining them and reducing the mobility of this pollutant (Quenea et al., 2009).

Although the variable pH showed discriminatory importance, it was not correlated with the other variables (Table 4), possibly due to the extractor used to assess the metal concentrations in the soil. pH is a key variable when assessing the availability of metals for plants because solubilization and increased availability may occur when the acidity of the medium increases.

The statistical dispersion of the points shown in Fig. 1 is indicated by the position of the points on the plane (i.e., the points agglomerated at the intersection of the axes), indicating that the three management types (CT, ST and NT) did not affect the metal concentration as evaluated by the USEPA 3050B method.

The NF points were distributed homogeneously, all located to the right of the plane, and had high SOM and Cd values compared with the other points. The high SOM concentration indicated good soil quality, likely because this area never experienced anthropogenic effects (Souza et al., 2010), whereas the high Cd concentration might be explained by the soil source material (Cai et al., 2015).

Notably, higher SOM levels help supply nutrients to plants, complex toxic elements and micronutrients and retain cations (Lima et al., 2009; Costa et al., 2010). In the present study, the lowest SOM levels were found in areas with a CT farming system. Increased SOM concentrations occur in the surface of soils with no-till farming (Cardoso et al., 2010; Santos et al., 2008), with the aforementioned implications for the metal concentrations in the NT areas.

Although the metal concentrations of the area mostly ranged within the prevention limits, the metals continue to accumulate in the soil and cause pollution (Quenea et al., 2009). Fig. 3 shows that the Cd, Cr and Ni concentrations in some small areas already exceeded the PVs and were within the range of the MVs, which indicated pollution. This contamination primarily resulted from the accumulation of these elements in the soil through intensive farming practices because phosphate fertilizers and sewage sludge are known sources of contamination (Mortvedt, 1996; Nogueira et al., 2008; Cai et al., 2015).

However, the source material of the study area, formed by alkaline rocks (Centurion et al., 1995), is a natural source for heavy metals. In Brazil, regional standards already exist (FEPAM, 2014) that indicate MVs based on soil source material. Additionally, as shown in Fig. 3, the highest concentrations of Cd, Cr and Ni occurred in the northern portion of the respective maps, which can

be explained by the presence of a textural gradient in the soil clay fraction, as indicated by Andrioli and Centurion (1999). Finally, water flows south-north across the experimental area, which causes soil particles to be transported, particularly clay. This transport process was probably intensified by the years of agricultural management of the area.

## 5. Conclusions

The Cd, Cr and Ni concentrations in the NF area were higher than the reference soil quality values in Brazilian legislation, indicating that the source material was the determining factor for the high metal concentrations in the study soils, especially for Cd. Portions of the experimental area are contaminated with these metals, with contents greater than the alert or PVs in the same legislation. The application of sewage sludge was the major contributor to the accumulation of Cd and Ni.

## Acknowledgments

The authors thank the Brazilian Federal Agency for the Support and Evaluation of Graduate Education (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - CAPES) for scholarship funding, the Postgraduate Program in Microbiologia Agropecuária from FCAV/ UNESP, São Paulo, CNPq (National Council for Scientific and Technological Development) for the granting of scholarships and financial support and the Teaching, Research and Extension Farm (Fazenda de Ensino, Pesquisa e Extensão - FEPE) staff at the School of Agricultural and Veterinary Sciences of São Paulo State University (Universidade Estadual Paulista “Júlio de Mesquita Filho” - UNESP), Jaboticabal Campus – São Paulo (SP) for assistance with soil collection.

