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Research article

Controls on accumulation and soil solution partitioning of heavy metals across upland sites in United Kingdom (UK)

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ABSTRACT

A significant body of knowledge suggests that soil solution pH and dissolved organic carbon (DOC) strongly influence metal concentrations and speciation in porewater, however, these effects vary between different metals. This study investigated the factors influencing soil and soil solution concentrations of copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) under field conditions in upland soils from UK having a wide range of pH, DOC and organic matter contents. The study primarily focussed on predicting soil and soil solution metal concentrations from the data on total soil metal concentrations (HNO_3 extracts) and soil and soil solution properties (pH, DOC and organic matter content). We tested the multiple regression models proposed by Tipping et al. (2003) to predict heavy metal concentrations in soil solutions and the results indicated a better fit (higher R^2 values) in both studies for Pb compared to the Zn and Cu concentrations. Both studies observed consistent negative relationships of metals with pH and loss on ignition (LOI) suggesting an increase in soil solution metal concentrations with increasing acidity. The positive relationship between Pb concentrations in porewater and HNO_3 extracts was similar for both studies, however, similar relationships were not found for the Zn and Cu concentrations because of the negative coefficients for these metals in our study. The results of this study conclude that the predictive equations of Tipping et al. (2003) may not be applicable to the field sites where the range of DOC and metal concentrations is much lower than their study. Our study also suggests that the extent to which metals are partitioned into soil solution is lower in soils with a higher organic matter contents due to binding of these metals to soil organic matter.

1. Introduction

Heavy metal concentrations in soil solution indicate their mobility, transformations, bioavailability and toxicity (Kalis et al., 2008). Leaching of toxic heavy metals into surface and groundwater, and soils has adverse effects on ecosystems (e.g. Yang et al., 2013; Shaheen et al., 2014; Valencia-Avallen et al., 2018). The application of critical loads methodology requires the understanding of biogeochemistry and bioavailability of metals so that the upland sites are protected from the toxic effects of metal deposition (Paĉes, 1998; Lawlor and Tipping, 2003; De Vries et al., 2015a). Tipping et al. (2003) analysed total dissolved metal concentrations and modelled free metal ion concentrations in soil samples from 98 upland UK sites and showed that 14 and 63 of these sites exceeded the critical limits for cadmium (Cd) and lead (Pb) respectively. Therefore, considering the very long residence periods of trace metals in most soils, it is important to assess the long-term legacy effects of such metals from metal deposition in UK upland soils.

Environmental risk assessment of metals depends on modelling the mobility of metals based on the soil – liquid partitioning coefficients. In the specific context of critical loads as a risk assessment method, it is generally assumed that a steady-state is eventually reached when metal inputs from the atmosphere deposition are balanced by the outputs through leaching, and uptake and removal in harvested vegetation (Hall et al., 2007, 2015; De Vries et al., 2015b). Since a strong relationship exists between the metal leaching and their concentrations in soil solution, the metal concentration will increase with increasing deposition until leaching and other losses balance the increased deposition (Bonten et al., 2012). In the critical loads approach,

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relationships between total and soil solution metal concentrations are important because they determine the proportion of the total soil metal pool which may be leached annually. Hence, the relationships to predict soil solution concentrations, which cannot be readily measured from the total soil metal concentrations, play a central role in calculations of critical loads of metals (RoTAP, 2012). The empirical critical loads are established with the help of field experiments to provide empirical evidence for the development of relationship between long-term deposition of a pollutant and its impact on ecology (Bobbink et al., 2015; Hettelingh et al., 2015). Nevertheless, there remains a wider uncertainty about how ecological risk assessment can most effectively be based on the bioavailable, rather than the total soil concentration, of contaminants (Kim et al., 2015; Cipullo et al., 2018).

Tipping et al. (2003) derived relationships between total and soil solution metal concentrations in and for UK upland soils using loss on ignition (LOI), dissolved organic carbon (DOC) and pH. The model was based on the following equation:

$$\log[\mathrm{M_{SS}}] = a\cdot\log[\mathrm{LOI}] + b\cdot\mathrm{pH} + c\cdot\log[\mathrm{M_{HNO_3}}] + d\cdot\log[\mathrm{DOC}] + e \quad (1)$$

Where, M_{SS} is the metal concentration in soil solution, M_{HNO3} is the total soil metal concentration, and a, b, c, d and e are constants.

These relationships were derived for Cd, copper (Cu), Pb and zinc (Zn), and the findings indicated that the transfer functions of metals could be used for predicting soil solution concentrations from soil properties and total soil metal concentrations. However, the findings of Tipping et al. (2003) were based on an artificial set-up of extracting soil solution using Rhizon samplers from the field-collected soil samples under laboratory conditions. Therefore, it is far from certain that the metal concentrations in soil solution, found using this method, were representative of real concentrations in the field.

