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Coupled mobilization of dissolved organic matter and metals (Cu and Zn) in soil columns

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Abstract

Dissolved organic carbon (DOC) is a key component involved in metal displacement in soils. In this study, we investigated the concentration profiles of soil-borne DOC, Cu and Zn at various irrigation rates with synthetic rain water under quasi steady-state conditions, using repacked soil columns with a metal-polluted topsoil and two unpolluted subsoils. Soil solution was collected using suction cups installed at centimeter intervals over depth. In the topsoil the concentrations of DOC, dissolved metals (Zn and Cu), major cations (Ca^{2+} and Mg^{2+}) and anions (NO_3^- and SO_4^{2-}) increased with depth. In the subsoil, the Cu and Zn concentrations dropped to background levels within 2 cm. All compounds were much faster mobilized in the first 4 cm than in the rest of the topsoil. DOC and Cu concentrations were higher at higher flow rates for a given depth, whereas the concentrations of the other ions decreased with increasing flow rate. The decomposition of soil organic matter resulted in the formation of DOC, SO_4^{2-}, and NO_3^- and was the main driver of the system. Regression analysis indicated that Cu mobilization was governed by DOC, whereas Zn mobilization was primarily determined by Ca and to a lesser extent by DOC. Labile Zn and Cu^{2+} concentrations were well predicted by the NICA-Donnan model. The results highlight the value of high-resolution in-situ measurements of DOC and metal mobilization in soil profiles.

1. INTRODUCTION

Dissolved organic carbon (DOC) mobilizes metals by forming strong complexes with metals in soil solutions (Römkens et al., 1999), whereas solid organic matter immobilizes metals. It is known that Cu forms stronger complexes with organic ligands (Florence, 1982) than Zn in soil solution (Milne et al., 2003). Therefore, the concentration of DOC is an important factor for the translocation of metals in soils (Antoniadis and Alloway, 2002; Tipping, 2002). DOC mobilization is mainly determined by adsorption/desorption reactions (Jardine et al., 1989; Gu et al., 1994; Kaiser and Zech, 1998) and microbial activity (Zsolnay and Steindl, 1991; Guggenberger et al., 1994; Godde et al., 1996). High temperature (Cronan and Aiken, 1985; Christ and David, 1996), elevated pH (Jardine et al., 1989; Godde et al., 1996), high water content (Christ and David, 1996; Tipping et al., 1999; Zsolnay et al., 1999), and low ionic strength (Davis, 1982) also increase the concentration of DOC.

The equilibration of DOC with the soil matrix has been found to be complete within 2–4 h (Kaiser and Zech, 1998). Therefore, non-equilibrium conditions could be expected to exist close to the soil surface during infiltration starts. With increasing depth they should disappear. Equilibrium conditions should be reached within shorter distances for lower than for higher infiltration rates in the case of homogeneous soil and uniform flow. Under field conditions, however, DOC concentration was reported to be positively related to runoff (Hornberger et al., 1994; Kalbitz and Knappe, 1997) and was also predicted to increase proportionally with water flux on a weekly basis in the model of Neff

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and Asner (2001). Increased rainfall may increase water content and decrease ionic strength, which may increase the concentration of DOC. Thus, increasing infiltration rate may result in higher DOC concentrations than in dilution, which may enhance metal leaching even more than the increase in proportion to the flow rate.

Because DOC mobilization is affected by a multitude of processes, it makes predictions of metal leaching from soils difficult. Various numerical models have been developed to describe the formation, transport and retention of DOC in soil profiles, such as DyDOC (Michalzik et al., 2003) based on humic substance fractions and the model of Neff and Asner (2001) utilizing C pools with different turnover times. Mechanistic models building on molecular-scale description of metal ion binding by humic substance, e.g. the NICA-Donnan model (Kinniburgh et al., 1996) and WHAM (Tipping, 1994), have been used to model DOC partitioning in soil (Oste et al., 2002; Weng et al., 2002b; Lumsdon et al., 2005).

