Chemosphere 185 (2017) 344–350

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Agricultural management of an Oxisol affects accumulation of heavy metals

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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 Eutroferric 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_3, H_2O_2 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^{-1}, 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.

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

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http://dx.doi.org/10.1016/j.chemosphere.2017.07.008
0045-6535/© 2017 Published by Elsevier Ltd.

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^{-1}, 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^{-1}. 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^{-1}; 20 g P kg^{-1}; 2.5 g K kg^{-1}; 0.19 g Cu kg^{-1}; 0.07 mg Mn kg^{-1}; 0.5 mg Zn kg^{-1}; 0.05 mg Cr kg^{-1}; 1.66 mg Cd kg^{-1}; 0.02 mg Ni kg^{-1} and 0.10 mg Pb kg^{-1}. 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 $CaCl_2$ and the soil organic matter (SOM) content were assessed according to Raij et al. (2001).

The United States Environmental Protection Agency (USEPA) method 3050B, which involves sample heating and open-system digestion with HNO_3, H_2O_2 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.