A significant body of knowledge demonstrates that the soil solution pH and DOC strongly influence metal concentrations and speciation in porewater, however, these effects vary strongly between different metals (e.g. Schneider et al., 2016; Kunhikrishnan et al., 2017). The strong complexation between DOC and heavy metals influence metal exchange between the soil and soil solution to control metal leaching and transport through the soil profile towards streams and ground water (Tipping and Hurley, 1992; Jones, 1998; Sauve et al., 2000). For example, Cu forms stronger complexes with organic ligands (Florence, 1982; Potysz et al., 2017) whereas immobilization of Zn occurs in soil solution due to its association with DOC (Milne et al., 2003; Guinoiseau et al., 2017). Hence, DOC exerts significant multiple effects on metal behaviours in soils (e.g. Antoniadis and Alloway, 2002; Tipping, 2002; Beesley et al., 2010; Uchimiya, 2014; Ren et al., 2015).

Soil pH is generally considered a predominant factor regulating the availability and plant uptake of many elements. For example, metal uptake by plants may be increased due to decreasing pH (Brown et al., 1994). Moreover, it is considered that both the complexing capacity of organic acids and low pH are major factors controlling the mobilization of metals in soil and their accumulation in plants (McGrath et al., 1997; Pérez-Esteban et al., 2014). The bioavailability of Cu and Zn is mainly controlled by pH and organic C contents while Ni depends on soil organic compounds, soil solution pH and DOC concentrations (Kuo et al., 1985; Bhogal et al., 1993). Changes in soil solution pH may also modify DOC which could have expanded structure at high pH values because the charges attempt to position themselves as far as possible (Rice et al., 2000). Under such scenario, when DOC becomes hydrophilic due to the presence of more negative charges, the adsorption and desorption mechanisms of metals associated with DOC are likely to be more pH-dependant (Jardine et al., 1989; Gu et al., 1994). In addition, the water-soluble materials are formed when degradation of organic matter occur due to enhanced activity of microbes in the soil dependent on high pH (Higashida and Takao, 1986; Park et al., 2011).

The specific three-fold objectives of this study, using the datasets of upland UK soils collected by van den Berg et al. (2012), therefore, were to:

- characterise the solid-solution partitioning of heavy metals (Pb, Zn, Ni and Cu) from regional survey datasets of sites with contrasting soil types, soil solution DOC and pH values;
- identify relationships between soil solution metal concentrations, total soil metal concentrations, and pH, LOI and DOC of soil solution, and specifically to assess whether decreasing pH and increasing DOC are associated with higher soil solution metal concentrations; and,
- compare the predictive relationships for soil solution metal concentrations in soil solution samples collected in the field in this study with those from Tipping et al. (2003) who extracted the soil solution in the laboratory.

2. Materials and methods

2.1. Description of study sites and data sources

This study partly used the data already collected for a regional survey of DOC concentrations during 2005–06 by van den Berg et al. (2012). The original survey contained the data from 41 sites with sampling and analysis conducted at three institutions. Out of these 41 sites from four habitats (grasslands, woodlands, moorlands and heathlands) and five soil classes (brown soils, lithomorphic soils, organic soils, podzolic soils and ground and surface water gley soils), 22 sites, representing four major soil classes were considered for this study (see Table S1). The analysis for these sites were performed at the University of York, UK and this approach made sure that the data were of consistent high quality because same analytical methods were used throughout the study. Furthermore, in contrast to van den Berg et al. (2012) who reported the data based on soil solution sample taken every 3 weeks throughout a year, the analyses described in this study were constrained to annual mean concentrations since these concentrations are generally used to apply transfer functions in mapping critical loads.

2.2. Soil solution and soil sampling at study sites

Soil solution samples were collected using Rhizon samplers (Eijkelkamp, Giesbeek Netherlands) following the procedure described by Knight et al. (1998) and Tye et al. (2003). The Rhizon samplers were placed horizontally in the field, under the vegetation, after piercing the soil with a wooden stick of diameter similar to the Rhizon sampler size. Samplers were installed horizontally in the middle of the A horizon in mineral soils or at 7.5 cm depth relative to the top of the O horizon in organic soils. Samplers were connected to a syringe which was pulled out to create a vacuum and the syringes were covered in aluminium foil to protect them from light. Porewater samples were collected every three weeks from the sampling locations by taking five replicates per location between May 2005 and April 2006. After collection, the volume obtained per sampler was noted and all individual samples were pooled to produce one sample for each sampling period per site. Immediately after pooling, the pH was measured, samples were filtered, and then samples were stored at 4 °C until further analysis. For metal analysis, 0.4 ml of 0.1 M citric acid was added to 10 ml of each sample to prevent metals from settling and the samples were frozen until further analyses.

At the start of the sampling period, in May 2005, five soil samples per site were taken to a depth of 10 cm using an auger and all samples were pooled prior to analysis and extraction. Soils were homogenized by hand, well mixed to avoid internal variation between sub samples, and roots and shoots were removed. The soil samples were then transported in a cooling box to the laboratory and stored at 4 °C until analysis in airtight plastic bags after removing as much air as possible. For non-metal determinants, the extraction and analytical methods for soils and soil solutions were described in detail by van den Berg et al. (2012).