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Influence of land use on human bioaccessibility of metals in smelter-impacted soils

Aurélie Pelfrêne [a,b,*], Christophe Waterlot [a,b], Francis Douay [a,b]

[a] Université Lille Nord de France, 59000 Lille, France
[b] Groupe ISA, Equipe Sols et Environnement, Laboratoire Génie Civil et géo-Environnement Lille Nord de France (LGCgE), EA 4515, 48 boulevard Vauban, 59046 Lille Cedex, France

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ABSTRACT

An investigation was undertaken to evaluate the empirical model developed by Pelfrêne et al. (2012), predicting the human bioaccessibility of Cd and Pb in smelter-contaminated agricultural topsoils, by including other soil uses: 50 urban and 65 woody habitat topsoils collected in the same area. The results showed that land use significantly affected the pseudototal metal concentrations and their oral bioaccessibility. However, whatever the soil's physicochemical parameters and degree of contamination, the 'agricultural' model can be used to simulate metal gastric bioaccessibility in urban and woody habitat soils. To simulate gastrointestinal bioaccessibility, this model can be used directly if the pseudototal metal concentrations are on the same order of magnitude as those usually recorded in the agricultural soils studied or after the use of a correction factor if these concentrations are greater. These results showed that the oral bioaccessibility predictions could be applicable for further environmental risk evaluation.

1. Introduction

Research on metal oral bioaccessibility relating to contaminated-land management has attracted attention at an international level and has been ongoing for more than 10 years (Basta and Gradwohl, 2000; Hamel et al., 1999; Juhasz et al., 2007; Pelfrêne et al., 2011; Roussel et al., 2010; Ruby et al., 1996; Van de Wiele et al., 2007; Yang et al., 2003). This is an important feature discussed by various authors. Indeed, at a given site, information on metal bioaccessibility (i.e., the fraction of contaminant that is soluble in the gastrointestinal environment and potentially available for absorption; Ruby et al., 1999) to humans, in contrast to total (or pseudototal, defined through the use of aqua regia digestion) contaminant concentrations, offers an effective decision-support tool and an opportunity to better refine contaminant exposure assessments and aid decision-making, and can therefore promote a more proportionate and cost-effective assessment of contaminated-land (Alexander, 2000; Brandon et al., 2006; Ollson et al., 2009; Pelfrêne et al., 2012; Wragg and Cave, 2003). One of the more widely accepted in vitro methods for assessing the bioaccessibility of inorganic elements along the oral exposure route, which has been successfully benchmarked against an available in vivo experiment (Denys et al., 2012), was developed by the BioAccessibility Research Group of Europe, providing bioaccessible metal concentrations (Cd, Pb and As) for both the gastric and gastrointestinal phases (Wragg et al., 2011).

Metals are associated with the various components in soils in different ways, and many authors have provided a summary of the main factors that control the bioaccessibility of these metals, e.g., the chemical speciation of the contaminants of concern, soil pH, and the soil contents in organic matter, carbonate minerals, clay, oxides of iron, manganese and aluminum, and phosphorus (Alloway, 1995, 2001; Basta et al., 2005; Caboche et al., 2010; Denys et al., 2007; Fairbrother et al., 2007; Nathanail and McCaffrey, 2003; Pelfrêne et al., 2012; Roussel et al., 2010; Ruby, 2004). Recently, statistical models have been proposed to predict metal bioaccessibility from total (or pseudototal) metal concentrations in soil and various soil properties (Appleton et al., 2012; Caboche et al., 2010; Pelfrêne et al., 2012; Poggio et al., 2009; Roussel et al., 2010). In a previous study (Pelfrêne et al., 2012), we developed a model predicting the oral bioaccessibility of Cd and Pb in agricultural topsoils located in an area highly affected by past atmospheric emissions of two lead and zinc smelters in northern France. An extended database of 390 soil samples was used to elaborate a robust model. As the in vitro tests are quite laborious, having a method by which the human bioaccessible fraction can be estimated from other soil data that are easier to obtain is very

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* Corresponding author.
E-mail address: aurelie.pelfrene@isa-lille.fr (A. Pelfrêne).

