Assessment of heavy metal pollution, spatial distribution and origin in agricultural soils along the Sinú River Basin, Colombia

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ABSTRACT

The presence of metals in agricultural soils from anthropogenic activities such as mining and agricultural use of metals and metal-containing compounds is a potential threat for human health through the food chain. In this study, the concentration of heavy metals in 83 agricultural soils irrigated by the Sinú River, in northern Colombia, affected by mining areas upstream and inundated during seasonal floods events were determined to evaluate their sources and levels of pollution. The average concentrations of Cu, Ni, Pb, Cd, Hg and Zn were 1149, 661, 0.071, 0.040, 0.159 and 1365 mg/kg respectively and exceeded the world normal averages, with the exception of Pb and Cd. Moreover, all values surpassed the background levels of soils in the same region. Soil pollution assessment was carried out using contamination factor (CF), enrichment factor (EF), geoaccumulation index (Igeo) and a risk assessment code (RAC). According to these indexes, the soils show a high degree of pollution of Ni and a moderate to high contamination of Zn and Cu; whereas, Pb, Cd and Hg present moderate pollution. However, based on the RAC index, a low environmental risk is found for all the analysed heavy metals. Multivariate statistical analyses, principal component and cluster analyses, suggest that soil contamination was mainly derived from agricultural practices, except for Hg, which was caused probably by atmospheric and river flow transport from upstream gold mining. Finally, high concentrations of Ni indicate a mixed pollution source from agricultural and ferronickel mining activities.

1. Introduction

Metal content in soils is the result of metals arising from human activities and natural processes. Inputs of metals from anthropogenic origins to the soil are much greater than the contribution of metals from natural sources (Desaules, 2012; Li et al., 2012; Teng et al., 2014). In agricultural soils, the presence of metals is of increasing concern because they have the potential to be accumulated in less soluble forms, transferred into soil solution and subsequently deteriorate groundwater and crop quality (Kelepertzis, 2014). Although fertilisers are essential for providing adequate nutrients and ensuring successful harvests, long-term repeated application of fertilisers and metal-containing pesticides and fungicides can gradually accumulate to potentially harmful levels in soils (Jiao et al., 2012). Additionally, because fertilisers tend to be local and ingredient specific, the chemical composition of soils receiving fertiliser inputs is expected to vary according to application rates and raw mineral sources (Nziguheba and Smolders, 2008).

The Sinú River is in northwestern Colombia and flows south to

north for 415 km, mostly through the Córdoba Department, until flowing into the Caribbean Sea. The soils of the Sinú Valley are primarily used for livestock and agriculture, and the sources of heavy metals are mainly influenced by parent materials, mining, application of agrochemical fertilizer and pesticides, and atmospheric deposition. Agricultural soils are mainly used for maize (548 km^2), cotton (227 km^2) and rice (96 km^2) but also for yucca, kidney beans, red pepper, sorghum, bananas and corn. Although regional surveys continue to monitor pesticide residues in water and sediments (Marrugo, 2005; Marrugo et al., 2014, studies on heavy metals in agricultural soils and degrees of pollution are not developed. Therefore, an intensive survey was conducted in the present study to profile the accumulation and sources of Cu, Pb, Zn, Ni, Cd and Hg in 83 soil plots within the agricultural system of the Sinú River Basin, covering an area of approximately 300 km^2. Several indexes, (i.e., enrichment factor, contamination factor and geoaccumulation index) and multivariate analyses were combined to investigate the current state of soil in this area and to identify the spatial patterns and possible sources of the heavy metals. Such research will be used to provide baseline informa-

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tion for the soil quality status in Colombian agricultural soils, as a basis for effectively targeting policies to protect soils from long-term accumulation of heavy metals and for ensuring food crop quality and protecting human health.

2. Materials and methods

2.1. Study area

The Sinú River Basin is located in northwest Colombia, South America, within the departments of Córdoba and Antioquia in the southwestern region of the Colombian Caribbean coast. The Sinú River Basin originates in the Paramillo Massif located between 7° 8′ 9″–9° 27′ 2″ N and 75° 55′ 31″–75° 58′ 18″ W. The Sinú River is the primary water system in the department of Córdoba and its valley is home to agricultural and livestock activities (Feria et al., 2010). Due to the annual flooding of the Sinú River, the Sinú Valley has some of the most fertile soil in Colombia (Marrugo et al., 2014). Rainfall in this area is highly seasonal, with a dry period between January and March, a rainy season between April and December and a short dry period around June. An average of 1100–2000 mm of rain falls in this region per year, with the southern parts of the valley being wetter than those in the north. The average annual temperature is between 26 and 30 °C (Ruiz et al., 2008). The valley of the Middle Sinú covers an area of 5178 km^2 and contains the municipalities of Monteria, Cereté, San Pelayo, Ciénaga de Oro and San Carlos. Most of this subregion is composed of alluvial plains derived from the dynamics of the Sinú River. In general, the soils are deep or very deep with moderate to high fertility and are suitable for temporary or permanent crops such as cotton, rice, maize, beans and pasture (Marrugo et al., 2014). The Lower Sinú valley covers an area of 1752 km^2 and contains the municipalities of Cotorra, Chimá, Momil, Lorica and Purisima. Soils are composed of recent alluvial deposits with moderate fertility and are used for agriculture and livestock. In this region, land use is divided as follows: 70% is used for livestock, 23% comprising extensive swamps and marshes, and the remaining 7% is dedicated to agriculture (Viloria de la Hoz, 2004).

