Chemosphere 90 (2013) 464–470

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Review

Localised mobilisation of metals, as measured by diffusive gradients in thin-films, in soil historically treated with sewage sludge

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HIGHLIGHTS

- ▶ Adjacent trace metal soil profiles were measured using DGT at 5 mm vertical intervals.
- ▶ The metals had sharp maxima within a two dimensional framework.
- ▶ Mobilisation of Cd, Co, Cu, Ni and Zn were strongly linked to mobilisation of Mn.
- ▶ There was a strong linkage between Pb and Fe mobilisation.
- ▶ Mobilisation was probably due to localised pH minima associated with fast C turnover.

ARTICLE INFO

Article history:
Received 3 May 2012
Received in revised form 27 July 2012
Accepted 29 July 2012
Available online 11 September 2012

Keywords:
Trace metals
Soil
Sewage sludge
Mn oxide
Diffusive gradients in thin-films
pH

ABSTRACT

The two dimensional, small-scale, distribution of labile trace metals was investigated in a sandy loam soil historically treated with sewage sludge. After deployment of two DGT (diffusive gradients in thin-films) probes, their 1.8 × 15 cm windows were sliced into 5 × 5 mm and 5 × 8 mm rectangles to provide three vertical profiles with 5 mm resolution. Both sets of profiles showed sharp maxima of Mn, Cd, Co, Cu, Ni and Zn, which varied systematically, both vertically and horizontally. The observed mobilisation of metals was highly localised, as each measurement corresponded to a volume of soil as little as 25–40 μL. Regression analysis indicated mobilisation of Cd, Co, Cu, Ni and Zn were strongly linked to mobilisation of Mn, while there was a strong linkage between Pb and Fe mobilisation. Localised reductive dissolution of Mn oxides or a localised lowering of pH were considered as possible mechanisms.

1. Introduction

Studies of the distribution of the chemical forms of metals with depth in soil profiles have used vertical resolutions of several centimetres to tens of centimetres (Kabala and Singh, 2001; Ruan et al., 2008). By contrast, quantitative tools linked to electron microscopy have been widely used during the last decade to describe the spatial heterogeneity of metals in soil aggregates at very fine (micron-scale) resolution (Cousin et al., 2005). There is little information at the mm or cm scale, even though uneven distributions of labile trace metals at this scale can potentially markedly affect their availability to plants. Chaudri et al. (2008) observed greater toxicity to free living rhizobia in soils treated with metals in sewage cake rather than an equivalent average concentration of directly added metals. They hypothesized that it was due to high concentrations of metals associated with the locally high concentrations of reactive organic material.

The spatial distribution of metals in sediments has been well studied and recent work using the emerging technique of DGT (diffusive gradients in thin-films) has shown highly localised structure at the mm scale (Fones et al., 2004). DGT probes perturb the solute equilibria at their surface in a well defined way while they are deployed in situ. The accumulated metal can be related to the average concentration in solution at the surface of the device, which in turn is related to the concentration in the undisturbed solution and the resupply of metal from solid phase to solution (Ernstberger et al., 2005).

The aim of this study was to investigate the two-dimensional distribution of available metals in the near-surface layer of a soil

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http://dx.doi.org/10.1016/j.chemosphere.2012.07.064

historically treated with sewage sludge. As previous studies have shown that mobile metals are most prevalent in the upper layers of such soils, measurements were performed with DGT deployed in the top 15 cm (Kabala and Singh, 2001; Ruan et al., 2008). Three adjacent vertical profiles were obtained from each probe, with a vertical resolution of 5 mm. The diffusion gradient in the soil at the surface of DGT probes seldom extends beyond 1 mm (Harper et al., 1998). Consequently, the sampled volume of soil that is effectively contributing to each measurement point is probably about 0.025–0.040 cm^3, which is more than three orders of magnitude less than the volume of soil usually sampled by traditional methods prior to pore water extraction. These measurements of a range of metals at this very small volumetric scale therefore have the potential to access small scale features in the pore water chemistry that have not previously been investigated.

2. Materials and methods

2.1. Soil sampling

Soil samples were collected from a site on the Christchurch Sewage Treatment farm at Bromley, New Zealand in December 2006. Sewage sludge, as an ~8% solids liquid, had been applied at intervals over 25 years to the soil surface, with the last application 7 years prior to sampling, and incorporated to a depth of 20–25 cm by rotavation (McLaren et al., 2007). The soil was sown to pasture (grass/clover). An undisturbed soil monolith was sampled and placed in a lysimeter 20 cm in diameter and 30 cm deep. The lysimeter soil was alkaline (pH 7.0–7.8) with high Ca (6–9.9 g kg^{-1}) and Mg (2.6–3.4 g kg^{-1}) and a moderate carbon content (4.4–8.3%) (Table S3). Mean concentrations of metals in mg kg^{-1} were: Cd, 1.7; Co, 11; Cu, 100; Fe, 5300; Mn, 200; Ni, 21; Pb, 81; Zn, 330. The design of the lysimeter casings and the method of sampling have been described in detail (Cameron et al., 1992). The lysimeter was exposed to normal weather conditions for 2 months prior to DGT deployment.

