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Predicting trace metal solubility and fractionation in Urban soils from isotopic exchangeability☆

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ABSTRACT

Metal-salt amended soils (MA, n = 23), and historically-contaminated urban soils from two English cities (Urban, n = 50), were investigated to assess the effects of soil properties and contaminant source on metal lability and solubility. A stable isotope dilution method, with and without a resin purification step, was used to measure the lability of Cd, Cu, Ni, Pb and Zn. For all five metals in MA soils, lability (%E-values) could be reasonably well predicted from soil pH value with a simple logistic equation. However, there was evidence of continuing time-dependent fixation of Cd and Zn in the MA soils, following more than a decade of storage under air-dried conditions, mainly in high pH soils. All five metals in MA soils remained much more labile than in Urban soils, strongly indicating an effect of contaminant source on metal lability in the latter. Metal solubility was predicted for both sets of soil by the geochemical speciation model WHAM-VII, using E-value as an input variable. For soils with low metal solution concentrations, over-estimation of Cd, Ni and Zn solubility was associated with binding to the Fe oxide fraction while accurate prediction of Cu solubility was dependent on humic acid content. Lead solubility was most poorly described, especially in the Urban soils. Generally, slightly poorer estimation of metal solubility was observed in Urban soils, possibly due to a greater incidence of high pH values. The use of isotopically exchangeable metal to predict solubility is appropriate both for historically contaminated soils and where amendment with soluble forms of metal is used, as in toxicological trials. However, the major limitation to predicting solubility may lie with the accuracy of model input variables such as humic acid and Fe oxide contents where there is often a reliance on relatively crude analytical estimations of these variables.

Trace metal reactivity in urban soils depends on both soil properties and the original source material; the WHAM geochemical model predicts solubility using isotopically exchangeable metal as an input.

1. Introduction

Accurate assessment of risk from trace metal contamination of the environment requires consideration of metal ‘reactivity’ or ‘lability’ in soils (Fairbrother et al., 1999; Lock and Janssen, 2001). Published literature (Degryse et al., 2004; Tack, 2010; Hammer et al., 2006) generally suggests that the lability of trace metals in soils is the net result of three factors: (i) soil properties, including soil physicochemical characteristics such as pH (e.g. McBride et al., 2006; Bonten et al., 2008) and redox potential (Borch et al., 2010) and the proportions of soil constituents such as Fe/Mn hydroxide and organic matter present (Tipping et al., 2003; Rodrigues et al., 2010); (ii) metal sources, which may vary greatly in their intrinsic metal lability (e.g. Atkinson et al., 2011; Mao et al., 2014) and (iii) soil-metal contact time, because there is a time-dependency to both metal fixation in soils (e.g. Tye et al., 2003; Ma et al., 2006b) and the release of trace metals from contaminant sources in soils (Kaste et al., 2006; Atkinson et al., 2011). Generally, low metal lability is more likely in soils with high pH values and following long contact times. Recent studies have focused on the concentrations and origins of trace metals in the urban environment (Manta et al., 2002; Cheng et al., 2014; Wei and Yang, 2010), but the effects

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on lability arising from characteristics of the original contaminant source are usually difficult to assess (Mao et al., 2014).

A range of techniques have been developed to measure the lability of trace element fractions in soils, among which isotope dilution is perhaps the most appropriate method (Degryse et al., 2009). This approach defines an amount of metal, distributed between the solution and solid phases, which is isotopically exchangeable, known as the E-value or M_E (Smolders et al., 1999; Young et al., 2000). Measurement is achieved by adding a small 'spike' of an enriched isotope of the analyte of interest to a pre-equilibrated soil suspension and measuring the isotopic abundance of the spike isotope in the separated solution phase. The extent to which the spike isotope has been able to mix with the indigenous soil metal quantifies the 'isotopically exchangeable' metal pool in the soil. The method has been modified to correct for the presence of non-labile metal in sub-micron colloidal particles (SCP-metal) by adding a resin purification step (Lombi et al., 2003). E-values can then be used as input variables to geochemical speciation models, such as WHAM (Windermere Humic Aqueous Model, Tipping et al., 2003) to predict metal fractionation and speciation in the solid and solution phases of soils respectively (Tipping et al., 2003; Shi et al., 2008; Almas et al., 2007; Buekers et al., 2008b; Marzouk et al., 2013b).

The primary aims of this study were to investigate how trace metal *lability* and *solubility* are affected by (i) soil properties, (ii) ageing and (iii) variable contamination sources in urban soils. To achieve this, objectives focussed on determination of the isotopically exchangeable fractions of Cd, Cu, Ni, Pb and Zn (M_E) in two distinct sets of soil samples. These included (i) soils, chosen for their range of land uses and soil properties, that had been incubated with metal nitrate salts (Cd, Cu, Ni, Pb and Zn) for several years and (ii) urban contaminated soils, from Nottingham and Wolverhampton (UK), chosen for their range of metal contaminant concentrations and sources. To reveal the effect of contaminant source, the 'lability' of soils from the two datasets were compared by normalising values of $\%M_E$ against soil pH; logistical models for describing metal lability with pH were parameterised. Secondary objectives included: (i) testing for non-labile SCP-metal (<0.22 μm) by comparing values of M_E with equivalent values following a resin cleaning procedure (M_{Er}); (ii) testing for metal *fixation* in air dried soil stored for more than a decade, (iii) comparing fractionation predicted by WHAM with fractionation by isotopic exchangeability and (iv) assessing the performance of the geochemical model, WHAM VII, to predict Cd, Cu, Ni, Pb and Zn solubility in both sets of soils.