2.2. Soil sampling and chemical analysis

A total of 83 topsoil samples (0–20 cm) were collected from agricultural and pasture areas from the Middle and Lower Sinú River Basin during January-March 2015 (dry season). The locations of the sampling sites are shown in Fig. 1. Each sample was a composite of 5 subsamples collected from a 10 m×10 m grid using a stainless steel hand trowel and transported to the laboratory. Soil samples were then air-dried, passed through a 2 mm polyethylene sieve and finally ground into fine powder with an agate mortar. The ground samples were stored in polyethylene zip-type bags for further analysis.

For Cu, Zn, Ni, Cd and Pb analysis, the soil samples (0.5 g) were digested with HNO_3/HCl 8:2 v/v in a microwave oven (in triplicate) using Method 3051 A (USEPA, 2007a). The Hg concentrations were determined following the US EPA Method 7471B (USEPA, 2007b), whereby 0.5 g of soil was digested with H_2SO_4/HNO_3 7:3 v/v and 5% w/v $KMnO_4$ at 100 °C for 1 h. All analyses were performed using a spectrometer Thermo Elemental Solaar S4 coupled cold-vapour (Hg), flame (Cu, Zn, Ni), and graphite furnace (Cd, Pb).

The method for heavy metal estimation was validated with the certified reference material 'Trace Metals Soil – Sediment' (CRM008-050: certified value; Hg 0.72 mg/kg, Cu 36.4 mg/kg, Ni 26 mg/kg, Pb 95.3 mg/kg, Cd 0.82 mg/kg). The percentages of recovery average for heavy metals were 98.4% (n=3). The sequential extraction method showed no statistically significant differences (P < 0.05) between the $\sum$ Heavy metal of the extracted fractions and the concentrations of heavy metals determined by digestion of the soils, demonstrating that the method shows good precision (< 2.5%) and accuracy (< 5.0%).

The organic matter was determined as the percentage loss on

ignition of 2.0g of sediment in an oven at 450 °C for 4 h (Coquery and Welbourn, 1995). The pH was determined in a relationship soil-water 1:1 with a combination glass electrode pH meter coupled to a computer (WTW, 330i). The soil texture was determined by measuring the proportions of clay, silt and sand particles present in the soil. These constituents were measured using the pipette method and the soil type was classified using the soil texture triangle (Pla, 1983). The cation exchange capacity (CEC) of the mineral soils was calculated as the sum of Ca+Mg+K+Na+Fe+Al+Mn extractable with 1 M of NH_4-acetate (IGAC 1979). A sequential extraction scheme was used to study the fractionation of metals in the soils and determine the bioavailability and speciation by employing the Bureau of Community Research (BCR) method (Rauret et al., 2000). Therefore, water-soluble and exchangeable metals (F1), reducible metals bound to Fe and Mn (F2), oxidisable metals bound to organic matter and sulphides (F3), and residual metals bound to silicate minerals (F4) were investigated. To 1.0g of soil sample, 40 mL of 0.11 mol L^{-1} acetic acid was added and shaken for 16 h at 25 °C in a mechanical shaker to extract water-soluble, exchangeable and carbonate-bound metals. The samples were centrifuged at 4000 rpm for 10 min and the supernatant passed through 0.45 mm filter. To the residue, 40 mL of 0.5 mol L^{-1} hydroxylamine hydrochloride was added and shaken for 16 h to extract the reducible metals. To the residue, 10 mL of 8.8 mol L^{-1} hydrogen peroxide was added and digested for an hour at 25 °C and left for another hour at 85 °C in a water bath. The solvent was evaporated and 50 mL of 1 mol L^{-1} ammonium acetate was added to the residue and shaken for 16 h to extract oxidisable metals at pH 2. Finally, aqua-regia digestion was carried out in a microwave digester to determine the status of the metals in the residue by atomic absorption analytical method.

2.3. Quantification of soil pollution

2.3.1. Contamination factor

The contamination factor (CF) is the ratio obtained by dividing the concentration of each metal in the soil by the baseline or background value:

$$CF = \frac{C_{heavy\ metal}}{C_{background}}$$

The contamination levels may be classified based on their intensities on a scale ranging from 1 to 6 (0=none, 1= none to medium, 2=moderate, 3=moderate to strong, 4=strongly polluted, 5=strong to very strong, 6=very strong) (Muller, 1969). The highest number indicates that the metal concentration is 100 times greater than what would be expected in the crust.

2.3.2. Enrichment factor

The enrichment factor (EF) for each metal is calculated by dividing its ratio to the normalising element by the same ratio found in the chosen baseline (Taylor, 1964):

$$EF = \frac{(metal/Al)_{sample}}{(metal/Al)_{background}}$$

The EF values close to unity indicate crustal origin and EFs > 10 are considered to be non-crustal source. EF > 1.0 suggest an anthropogenic origin and those < 1.0 suggest a possible mobilisation or depletion of metals (Zsefer et al., 1996). The degree of metal pollution was based on seven enrichment factor classes (Taylor, 1964). Accordingly, an EF value of 50 corresponds to extremely severe enrichment; EF=25 − < 50 to very severe enrichment; EF=10 − < 25 to severe enrichment; EF=5 − < 10 to moderately severe enrichment; EF=3 − < 5 to moderate enrichment; EF=1 − < 3 to minor enrichment and EF < 1 to no enrichment. For most heavy metals of environmental interest, concentrations in soil easily vary over two to three orders of magnitude depending on the parent materials (Blaser et al., 2000). In