



Background levels of potentially toxic elements in soils: A case study in Catamarca (a semiarid region in Argentina)

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ABSTRACT

Thirty soil profiles from the agricultural area of Fray Mamerto Esquiú (Catamarca, Argentina) were investigated, and the variability in the natural background levels of seven heavy metals (e.g., Cd, Cr, Cu, Mn, Ni, Pb and Zn) was examined. Sampling sites with minimal anthropogenic influence were selected, and soil profile samples were analysed for major and trace element content. The soil samples were collected from every horizon in each profile, and the samples were digested using the *aqua regia* and DTPA methods for pseudo-total and available heavy metals, respectively. A clear distinction was found between the metal content of the soils developed in each Reference Soil Group: the A-horizon reflects the complex interplay between the atmosphere, biosphere and lithosphere; the B-horizon can be used to study the influence of soil-forming processes; and the C-horizon represents the composition of the parent material at each sample site. The occasional or continuous addition of sediments to soil profiles, as well as organic matter accumulation and humification, make up the soil-forming processes of the greatest importance to the distribution of pseudototal heavy metals. The upper limits of the background levels, which help distinguish between natural and anomalous element concentrations, are presented. The heavy metal with the greatest number of samples and slight enrichment anomalies is Cd. Slight enrichment anomalies in Cd, Cr, Cu, Pb and Zn were detected in profile 29, confirming anthropogenic contamination. The results of this study confirm the importance of the local determination of background concentrations. The percentage of organic matter is the determining factor in the presence and distribution of the metals (Cu, Fe, Mn and Zn) available in the soils of the studied area, the top horizon having the greatest accumulation. Zn_{DTPA} is the only available metal that also shows differences associated with soil salinity. However, the geochemical soil conditions imply low extractability, suggesting the plants in Fray Mamerto Esquiú have difficulty with micronutrient absorption.

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1. Introduction

Knowing the concentrations of trace elements in soils is essential to maintaining environmental quality. In recent years, separating background values from baseline values to discriminate between anthropogenic contamination and natural (geogenic) sources has arguably become even more crucial than distinguishing background values from anomalies when conducting geochemical prospecting for mineral exploration (Albanese et al., 2007). The term “geochemical baseline” indicates the actual content of an element in a superficial environment at a given point in time, as defined by Salminen and

Gregorauskiene (2000). The determination of background values (as geogenic natural content), in contrast to baseline values, is crucial when defining the extent of contamination in areas where environmental legislation has not yet established intervention limits for all environmental matrices (Albanese et al., 2007).

The background levels of a given element in a particular soil are highly dependent on the mineralogical composition of the parent material (Prabhakaran and Cottenie, 1971) in the soil and the weathering processes that led to the formation of the soil (Klassen, 1998). The grain size is also important (Salminen and Tarvainen, 1997), as well as clay and organic matter content (Mellum et al., 1998; Tack et al., 1997). Because the heavy metal content of soils varies widely, background values are characterised by regional variability and are a function of time (Matschullat et al., 2000). Therefore, it is inappropriate to use universal background concentrations or report normal content, as the native concentrations of metals in a specific soil may exceed the ranges listed (Horckmans et al., 2005).

Different approaches have been used to establish the background levels of trace elements in soils (Tobías et al., 1997). Therefore, in

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this study, descriptive statistics and normal ranges were calculated from the background populations. These populations were obtained by dividing the raw data set, which contains normal and anomalous values, into its constituent populations using different statistical techniques to yield realistic and plausible values. In most statistical tests, it is helpful to eliminate outliers and thus reduce the original data set to a “clean” data set (Matschullat et al., 2000). Moreover, in the present study, background concentrations were determined by analysing soils considered unaffected or, at least, minimally affected by man.

There is also a practical reason for defining the border between the concentration of a chemical element or component that naturally occurs and the concentration of the same analyte when present as a result of anthropogenic activities. A deficit or excess of these elements can have serious implications for plant growth and animal and/or human health (Tiller, 1989). Nriagu and Pacyna (1988) believe that the mobilisation of heavy metals in the biosphere caused by human activity has significantly increased the circulation of toxic metals throughout the environment. However, knowing the total amount of heavy metals in the biosphere does not indicate the amount of metals available to plants. Metals accumulate in the tissues of living organisms because they are not, as are the majority of organic compounds, subject to metabolic breakdown. High levels of heavy metals in a soil may result in increased levels of metals in plants, but plant uptake is dependent on various soil properties (McGrath, 1996). However, this accumulation will not necessarily demonstrate itself as toxicity, as certain metals form highly stable compounds or are rendered inactive in different ways (Romic and Romic, 2003). Therefore, single extraction tests are commonly used to study the ecotoxicity and mobility of metals in soils and to assess the proportion of metals available to plants. However, the lack of procedural uniformity prevents a worldwide comparison of results and validation of procedures (Quevauviller et al., 1996). Knowledge of the relationship between extractable metals and their concentrations in plants can be improved by including other soil properties known to affect availability. The soil factors that affect this relationship depend on the chemical composition of the solution utilised (He and Singh, 1993). Neutral salt solutions and complex-forming reagents have been found to be good for the assessment of plant-available heavy metals (Mellum et al., 1998).