2. Material and methods

2.1. Soil sampling

Two sets of soils were used in this study. The first set comprised 23 metal-amended topsoils (MA soils), from sites with contrasting land uses and parent materials, to provide a wide range of soil properties (pH, soil organic matter, mineral (hydr)oxides content and texture). These soils were collected for a previous study of trace metal fixation and solubility (Tye et al., 2003, 2004) and had been amended with metal nitrate salts to the limits prescribed by the UK Sludge Regulations (MAFF, 1993) (Cd = 3, Cu = 135, Ni = 75, Pb = 300 and Zn = 300 mg kg^{-1}) before being incubated at 16 °C and 80% field capacity (FC) for ~3 years (Tye et al., 2003), air-dried, and then stored for ~12 years prior to the current study. The second set (Urban soils) consisted of 50 topsoils collected in the cities of Wolverhampton (WV) and Nottingham (NG), UK. Site selection included consideration of historical and recent industrial and domestic land use and locations included brownfield sites, rail transport sidings, urban roadsides, waste disposal facilities, recreational areas, gardens, urban nature reserves and woodland and parkland areas. Data relating to these soils has been published previously in an investigation of metal speciation and bioavailability in risk assessment (Thornton et al., 2008; Hough et al., 2005).

2.2. Soil characterization

Some of the soil properties originally determined were re-measured to identify changes during storage and to provide a more complete input dataset for subsequent modelling (Section 2.6). Soil pH was measured on suspensions (1 g soil: 30 mL of 0.01 M $Ca(NO_3)_2$) using a pH meter with combined Ag/AgCl glass electrode (Model pH 209, HANNA Instruments, Bedford, UK). Total organic matter content was estimated using a LECO combustion analyser (Tye et al., 2003) for MA soils. For Urban soils total organic matter content was calculated from the difference between total soil carbon (SC) content measured using an Elemental Analyser (CE Instruments model Flash EA1112) and calibrated using a range of certified soils, and carbonate content determined by manometric assay using the Collins' calcimeter method (Piper, 1954). Alkaline extraction was used to determine humic acid (HA) and fulvic acid (FA) content in all soils. Organic carbon content in HA and FA was measured using a Shimadzu TOC-Vcp analyser. Clay content (%) was estimated from the soil texture classification provided by Tye et al. (2003) for MA soils. Iron, Al and Mn oxide concentrations were determined following extraction with a mixture of sodium dithionite, sodium citrate and sodium bicarbonate (DCB extraction, Anschutz et al., 1998). Total Cd, Cu, Ni, Pb and Zn concentrations in soil were determined following digestion of 200 mg of finely ground soil with HF (40% AR), HNO_3 (70% TAG) and $HClO_4$ (70% AR) in a block digester (Model A3, Analysco Ltd, Chipping Norton, UK). Iron, Al and Mn in DCB extractants and trace metals in acid digests were analysed by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS; Thermo-Fisher Scientific X-Series^{II}) operating in 'collision cell mode' (7% hydrogen in helium) to reduce polyatomic interferences.

2.3. Cadmium, Cu, Ni, Zn, and Pb lability measured by isotopic dilution (E-value)

2.3.1. Sample preparation

The stable isotopic dilution method used in this study was adapted from Atkinson et al. (2011). Soils were pre-equilibrated in 0.01 M $Ca(NO_3)_2$ (1 g: 30 mL) on an end-over-end shaker for 3 days; 4 suspensions were made for each soil. An aliquot (0.4 mL) of enriched stable isotope stock solution (ISOFLEX, San Francisco CA, USA) in ~2% HNO_3, with known isotopic abundances (IA) for ^{108}Cd (IA = 69.7%), ^{65}Cu (IA = 99.0%), ^{62}Ni (IA = 98.2%), ^{204}Pb (IA = 98.8%) and ^{70}Zn (IA = 92.7%) was added to two of the suspensions and the other two were used as control samples to derive the natural isotopic abundance of the labile metal. The spike isotopes used were, with the exception of ^{65}Cu, chosen because they have relatively low natural isotopic abundance (De Bievre and Barnes, 1985). Therefore, only a small addition to the system was required to produce a significant increase in IA from the background level. To reduce the number of individual operations and to avoid adding different amounts of isotopes to each soil, the samples were classified into several groups according to their soil metal content. The level of isotope tracer to be added was determined from the highest concentration of metal in each group to ensure that the difference in isotopic ratio between the spiked and un-spiked samples was at least 20%. After spiking, the suspensions were shaken for a further 3 days; the solution and solid phases were then separated by

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