## References

- Ali, S.M., Malik, R.N., 2011. Spatial distribution of metals in top soils of Islamabad City, Pakistan. *Environ. Monit. Assess.* 172, 1–16. <http://dx.doi.org/10.1007/s10661-010-1314-x>.
- Alleoni, L.R.F., Borba, R.P., Camargo, A.O., 2005. Metais pesados: da cosmogênese aos solos brasileiros. *Tópicos em Ciência do Solo* 4, 1–42.
- Amaral Sobrinho, N.M.B., Costa, L.M., Oliveira, C., Velloso, A.C.X., 1992. Metais pesados em alguns fertilizantes e corretivos. *Rev. Bras. Cienc. Solo* 16, 271–276.
- Andrioli, I., Centurion, J.F., 1999. Levantamento detalhado dos solos da Faculdade de Ciências Agrárias e Veterinárias de Jaboticabal. *Congr. Bras. Ciência do Solo Ann.* 27.
- Bai, Ling-yu, Zeng, Xi-bai, Li, Liang-fang, Pen, C., Li, Shu-hui, 2010. Effects of land use on heavy metal accumulation in soils and sources analysis. *Agric. Sci. China* 9, 1650–1658. [http://dx.doi.org/10.1016/S1671-2927\(09\)60262-5](http://dx.doi.org/10.1016/S1671-2927(09)60262-5).
- Bayer, C., Martin-Neto, L., Mielniczuk, J., Pavinato, A., Dieckow, J., 2006. Carbon sequestration in two Brazilian Cerrado soils under no-till. *Soil Till Res.* 86, 237–245. <http://dx.doi.org/10.1016/j.still.2005.02.023>.
- Brandt, H.B., 2005. *Heavy Metals in the Environment: Origin, Interaction and Remediation*. Elsevier Academic Press, Amsterdam; Boston.
- Brasil, 2009. Conselho Nacional do Meio Ambiente. Resolução 420, de 28 de dezembro de 2009 [internet]. Conselho Nacional do Meio Ambiente, Brasília, DF. <http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620> (Accessed 10 July 2015).
- Buol, S.W., Eswaran, H., 2000. Oxisols. *Adv. Agron.* 68, 151–195.
- Cai, L., Xu, Z., Bao, P., He, M., Dou, L., Chen, L., Zhou, Y., Zhu, Y., 2015. Multivariate and geostatistical analyses of the spatial distribution and source of arsenic and heavy metals in the agricultural soils in Shunde, Southeast China. *J. Geochem Explor* 148, 189–195. <http://dx.doi.org/10.1016/j.gexplo.2014.09.010>.
- Calegari, A., Hargrove, W.L., Rheinheimer, D.D.S., Ralisch, R., Tessier, D., de Tourdonnet, S., de Fatima Guimarães, M., 2008. Impact of long-term no-tillage and cropping system management on soil organic carbon in an Oxisol: a model for sustainability. *Agron. J.* 100, 1013–1019. <http://dx.doi.org/10.2134/agronj2007.0121>.
- Camara, G., Souza, R.C.M., Freitas, U.M., Garrido, J., 1996. SPRING: integrating remote sensing and GIS by object-oriented data modelling. *Comput. Graph* 20, 395–403. [http://dx.doi.org/10.1016/0097-8493\(96\)00008-8](http://dx.doi.org/10.1016/0097-8493(96)00008-8).
- Campos, M.L., Pierangeli, M.A.P., Guilherme, L.R.G., Marques, J.J., Curi, N., 2003. Baseline concentration of heavy metals in Brazilian Oxisols. *Commun. Soil Sci. Plan.* 34, 547–557.
- Campos, M.L., Silva, F.D., Furtini Neto, A.E., Guilherme, L.R.G., Marques, J.J.,