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advantageous. In Pelfrêne et al. (2012), results were obtained only for agricultural topsoils. Inclusion of other soil uses in this area (e.g., urban soils, woody habitat soils) is needed to: (i) evaluate this empirical model, (ii) compare the contamination levels and physicochemical parameters of these soils located in a similar environmental context, and (iii) better assess the associated potential health risk for local inhabitants. Indeed, this may be of particular importance for human risk assessment because these land uses comprise residential, recreational, or food production areas and are intensively frequented by people.

It is often assumed that urban areas are more contaminated than rural areas due to the high number of the potential sources (Aelion et al., 2008; Douay et al., 2008, 2009; Li et al., 2004; Madrid et al., 2002; Wong et al., 2009). Urban soils were often developed on composite materials and their spatial heterogeneity is a typical feature. Their physicochemical parameters are generally known to be strongly affected by anthropogenic actions, the outcomes of which include compaction of deeper layers, low biodiversity, presence of fragments of various materials and often high concentrations of pollutants. Urban soils, in particular kitchen garden soils, are often subjected to intensive cultural practices and are characterized on average by higher contents of organic matter, total phosphorus, nitrates and nutrients compared to agricultural soils. Land-use change can have significant impacts on soil conditions and could influence the oral bioaccessibility of metals. Moreover, other ecosystems, such as the soils of woody habitats, are less often considered in the literature, even though they are present in the landscape composition. Globally, woody habitats correspond to small groves, woods, poplar groves, anthropogenic linear wooded creations (road embankments, hedges, old railways linked to coal mining, etc.) and forests. The woody habitat features may also influence pollutant deposition and thus local environmental contamination. Ettler et al. (2005) and Mageria and Zawadzki (2007) showed higher metal concentrations in soils of woodlands compared to open lands. Some woody habitat soils, particularly forest areas, presented particular characteristics, such as high organic matter contents (Bergkvist, 2001) and/or soil acidity (Courchesne et al., 2006).

The situation is more complex in industrialized and urban areas such as the North of France where anthropogenic pressures have strongly influenced landscapes and soils (Douay et al., 2008, 2009, 2013). The soils investigated in the present study were sampled from an area of northern France where smelting activities from the latter part of the nineteenth through much of the twentieth century have brought about extensive soil contamination by metals and caused a health risk for the population. Recent studies in this area showed that the patterns and levels of metal contamination differed between agricultural, urban and woody habitat topsoils. Douay et al. (2008, 2009) underlined the very large spatial variability of urban soils and, above all, their high contamination. Douay et al. (2009) and Fritsch et al. (2010) reported that the habitat soils corresponding to hedges showed medium to high anthropization. Soil anthropization was less frequent in groves and woods; conversely, it was low, or even absent for forest land. Therefore, the specificities of the physicochemical parameters of urban and woody habitat soils could lead to oral metal bioaccessibility different from what is observed in agricultural soils. On the area studied, and to our knowledge in the literature, woody habitats are never taken into account in the determination of metal bioaccessibility and in the assessment of population exposure.

The purpose of this study was to evaluate the effects of land uses on the bioaccessibility of metals. Specifically, the study was conducted on both urban and woody habitat soils as follows: (i) determination of Cd and Pb bioaccessibility in the gastric and intestinal phases; and (ii) testing the ability of the model established on agricultural soils to simulate metal bioaccessibility in these soils.

2. Materials and methods

2.1. Sampling sites

The study area is located in the former coal-mining area of northern France where considerable atmospheric emissions of dust were generated by two smelters (the lead smelter Metaleurop Nord at Noyelles-Godault and the zinc smelter Nyrstar at Auby; Fig. 1). These atmospheric discharges highly contaminated the soils around the smelters (Sterckeman et al., 2002; Douay et al., 2008, 2009, 2013).

A 180-km^2 surface was defined as the study area and 505 topsoil samples were collected surrounding two neighboring smelters (Fig. 1). The locations were classified into three land-use groups: agricultural, urban and woody habitat sites. In Pelfrêne et al. (2012), 390 sites were chosen randomly according to the agricultural land management. In the present study, 50 urban (kitchen gardens and lawns) and 65 woody habitat (hedges, wooded creations, forests, groves) topsoil samples were collected. The sampling sites were chosen in order to represent large-scale metal contamination of soil and to reflect contamination caused by both smelters.

