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Evaluation of the bioaccessible gastric and intestinal fractions of heavy metals in contaminated soils by means of a simple bioaccessibility extraction test

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HIGHLIGHTS

- SBET allows evaluating the gastric and intestinal bioaccessibility of metal in soils.
- Copper is highly bioaccessible in gastric and intestinal phase of contaminated soils.
- Chemical form of the metal has a remarkable impact on the bioaccessibility in soils.

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ABSTRACT

A study is made to evaluate the bioaccessibility of heavy metals in contaminated soils through a simple bioaccessibility extraction test (SBET), applied to the analysis of both the gastric and intestinal phases. Soils with high metal content of the Mapocho, Cachapoal, and Rancagua series were studied; they are located in suburban areas of large cities in the central valley of Chile. The bioaccessible concentrations of Cd, Cr, Cu, Ni, Pb, and Zn were related to the main physicochemical characteristics of the soils and to the chemical forms obtained by sequential extraction.

The elements Cd, Cu, Ni, and Zn are distributed in the soils between the exchangeable fractions, bound to oxides, to organic matter, and in the residual fraction. On the other hand, Cr and Pb are found mainly in the fractions bound to organic matter and in the residual fraction. The three soils have a high Cu content, (640–2060 mg/kg), in the order Cachapoal > Rancagua > Mapocho. The SBET test allowed establishing a different bioaccessibility for the elements in the soil. Cu was notoriously bioaccessible in both the gastric and intestinal phases in the three soils, reaching more than 50% in the Cachapoal and Rancagua soils. The other elements, regardless of the soil, were bioaccessible only in one of the phases, more frequently in the gastric phase. The multiple correlation study indicates that the metal forms have a higher incidence than the soil's physicochemical factors on the extractability to evaluate the human oral bioaccessibility of the metals.

1. Introduction

The soil plays a fundamental role in the mobility of contaminants to groundwater, food, and directly to humans. In this context, the heavy metals get to the soil through weathering processes of the parent material, but human activity has accelerated this process, causing some metals or their species to reach concentrations that put the ecosystems at risk, leading to their accumulation in soils and sediments (Wuana and Okieimen, 2011; Li et al., 2014a).

From the relation between the presence of high concentrations of heavy metals in the soil and the risk to human health, International Soil Quality Guidelines based mainly on the total concentration of the metals have been established (Barrios et al., 2006). The maximum allowed limits of heavy metals to ensure the quality of the soils have been determined in terms of their use (residential, agricultural, and industrial). In this context, these limits are established as hypothetical relations between the use of the soil,

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and the transport and toxicology of the pollutants (Wragg and Cave, 2003). However, the determination of the total metal content in the soil is not representative of the quality of the soils and their relation with the risk to public health (Wragg and Cave, 2003) because the heavy metals associate with the soil components, and the ecological effect of the pollutant is related to that association (Rodriguez et al., 2009).

For the study of the metals in the soil several selective chemical extraction methods have been developed which group the chemical species or forms according to their general function or characteristics, such as phytoavailable, exchangeable, labile species, among others. At the same time, sequential extraction methods have been developed to determine the forms of an element associated with the different fractions that compose the soils (Hass and Fine, 2010). One of the most widely studied sequential extraction methods is the one proposed by the Community Bureau of Reference (BCR) of the European Community (Sutherland, 2010; Fernandez-Ondono et al., 2017). However, with the development of new techniques for the structural analysis of materials, such as synchrotron-based techniques (XANES, EXAFS, μ-XRF, STXM), new information has been provided on which would be the main associations of the metals with the soil's components (Sun et al., 2017; Yang et al., 2014; Minkina et al., 2016).

