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Mobility of metals and metalloids in a multi-element contaminated soil 20 years after cessation of the pollution source activity

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Soil pore water collected in situ provided realistic information on metal and metalloid mobility in the profile of a contaminated woodland soil.

Abstract

Knowledge of trace element concentrations and mobility is important in the ecotoxicological assessment of contaminated soils. We analysed soil pore water under field conditions to provide new insights into the mobility of residual contaminants in the surface 50 cm of a highly contaminated woodland soil. Cadmium and Zn were highly mobile in the acidic soil, concentrations increasing with depth in soil pore water, showing considerable downward mobility. High levels of surface organic matter restricted the solubility of Cu, Pb and Sb, with highest concentrations being found close to the surface. Dissolved organic carbon in pore water had a strong influence on mobility of Cu, Zn, Pb and Sb. Elevated As had moved from the organic surface horizons but was largely immobilised in deeper layers and associated with Fe and Al oxides. The measured differential mobility of pollutants in the present study is highly relevant to protection of groundwater and other receptors.

Keywords: Heavy metals; Arsenic; Antimony; Soil pore water; Temporal change

1. Introduction

Intense industrial activity and the lack of effective environmental protection during the first half of the last century gave rise to many contaminated areas in NW England. Poorly regulated metal processing industries and inefficient industrial processes resulted in sites contaminated with metals (Zn, Cu, Pb, Cd, Ni, Cr, Hg, and Sn) and metalloids (mainly As). Metalloids (i.e., B, Si, Ge, As, Sb, Te, Po) have properties of both metals and non-metals.

Monitoring the mobility of inorganic pollutants in a naturally remediated (or revegetated) site near a former industrial pollution source at a finite time after emissions ceased potentially provides important information regarding the fate of the contaminants in the environment, time-dependent changes in speciation, mobility towards the water table and the likely long-term effectiveness of monitored natural attenuation (Environmental Agency, 2004; Mulligan and Yong, 2004). Reliance on non-degradative attenuation mechanisms and unenhanced natural processes may be an important option for some sites, depending on site-specific risks and end use (Werner et al., 2004).

Risk assessment for soils should consider both mobile and bioavailable fractions of pollutants (Wahle and Kördel, 1997). Total concentrations of metals in soils are poor indicators of metal toxicity since metals exist in different solid-phase forms that vary considerably in terms of bioavailability (Nolan et al., 2003). The extraction of interstitial soil pore water (soil solution) is potentially an important step in the ecotoxicological assessment of a polluted soil (Tiensing et al., 2001) as it isolates the aqueous phase to which plant roots and microorganisms are exposed (Nolan et al., 2003). Isolation of soil

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pore water (or soil solution) has been carried out satisfactorily in numerous column/pot experiments in both laboratory and greenhouse conditions (Knight et al., 1998; Meers et al., 2007b). 'Rhizon' samplers can be used to remove soil water from the pores whilst the physical structure of the soil remains intact (Tiensing et al., 2001). This technique has proved to be effective, relatively straightforward and inexpensive compared to other procedures for extracting soil solution (Datta and Young, 2005). Pore water removed by Rhizon samplers probably represents the fraction of soil water that is taken up by plants and such pore water samples have been recommended for use in ecotoxicity tests (Tiensing et al., 2001). However, there are surprisingly few reports of the use of Rhizon samplers in soils in the field (Farley and Fitter, 1999; Geibe et al., 2006).

The aim of the present work was to use pore water sampling to study the mobility of metals and metalloids down the soil profile in a long-term naturally-attenuated woodland ecosystem by sampling at different depths. These were compared with chemical analysis and sequential extraction of soil to provide information on the long-term fate of trace elements in terms of mobility within the soil profile following the cessation of emissions from specific pollution sources.