- Antunes, A.S., 2005. Determinação de cádmio, cobre, cromo, níquel, chumbo e zinco em fosfatos de rocha. *Pesqui. Agropecu. Bras.* 40, 361–367. <http://dx.doi.org/10.1590/S0100-204X2005000400007>.
- Cardoso, E.L., Silva, M.L.N., Silva, C.A., Curi, N., Freitas, D.A.F., 2010. Estoques de carbono e nitrogênio em solo sob florestas nativas e pastagens no bioma Pantanal. *Pesqui. Agropecu. Bras.* 45, 1028–1035. <http://dx.doi.org/10.1590/S0100-204X2010000900013>.
- Carvalho, V.G.B., Nascimento, C.W.A., Biondi, C.M., 2012. Potential de fertilizantes e corretivos no aporte de micronutrientes ao solo. *Rev. Bras. Cienc. Solo* 36, 931–938. <http://dx.doi.org/10.1590/S0100-06832012000300023>.
- Centurion, J.F., Andrioli, I., Marques Jr., J., Marchiori, D.G., 1995. Características de Latossolos Roxos desenvolvidos de rochas alcalinas e básicas de Jaboticabal. *SP. Sci. Agric.* 52, 226–232.
- CETESB - Companhia de Tecnologia de Saneamento Ambiental, 2014. Decisão de Diretoria nº 045-2014-E-C-I em 20-02-2014 [decisão na internet]. São Paulo (Accessed 10 July 2015). Available in: [www.cetesb.sp.gov.br/wp-content/uploads/sites/11/2013/11/DD-045-2014-P53.pdf](http://www.cetesb.sp.gov.br/wp-content/uploads/sites/11/2013/11/DD-045-2014-P53.pdf).
- Chandrasekaran, A., Ravisankar, R., Hari Krishnan, N., Satapathy, K.K., Prasad, M.V.R., Kanagasabapathy, K.V., 2015. Multivariate statistical analysis of heavy metal concentration in soils of Yelagiri Hills, Tamilnadu, India – spectroscopic approach. *Petrochim Acta Part A Mol. Biomol. Spectrosc.* 137, 589–600. <http://dx.doi.org/10.1016/j.saa.2014.08.093>.
- Chen, T., Liu, X.M., Zhu, M.Z., Zhao, K.L., Wu, J.J., Xu, J.M., Huang, P.M., 2008. Identification of trace element sources and associated risk assessment in vegetable soils of the urban-rural transitional area of Hangzhou, China. *Environ. Pollut.* 151, 67–78. <http://dx.doi.org/10.1016/j.envpol.2007.03.004>.
- Coscione, A.R., Silva, L.F.M., De Maria, I.C., Andrade, C.A., Ferracini, V.L., 2014. Solução do solo e análise de componentes principais para monitoramento da aplicação de lodo de esgoto. *Rev. Bras. Cienc. Solo* 38, 1654–1662. <http://dx.doi.org/10.1590/S0100-06832014000500030>.
- Costa, F.X.X., Beltrão, N.M.E.M., Cruz, O., Silva, F.E.A.A., Filho, J.S.M.M., Silva, M.A.S., 2010. Disponibilidade de nutrientes no solo em função de doses de matéria orgânica no plantio da mamona. *R. Verde Agroecol. Desenv. Sust.* 5, 204–212.
- Fagbote, E.O., Olanipekun, E.O., 2010. Evaluation of the status of heavy metal pollution of soil and plant (*Chromolaena odorata*) of Agbabu bitumen deposit area, Nigeria. *Am-Eurasian J. Sci. Res.* 4, 241–248.
- FEPAM – Fundação Estadual de Proteção Ambiental Henrique Luiz Rossler/RS, 2014. Portaria FEPAM 85/2014. Porto Alegre. <http://www.fepam.rs.gov.br/legislacao/arq/Portaria085-2014.pdf> (Accessed 17 May 2017).
- Gabe, U., Rodella, A.A., 1999. Trace elements in Brazilian agricultural limestones and mineral fertilizers. *Commun. Soil Sci. Plan.* 30, 605–620. <http://dx.doi.org/10.1080/00103629909370231>.
- Ghreat, H.A., Rukah, Y.A., Rosen, M.A., 2011. Application of geoaccumulation index and enrichment factor for assessing metal contamination in the sediments of Kafra Dam, Jordan. *Environ. Monit. Assess.* 178, 95–109. <http://dx.doi.org/10.1007/s10661-010-1675-1>.
- Gonçalves Junior, A.C., Luchese, E.B., Lenzi, E., 1999. Avaliação da fitodisponibilidade de cádmio, chumbo e cromo, em soja cultivada em latossolo vermelho escuro tratado com fertilizantes comerciais. *Quím. Nova* 23, 173–177.