2.2. DGT probe devices and measurement

The rectangular DGT probes consist of a plastic backing plate, a resin-embedded gel layer, a 0.8 mm thick ion-permeable diffusive gel layer, a 0.14 mm thick, 0.45 μm hydrophilic polyethersulfone membrane to prevent adherence of the soil particles to the gels, and a front plate, with a 1.8 × 15 cm window, that clips to the backing plate and holds all the layers tightly together (Tankere-Muller et al., 2007). The gels were prepared according to the standard procedures for DGT (Warnken et al., 2006). The diffusive gel was polyacrylamide with 0.3% agarose-derived cross linker, while the binding layer was a similar gel, but incorporating Chelex-100 ion-exchange resin.

The soil column of the lysimeter was cleaved vertically with a clean stainless steel blade and the windows of a DGT probe firmly pressed on each exposed face, ensuring good contact with the soil. The two soil faces sampled by DGT were not immediately opposite one another, but were laterally displaced by a few cm. The upper boundary of the window area was level with the soil surface. Before DGT deployment, the soil column was saturated with ultra-pure water (Milli-Q, Millipore), known here as MQ water and allowed to drain for 24 h. The water holding capacity was 25% v/v. The probes were deployed for 24 h, while the temperature of the soils was maintained at approximately 20 °C. One probe, not deployed, served as a blank.

Upon retrieval, the window area of each probe was thoroughly rinsed using MQ water, to ensure that there were no adhering soil particles. Probes were stored until analysis in separate clean plastic bags in a refrigerator. The exposed gels and filter membrane layers were cut from the window area using a Teflon-coated razor blade. Using a micro-manipulator guillotine with a Teflon-coated blade, the binding gel was sliced into three columns, two of 5 × 5 mm squares and one of 5 × 8 mm rectangles.

Each segment was placed in a 0.5 mL centrifuge tube containing 0.2 mL of 1 M HNO_3 solution. After at least 24 h, the acid eluate was diluted prior to analysis by ICP-MS (Thermo-Fisher X7). Care was taken to prevent any contamination during assembly, deployment and analysis of DGT probes, with use of a class 100 laminar flow cabinet where appropriate and clean room protocols.

Probes for blank determinations were treated in the same way as samples except for deployment. Twenty 5 × 5 mm resin-gel segments were analysed and concentrations for metals calculated using a notional deployment time of 24 h (see below). For Mn, Ni and Al, the lowest concentrations were greater than the DGT detection limits (3 × standard deviation of DGT blank) (Table S1). More than 96% of the data points were greater than the DGT detection limits for all metals analysed.

2.3. Routine soil analysis

Soil samples were collected from the lysimeter at 1 cm depth intervals. They were bulked to provide average samples for the depths: 0–3, 3–6, 6–9 and 9–12 cm. Total major cation and trace metal concentrations were determined by ICP-OES (Varian 720-ES) following acid digestion of 1 g samples (Kovacs et al., 2000). Organic carbon was determined using a LECO CNS 2000 Analyser. Soil solution, extracted from a 1:1 mixture of soil and water equilibrated for 1 d, was used to measure pH.

2.4. EDTA-extractable metals

Following retrieval of the DGT probes from the soil columns, soil in the vicinity of the probe positions was sampled at 1 cm depth intervals vertically from the original soil surface. Samples were taken to a depth of 2.5 cm below the surface on which the probe had been deployed (in effect horizontally with respect to the soil column). As the freely draining soils were oxygenated, no special precaution was taken to exclude air. The ~50 mL soil samples were air dried and homogenised. Ten g of each 1 cm depth sample were placed into a 50 mL centrifuge tube and 25 mL of 0.04 M EDTA at pH 6.0 were added prior to shaking for 2 h (McLaren et al., 2005). The tubes were then centrifuged at 4500 rpm for 15 min. The supernatant of the extraction solution was syringe-filtered (0.45 μm) and analysed for metals using atomic absorption spectrophotometry (GBC Avanta).

2.5. Interpretation of DGT data

The mass of metals in the resin gel (M) can be calculated using the following equation:

$$M = C_e(V_e + V_{gel})/f_e \quad (1)$$

The concentration of metals, measured by ICP-MS, in the eluate of volume, V_e, is C_e, V_{gel} is the volume of resin gel, and f_e is the elution factor for each metal (typically 0.8) (Zhang et al., 2002). The time averaged concentration of metals at the interface of the soil and the DGT device can be obtained using the following equation:

$$C_{DGT} = M\Delta g/(DAt) \quad (2)$$

The combined thickness of the diffusive gel and filter membrane is Δg, D is the diffusion coefficient of metals in the gel, t is the deployment time and A is the area of each gel segment.