Data are scarce on the qualitative and quantitative trace element content of Argentinian soils. Recently, Lavado et al. (2004) determined the baseline levels of potentially toxic elements in Pampean soils. The soils of Catamarca province, located in northwestern Argentina, are generally thought to be uncontaminated. Nevertheless, the intensive urbanisation of agricultural soils around Catamarca's provincial capital has led to a situation in which agricultural soils are trapped within suburban areas. Therefore, the influence of urban and industrialised environments on the accumulation of metals in agricultural soils needs to be investigated.

The objectives of this study were the following: 1) to determine the pseudototal and available content of eight heavy metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in agricultural soils trapped within suburban areas; 2) to assess the role of soil properties in the adsorption, accumulation or translocation of heavy metals; and 3) to evaluate the natural backgrounds of the soil samples selected using the *4 σ -outlier test*, *iterative 2 σ -outlier test* and *calculated distribution function* described by Matschullat et al. (2000).

2. Material and methods

2.1. Area description

The area studied is 40 km² and is located 20 km NW of San Fernando del Valle de Catamarca in the municipal district of Fray Mamerto Esquíu, Argentina (28° 2'–28° 25' S, 65° 42'–65° 44' W). This area belongs to the geologic province of the Pampean Sierras

(Blasco et al., 1995), which is characterised by Precambrian and Palaeozoic schist and a gneiss basement. The area is a deep river valley covered by alluvial Quaternary deposits and surrounded by the Sierras, with a maximum elevation of 1000 m (Fig. 1). The climate here is arid, with 364 mm rainfall in the summertime. The average winter temperature is 11 °C, while summers are warm (27 °C). The natural vegetation is shrubland that is modified, in places, by agriculture or urban use.

The soils, developed in the Quaternary sediments, are young and have secondary CaCO₃ accumulation. Some soils are saline in the upper horizons. Organic carbon content generally decreases irregularly with depth, yet it remains high at a depth of 1 m (Table 1). The soils are classified according to the Soil Taxonomy (Soil Survey Staff, 2010) at the subgroup level and WRB (IUSS Working Group WRB, 2006) (Table 2).

2.2. Sample collection

An initial soil survey was undertaken to establish the soil boundaries. Then, a set of 30 profiles were sampled at representative sites in order to cover all the soil types. Different strategies can be followed for sampling soil profiles at various depths (Ferguson, 1993); sampling can be made at fixed depth, which does not require identification of the type of horizon, or by type of horizon (horizon A, horizon B, etc.). This work has adopted the second strategy, which is more accurate with regard to the irregular metal distribution with depth (Bini et al., 2011). All hemi-organic surface horizons and inorganic subsurface horizons of the soil have been sampled.

Parameters such as organic carbon content, pH, calcium carbonate content and particle size distribution were determined with the aim of obtaining a more complete picture of the soils and their subsequent classification.

Organic carbon content was determined with the Walkley and Black titration method (Burt, 2004). The amount of calcium carbonate equivalent in the soils was measured by treating the samples with HCl. The evolved CO₂ was measured nanometrically. The amount of carbonate was then calculated as the percent CaCO₃. Soil acidity (pH) was measured in a soil–water suspension with a 1:2.5 ratio and was stirred for 30 min. Particle size analysis was determined by the pipette method. The electrical conductivity (EC) and soluble salts of the saturation extract were measured (Burt, 2004). The cation exchange capacity (CEC) was determined with ammonium acetate, pH 7, using a mechanical vacuum extractor, steam distillation and titration to determine NH₄⁺. The exchangeable cations Ca²⁺ and Mg²⁺ were determined by EDTA titration and Na⁺ and K⁺ by flame emission spectrophotometry (Pauwels et al., 1992).

2.3. Determination of metal content

To determine the pseudototal heavy metal content, approximately 3 g (to the nearest 0.001 g) of the dried and ground samples with particle sizes of less than 150 μm were transferred to a 250-ml reaction vessel. After moistening, 21 ml hydrochloric acid and 7 ml nitric acid were added as drops to reduce foaming. The samples were allowed to stand for 16 h at room temperature with a condenser connected. The reaction vessel was then heated at 116 °C under reflux conditions for 2 h, ensuring that the condensation zone was lower than 1/3 of the height of the condenser. After 2 h, the contents of the reaction vessel were filtered by gravity through Whatman no. 42 filter paper into a 100-ml graduated flask, using nitric acid to wash the reaction vessel (ISO/CD 11466, 1995). Copper, Cr and Mn were measured with an inductively coupled plasma spectrometer (Polyscan 61E spectrometer), and Cd, Ni, Pb and Zn were analysed with an inductively coupled plasma-mass spectrometer (ICP-MS Perking Elmer Elaw 6000). The detection limits for the analysed metals were 0.007 mg kg⁻¹ for Cd, 3.3 for Cr and Cu, 1.7 mg kg⁻¹ for Mn, 5.5 mg kg⁻¹ for Ni, 0.03 for Pb and, finally, 0.09 mg kg⁻¹ for Zn.

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