2.2. Characterization of topsoils

The characterization of agricultural topsoils (390 samples) was detailed in Pelfrêne et al. (2012). The same protocols were used to characterize the urban and woody habitat topsoils. In brief, for each site, a composite sample was constituted from the surface layer (0–25 cm). In most situations the vegetative cover and plant roots were not considered part of the surface soil sample and were removed in the field. The soil samples were prepared according to the ISO 11464 standard. The samples were air-dried at a temperature below 40 °C and crushed to pass through a 2-mm stainless steel sieve. Particle-size distribution was obtained through sedimentation and sieving (NF X 31-107). Soil pH was measured in a water suspension (NF ISO 10390), and organic matter content was obtained by the NF ISO 10694 standard. Total carbonate content was obtained by measuring the volume of CO_2 released after a reaction with HCl (NF ISO 10693). Assimilated P (expressed in g P_2O_5 kg^{-1} of soil) was measured using an extraction by ammonium oxalate solution and spectrocolorimetric determination (NF X 31-161). All these analyzes were performed by the INRA Soil Analysis Laboratory (Arras, France) accredited by COFRAC according to the ISO 17025 standard.

For each of the soil samples, a representative subsample was obtained with an automatic sieve used with an ultracentrifugal mill <250 μm (Retsch type ZM 200, Germany). The pseudototal element concentrations (Cd, Pb, Fe, Mn, and Al) in the soil subsamples were obtained by Hot Block system-assisted digestion (Environmental Express® SC100, Charleston, SC, USA). For this, 300 mg of soil subsamples was digested in a mixture of 1.5 mL nitric acid (70%) and 4.5 mL HCl (37%) (aqua regia). Quality control was based on a certified sample (BCR CRM 141R) and provided good recoveries for Cd, Pb, Zn, and Mn (91–105%, $n = 5$). For Al and Fe, there are no certified values. However, the recovery for Fe was compared to an indicative value (Waterlot et al., 2011) and was 95%. A single extraction was done with a mix of solutions (0.111 mol L^{-1} sodium bicarbonate, 0.267 mol L^{-1} sodium tricitrate, and 200 g L^{-1} sodium dithionite) to extract free Fe, Mn, and Al oxides (Mehra and Jackson, 1958). The concentrations were measured by atomic absorption spectrometry (AAS, AA-6800, Shimadzu, Japan) using a flame (FAAS).

2.3. In vitro oral bioaccessibility measurement

A total of 505 soil samples within the study's data set (dried and sieved to less than 250 μm particle-size) were tested by applying the Unified Bioaccessibility Method (UBM; Wragg et al., 2011). The UBM procedure was carried out according to the methodology previously described in full by Roussel et al. (2010), Pelfrêne et al. (2011, 2012), and Wragg et al. (2011). The UBM test consisted in two parallel sequential extractions and provided samples for analysis from both the gastric (G) and gastrointestinal (GI) phases. Although both phases have been shown to be correlated with animal bioavailability (Denys et al., 2012), the G phase gives a more conservative bioaccessible fraction than the GI phase, mainly because of the low pH conditions found in the stomach. For the purposes of the discussion in this paper, the results in both phases were presented, although the gastric phase samples were chosen as being most suitable.

The metal concentrations in the bioaccessibility extracts were measured using FAAS. For every ten soil samples analyzed from the study set, a triplicate soil, a standard control soil (NIST 2710), and a blank were included in the sample batch tested. The values obtained for Cd and Pb in the NIST 2710 reference material ($n = 12$) were 14.52 ± 0.56 mg kg^{-1} and 3969 ± 293 mg kg^{-1}, respectively, for the G phase, and 7.88 ± 0.60 mg kg^{-1} and 1290 ± 235 mg kg^{-1}, respectively, for the GI phase, and were in good agreement with the current consensus values of 14.80 ± 1.09 mg kg^{-1} and 3785 ± 469 mg kg^{-1}, respectively, for the G phase, and 7.86 ± 1.81 mg kg^{-1} and 1138 ± 910 mg kg^{-1}, respectively, for the GI phase (Wragg et al., 2011).