Leachates collected from pot or column experiments have shown that complexation with DOC increased the leaching of metals (Chanmugathas and Bollag, 1988; Camobreco et al., 1996; Antoniadis and Alloway, 2002). Such experiments, however, do not yield spatially resolved information on DOC and metal mobilization within the soil. Thus, they do not allow separating the influence of processes acting at different depths on the leaching characteristics of a soil profile. Using zero-tension lysimeters or porous materials under suction is a way to continuously sample soil solution. This technique has been applied for years in the field to determine the changes in soil solution composition with depth in different soil horizons and over time (Vance and David, 1991; Tipping et al., 1999; Camobreco et al., 1996; Antoniadis and Alloway, 2002; Hoffmann et al., 2002; Rais, 2005). In these studies, it was found that DOC concentrations in the topsoil were in most cases much higher than in the subsoil and the DOC leached from the topsoil was immobilized by adsorption in the subsoil. Likewise, mobile metals leached from the topsoil were retained in the subsoil. The changes in the soil solution composition were mostly related to the different soil horizons in the profile. However, changes in soil solution composition over small distances and across soil layer boundaries are poorly studied. To understand the leaching processes of DOC and metals, it is necessary to reveal the composition of the soil solution and its gradual variation over time and depth.

The aim of this study was to investigate in-situ the mobilization of DOC and coupled release of Cu and Zn, from contaminated topsoil into and through two different types of subsoil (acidic vs. calcareous) under different irrigation rates. We installed suction cups at vertical distances of a few cm in large soil columns to obtain soil solution samples continuously with high spatial resolution through the soil profile without disturbing the experimental system (Zhao et al., 2007). We analyzed the concentration of DOC along with those of total and labile Cu and Zn and those of major cations and anions in soil solution and interpreted the changes along the soil profile with the NICA-Donnan model. Our hypotheses were that: (1) the mobilization of DOC and Ca influences the mobilization of Cu and Zn; (2) DOC mobilization is enhanced with increasing irrigation rate, which may be the key process to enhance metal leaching; and (3) immobilization reactions in the subsoils reduce the concentrations of the mobilized metals.

2. MATERIALS AND METHODS

2.1. Soils

The soils were sampled in 2004 from a model ecosystem experiment, in which the relationships between metal pollution and its effect on soil and vegetation had been investigated for three years (details in Nowack et al., 2006). The topsoil was a weakly acid loam, originating from an agricultural field (Luvisol). Part of the topsoil had been pretreated artificially with filter dust from a non-ferrous metal smelter in 2000. Total Cu, Zn, Cd and Pb concentrations averaged 640, 3000, 10, and 90 mg/kg, respectively. For our experiment, the polluted topsoil was mixed with unpolluted topsoil (ratio 1:4) to lower the metal concentrations. The subsoil was either acidic loamy sand from a Haplic Alisol or a calcareous sandy loam originating from a Calcaric Fluvisol. The soil properties are given in Table 1. Total metals were measured by X-ray Fluorescence Spectrometer (SPECTRO X-LAB 2000, Spectro, Germany). The soil was sieved through 2 mm and kept moist at a temperature of 15 °C before use.

2.2. Column set-up

Four large soil columns were packed with metal-polluted topsoil and unpolluted subsoil (acidic subsoil in two columns and calcareous subsoil in the other two columns). The scheme of the column setup is shown in Fig. 1. Each PVC column of 62 cm length and 20 cm diameter was filled with 2 cm quartz sand (grain size < 0.5 mm) at the bottom, 35 cm subsoil (either acidic or calcareous) and 23 cm polluted topsoil in the middle and another 2 cm quartz sand on the surface. The column bottom was sealed by a polyamide mesh (mesh size 200 μm) placed on a PVC plate with holes (diameter 6 mm). Subsoil and topsoil were separated by a polyamide mesh (mesh size 60 μm), fixed by plastic tape and plastic glue to the column wall. In each column fifteen coiled suction cups (50 cm long Rhizon samplers, Rhizosphere Research Products, the Netherlands) were installed at 4, 10, 13, 16, 18, 20 and 22 cm depth (A depth of 0 cm refers to the topsoil surface) in the topsoil, and at 24, 26, 28, 30, 33, 38, 44 and 50 cm depth in the subsoil during filling of the column. The suction cups were curved in a spiral and fixed by a plastic stick to hold them in place and shape. To investigate the changes of soil solution across the soil layer boundary, the distance between the suction cups was smaller above and below the mesh than in the rest of column. A 100 cm long suction cup (Rhizon samplers, Rhizosphere Research Products, the Netherlands) was installed at 56 cm depth in the sand layer to continuously collect the leachate. All suction cups were cleaned prior to installation with nitric acid (0.01 M). This type suction cup only sorbs metals weakly and has no effect on major cations and anions (Rais et al., 2006).