- Harmanescu, M., Liana, M.A., Despina, M.B., Ioan, G., Iosif, G., 2011. Heavy metals health risk assessment for population via consumption of vegetables grown in old mining area; a case study: banat County, Romania. *Chem. Cent. J.* 5, 1–10. doi: [journal.chemistrycentral.com/content/5.1.64](http://journal.chemistrycentral.com/content/5.1.64).
- Herbert Jr., R.B., 1997. Partitioning of heavy metals in podzol soils contaminated by mine drainage water, Dalarna, Sweden. *Water Air Soil Poll.* 96, 39–59. <http://dx.doi.org/10.1023/A:1026461612610>.
- Instituto Nacional de Pesquisas Espaciais – INPE, 2014. Spring (Sistema para Processamento de Informações Georeferenciadas), version 5.2.7. <http://www.dpi.inpe.br/spring/portugues/download.php> (Accessed 25 October 2015).
- Jiao, W., Chen, W., Chang, A.C., Page, A.L., 2012. Environmental risks of trace elements associated with long-term phosphate fertilizers applications: a review. *Environ. Pollut.* 168, 44–53. <http://dx.doi.org/10.1016/j.envpol.2012.03.052>.
- Kaiser, H.F., 1958. The varimax criterion for analytic rotation in factor analysis. *Psychometrika* 23, 187–200. <http://dx.doi.org/10.1007/BF02289233>.
- Lado, L.R., Hengl, T., Reuter, H.I., 2008. Heavy metals in European soils: a geo-statistical analysis of the FOREGS Geochemical database. *Geoderma* 148, 189–199. <http://dx.doi.org/10.1016/j.geoderma.2008.09.020>.
- Lavres Jr., J., Reis, A.R., Nogueira, T.A.R., Cabral, C.P., Malavolta, E., 2011. Phosphorus uptake by upland rice from superphosphate fertilizers produced with sulfuric acid treatments of Brazilian phosphate rocks. *Commun. Soil Sci. Plan.* 42, 1390–1403. <http://dx.doi.org/10.1080/00103624.2011.577859>.
- Lima, R.L.S., Severino, L.S., Albuquerque, R.C., Ferreira, G.B., Sampaio, L.R., Beltrão, N.E.M., 2009. Capacidade da cinza de madeira e do esterco bovino para neutralizar o alumínio trocável e promover o crescimento da mamoneira. *Rev. Bras. Ol. Fibras* 13, 9–17.
- McBride, M.B., 2003. Toxic metals in sewage sludge-amended soils: has promotion of beneficial use discounted the risks? *Adv. Environ. Res.* 8, 5–19. [http://dx.doi.org/10.1016/S1093-0191\(02\)00141-7](http://dx.doi.org/10.1016/S1093-0191(02)00141-7).
- Melo, W.J., Aguiar, P.S., Melo, G.M.P., Melo, V.P., 2007. Nickel in a tropical soil treated with sewage sludge and cropped with maize in a long-term field study. *Soil Biol. Biochem.* 39, 1341–1347. doi: [10.1016/j.soilbio.2006.12.010](https://doi.org/10.1016/j.soilbio.2006.12.010).
- Merlino, L.C.S., Melo, W.J., Macedo, F.G., Guedes, A.C.T.P., Ribeiro, M.H., Melo, V.P., Melo, G.P., 2010. Bário, cádmio, cromo e chumbo em plantas de milho e em Latossolo após onze aplicações anuais de LE. *Rev. Bras. Cienc. Solo* 34, 2031–2039. <http://dx.doi.org/10.1590/S0100-06832010000600027>.
- Micó, C., Peris, M., Sánchez, J., Recatalá, L., 2006. Heavy metal content of agricultural soils in a Mediterranean semiarid area: the Segura River Valley (Alicante, Spain). *Span. J. Agric. Res.* 4, 363–372. <http://dx.doi.org/10.5424/sjar/2006044-213>.
- Mortvedt, J.J., 1996. Heavy metal contaminants in inorganic and organic fertilizers. *Fert. Res.* 43, 55–61. <http://dx.doi.org/10.1007/BF00747683>.
- Nagajyoti, P.C., Lee, K.D., Sreekanth, T.V.M., 2010. Heavy metals, occurrence and toxicity for plants: a review. *Environ. Chem. Lett.* 8, 199–216. <http://dx.doi.org/10.1007/s10311-010-0297-8>.
- Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* 311, 205–219. [http://dx.doi.org/10.1016/S0048-9697\(03\)00139-6](http://dx.doi.org/10.1016/S0048-9697(03)00139-6).
- Nogueira, T.A.R., Oliveira, L.R., Melo, W.J., Fonseca, I.M., Melo, G.M.P., Melo, V.P., Marques, M.O., 2008. Cádmio, cromo, chumbo e zinco em plantas de milho e em Latossolo após nove aplicações anuais de lodo de esgoto. *Rev. Bras. Cienc. Solo* 32, 2195–2207. <http://dx.doi.org/10.1590/S0100-06832008000500040>.
- Quenea, K., Lamy, I., Winterton, P., Bermond, A., Dumat, C., 2009. Interactions between metals and soil organic matter in various particle size fractions of soil contaminated with waste water. *Geoderma* 149, 217–223. <http://dx.doi.org/10.1016/j.geoderma.2008.11.037>.
- Raij, B., van, Andrade, J.C., Cantarella, H., Quaggio, J.A., 2001. Análise química para avaliação da fertilidade de solos tropicais. Instituto Agronômico, Campinas, 2001. (Boletim Técnico, 100).
- Santos, S.N., Alleoni, L.R.F., 2013. Methods for extracting heavy metals in soils from the Southwestern Amazon, Brazil. *Water Air Soil Poll.* 224, 1–16. <http://dx.doi.org/10.1007/s11270-012-1430-z>.
- Santos, H.P., Spera, S.T., Tomm, G.O., Kochann, R.A., Ávila, A., 2008. Efeito de sistemas de manejo de solo e de rotação de culturas na fertilidade do solo, após vinte anos. *Bragantia* 67, 441–454. <http://dx.doi.org/10.1590/S0006-87052008000200020>.
- Singh, R.P., Agrawal, M., 2008. Potential benefits and risks of land application of sewage sludge. *Waste Manag.* 28, 347–358. <http://dx.doi.org/10.1016/j.wasman.2006.12.010>.
- Soares, A.P., Weber, O.L.S., Espírito Santo, O., 2015. Metais pesados em calcários do Estado de Mato Grosso. *Geociências* 34, 465–474.
- Sousa, D.M.G., Lobato, E. (Eds.), 2004. Cerrado – correção do solo e adubação, 2.ed. Embrapa Informação Tecnológica, Brasília.
- Souza, E.D., Costa, S.E.V.G.A., Anghinoni, I., Carvalho, P.C.F., Oliveira, E.V.F., Martins, A.P., Cao, E., Andrighetti, M., 2010. Soil aggregation in a crop-livestock integration system under no-tillage. *Rev. Bras. Cienc. Solo* 34, 1365–1374. <http://dx.doi.org/10.1590/S0100-06832010000400033>.
- Statsoft, 2004. Statistica (Data Analysis Software System), Version 7 [internet]. <http://www.statsoft.com> (Accessed 25 May 2015).
- United States Environmental Protection Agency – USEPA, 1996. USEPA 3050B, Revision 2 [internet]. United States Environmental Protection Agency 3050B, US. <http://www3.epa.gov/epawaste/hazard/testmethods/sw846/NFts/3050b.NTF> (Accessed 23 April 2015).
- Wei, B., Yang, L., 2010. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. *Microchem. J.* 94, 99–107. <http://dx.doi.org/10.1016/j.microc.2009.09.014>.
- Weirich-Neto, P.H., Caires, E.F., Justino, A., Dias, J., 2000. Correction of soil acidity in function of lime incorporation manners. *Cienc. Rural.* 30, 257–261. <http://dx.doi.org/10.1590/S0103-84782000000200010>.
- Zhang, X.P., Deng, W., Yang, X.M., 2002. The background concentrations of 13 soil trace elements and their relationships to parent materials and vegetation in Xizang (Tibet), China. *J. Asian Earth Sci.* 21, 167–174. [http://dx.doi.org/10.1016/S1367-9120\(02\)00026-3](http://dx.doi.org/10.1016/S1367-9120(02)00026-3).
- Zheng, L.G., Liu, G.J., Kang, Y., Yang, R.K., 2010. Some potential hazardous trace elements contamination and their ecological risk in sediments of western Chaohu Lake, China. *Environ. Monit. Assess.* 166, 379–386. <http://dx.doi.org/10.1007/s10661-009-1009-3>.