Exposure of the human population to the pollutants can take place through a wide variety of routes that include inhalation, oral ingestion, or skin absorption. One of the most important routes of exposure to a pollutant, after the diet, is the accidental ingestion of polluted soil (Luo et al., 2012). To simulate the heavy metal release processes in the gastrointestinal tract, several in vitro methods have been developed which are based on the use of extractant solutions to simulate digestion in the stomach and small intestine (Wragg and Cave, 2003). These methods allow the determination of the bioaccessibility of a contaminant, and its main advantage is the speed of the analyses and the low cost compared to in vivo methods. Recently, various studies have related bioaccessibility with the different chemical forms of the metals and metalloids present in the soils (Zong et al., 2016; Cui et al., 2016; Bavec and Gosar, 2016). One of the most widely used in vitro methods is the physiologically based extraction test (PBET) (Ruby et al., 1996; Li and Zhang, 2013). Various studies have shown that there is a high correlation between the gastric phase of the PBET with in vivo studies made with young pigs (Wragg and Cave, 2003; Deshommes et al., 2012). Considering this, Drexler and Brattin (2007) using a single extractant, have optimized and validated a simple bioaccessibility extraction test (SBET) for the estimation of bioaccessible lead in the gastric phase. This method has also had good results for the evaluation of the gastric bioaccessibility of various metals in the soil (Pedron et al., 2014; Izquierdo et al., 2015). In contrast with this, the use of a single extractant has been scarcely studied to simulate the availability of metals in the intestinal phase of the digestion process. In this respect, Poggio el al. (2009) have extended the use of the extractant glycine, often used in SBET, to study also the bioaccessibility of metals in the intestinal phase. In that sense, we hypothesize that the SBET method can explain well the bioaccessibility of metals in the intestinal phase, the same as it occurs in the gastric phase.

Copper mining is one of the main economic activities of Chile. Heavy metal pollution is associated with the operating centers of Cu mining, located in the county's north and center regions (Codelco, 2016). However, the high levels of Cu and other elements are not confined to the areas in which these activities have developed historically, but also to agricultural soils located several kilometers away from them. This is due to the transport of the pollutants by the particulate matter emitted into the air or the water of the rivers by the mining processes (González et al., 2014).

The suburban soils of the cities of Santiago and Rancagua have been exposed for decades to pollution by heavy metals from either irrigation with wastewater, water that contains mining wastes, or through the deposition of polluted particles carried by the air. Currently these areas are going through a process of urbanization and demographic increase, with a high percentage of child population.

The objective of the present work was to make an estimation of the fraction of heavy metals that are orally bioaccessible to humans in contaminated soils, evaluating this fraction with a SBET test applied to both the gastric and the intestinal phases in order to provide information on the applicability of a simplified method to study jointly the gastric and the intestinal phases. Furthermore, the relation between these bioaccessible fractions with the physicochemical properties of the soil and the forms in which the metals are found more frequently in the soil will be studied.

2. Materials and methods

2.1. Selection of soils and physicochemical characterization

Three soils from the suburban areas of the cities of Santiago and Rancagua in the central valley of Chile were selected. The cities are 80 km apart from one another and highly populated, representing together a population of 6.4 million inhabitants. Soils of the Mapocho series (order Mollisol) of Santiago and the Rancagua (order Mollisol) and Cachapoal (order Inceptisol) series of Rancagua were chosen.

For this study soils were collected from the surface horizon of the three sites (0–20 cm depth), and they were air dried, then ground, and sieved through a 2 mm mesh. These soils were chosen on the basis of their high Cu concentration. Additionally, for the study of the Cd, Cu and Zn metals, the Mapocho series soil was chosen because the order mollisol is one of the orders most frequently found in the soils of Chile, and because of its proximity to the city of Santiago, which is more highly populated. This soil was spiked with Cd, Pb, or Zn by adding solutions of $Cd(NO_3)_2$, $Pb(NO_3)_2$, or $Zn(NO_3)_2$ at pH 6.0 in sufficient quantity to triplicate the initial concentration (basal) of each metal. Then the soils were moistened to their field capacity and stabilized for 30 days at ambient temperature (±22 °C) keeping their moisture. After this period, they were air dried, ground in a mortar, and sieved through a 2 mm mesh.

The characterization of the soils considered the determination of residual humidity, organic matter (OM), texture, pH, cation exchange capacity (CEC), electric conductivity, and total metal content using standardized methods for soil analysis (Blakemore et al., 1987). To determine the total concentration of metal in the soils, they were digested by the wet method by means of microwaves (Milestone MLS 1200 Mega) in teflon beakers with a 2:1:1 v/v/v mixture of HNO_3:H_2O_2:HF. The solutions were dried on a hot plate to remove the HF completely, and then the residue was dissolved in HCl. The solutions obtained were analyzed by flame atomic absorption spectroscopy (FAAS) to determine the metal content.

2.2. Sequential extraction

The method of the European Community Bureau of Reference (BCR) as described by Luo and Christie (1998) was used for the sequential extraction of the metals from the soil. This method consists of three stages: the first stage represents the exchangeable metal, soluble in water or weakly linked with carbonates, and it was obtained with 0.11 mol/L acid acetic; the second stage represents the metal linked with iron and manganese oxides, obtained with 0.1 mol/L hydroxylamine at pH 2, and the third stage represents the