2. Materials and methods

2.1. Field site

Prescot in Merseyside, UK, has a lengthy history of atmospheric pollution from a group of metallurgical processes consisting of a copper refinery, a cadmium alloying plant and a brass foundry that operated for over a hundred years (Dickinson et al., 1996). The brass foundry was finally closed in 1991, and only a new copper rod-rolling plant, located 1 km from the original site, is now active, with some very localized stack loss of flue dust containing copper oxides (Lepp et al., 1997).

The area adjacent to this complex has been subjected to considerable ecological and environmental research since the 1970s. The findings from this body of work were reviewed by Dickinson et al. (1996), focussing on the ecotoxicological impact of metal processing. They reported that soils in the vicinity of the complex, and to a distance of 1.5 km, had substantially elevated levels of copper, cadmium, zinc and lead to depths of 1 m. Potentially toxic concentrations of Cu and Cd were found to be widespread in the affected soils, giving cause for concern. No other elements were determined in these soils. The present field site is located within the walled wooded garden of the Prescot vicarage (53°25′39″N, 02°48′29″W), Merseyside, UK. The site consists of a mature, planted and self-established woodland, whose presence predates the pollution source, dominated by non-UK native species of varying age such as Sycamore (*Acer pseudoplatanus*) and Horse Chestnut (*Aesculus hippocastaneum*). The ground flora is poorly developed, due to a combination of the dense tree canopy and previous pollution. An extensive litter layer has formed on the ground surface.

The soil is a sandy loam (76% coarse sand, 21% fine sand, 2.5% silt and clay) derived from unmineralized strata with naturally low background concentrations of copper, cadmium, lead, and zinc that are typical of unpolluted soils in the UK (Watmough, 1994). Soils in the area have been found repeatedly to be heavily copper contaminated, with elevated levels of cadmium, zinc and lead also present (Dickinson et al., 1996).

2.2. Soil and 'pore water' samples

The sampling site was selected at a point between large trees, sufficiently secluded from public attention. Composite soil samples were taken at 0–10, 10–30 and 30–60 cm depth intervals (May 2006). On excavation, the soil profile had a deep (15–20 cm) organic layer overlying strata of 'made ground' (soil showing clear human interference and debris). Given this heterogeneous profile, this was taken as a representative profile for the woodland part of this site. In view of this, samples were taken that corresponded to different depths down the profile as opposed to representative soil horizons. Permission was given to excavate a single substantial soil pit (1 m × 1 m) to a depth of 75 cm in the sampling site, leaving a straight, exposed face for experimental purposes (June 2006). Whilst further replication would have been desirable, this was not possible on grounds of health and safety.

Pairs of 'Rhizon' soil pore water samplers (Eijkelkamp Agrisearch Equipment, The Netherlands) were inserted horizontally into the soil at an angle of approximately 45° at 10 cm intervals down the soil profile to a final depth of 50 cm, in the straight face of the pit (Fig. 1). These consist of a 10 cm porous polymer tube at one end that is inserted in the soil. This is connected to a 10 cm PVC tube and a Luer-Lock connector, from which the pore water is obtained using either a syringe or needles and vacuum tubes. The Rhizon samplers were left in situ to equilibrate for 4 weeks, and then sampled (Sampling 1, July 2006). All except one of the samplers worked, producing up to 10 ml of soil pore water. The malfunctioning sampler was replaced and a further series of samples were taken 3 months later (Sampling 2, October 2006). Subsequently more detailed soil profile sampling was performed from the same soil pit, in order to obtain soil samples at 10 cm intervals to a depth of 50 cm. These samples were analysed for pH, total organic carbon (TOC) and pseudo-total metal and metalloid concentrations. The concentrations of the different elements in soil pore water (in micrograms per millilitre) were transformed to a soil weight basis (micrograms per milligram) by multiplying with the water holding capacity of the soils (in millilitres per milligram). This conversion enabled the estimation of the percent total soil carbon, metal and metalloid pools present in soil solution (percent of dissolved element). Pore water samples were collected after heavy rain days, so it was considered

Fig. 1. Pore water collection in situ in the sampling site.