A scale-dependent approach to study pollution control processes in wetland soils using three different techniques

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ARTICLE INFO

ABSTRACT

The Elbe River, Germany, has received heavy metals and arsenic from the discharge of urban industrial, and agricultural effluent. During periods of inundation, these contaminants were transported with water into floodplain ecosystems, where they settled and accumulated predominantly in depressions and low-lying terraces. Markedly elevated arsenic concentration in soil solution during floods exceeded the inspection value of $10 \, \mu g \, L^{-1}$ of the German soil protection ordinance. Highly variable hydrological conditions in floodplains can affect the dynamics of pollutants. The study of processes controlling the dynamics of pollutants is challenging because the results are required to answer both scientific and practical questions regarding protection of groundwater and plants, sustainable management of floodplains or explain the fate of environmentally harmful substances.

Our experiments in small groundwater lysimeter and biogeochemical microcosms tended to yield similar results regarding the functional relationships among the investigated site parameters. But the results of the field experiments, carried out at a floodplain site of the middle course of the Elbe River, Germany, are often characterized by complex and varying factors. Whereas arsenic tended to be mobilized during flooding due to decreasing redox potential (E_H), chromium showed the opposite trend, with peak concentrations at the highest E_H values. Our approach at three different spatiotemporally scale levels, ranging from 23 days (microcosms) to two-and-a-half years (field soil hydrological facility) allows us to overcome process interferences observed in field studies.

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1. Introduction

Wetlands, especially floodplains, offer a variety of ecosystem functions. One of the most important is their ability to act as water regulator by buffering the extremes associated with the discharge of rivers (de Groot et al., 2002; Golladay and Battle, 2002). Floodplains also fulfil important retention functions in relation to the cycling of nutrients and the treatment of contaminants transported in the river system (Costanza et al., 1997; Venterink et al., 2003). Contamination hot spots emerge in selected floodplain areas as a consequence of contaminated sediment deposition (Martin, 2000; Middelkoop, 2000; Krüger et al., 2005; Benson, 2006; Baborowski et al., 2007; Overesch et al., 2007; Rinklebe et al., 2007).

The tolerable concentrations of heavy metals and arsenic (As) in soil and pore water according to the precaution and action values of the German soil protection ordinance (BBodSchV, 1999) are

often exceeded in these areas (Krüger et al., 2005; Rinklebe et al., 2007; Rennert and Rinklebe, 2010). The BBodSchV (1999) is a comprehensive law whereby different limits are defined; these are inspection value, action value, and precaution value. Examination and analytical methods are governed by this control instrument and exposure pathways are differentiated into soil–human being, soil–plant transfer, and soil–groundwater. This law is also applicable to the contamination of floodplain soils and soil pore waters. An action value for As content in soils of $50 \, mg \, kg^{-1}$ dry matter was ascertained for the exposure pathway soil–agricultural crop. The soil protection ordinance also defines precautionary values of 10 and $50 \, \mu g \, L^{-1}$ for As and chromium (Cr) in pore water, respectively, for the exposure pathway soil–groundwater.

The accumulation of heavy metals in floodplains and their adverse effects on ecosystem quality are problems not unique to the Elbe River. River systems all over the world suffer from these accumulations (Taylor, 1996; Martin, 2000; Hudson-Edwards et al., 2001; Hobbelen et al., 2004; Thon, 2006). Typically, floodplains are characterized by a highly dynamic and variable hydrological regime. Dry spells alternate with inundations. These variable hydrological conditions have a considerable impact on

the geochemical conditions and consequently on the processes of nutrient or heavy metal and As mobilization or immobilization (Sánchez-Pérez and Trémolières, 2003; Yoo and James, 2003; van Griethuysen et al., 2005). The mobility of metals in wetlands is determined by a complex of soil factors and processes; e.g., adsorption/desorption reactions, salinity, organic matter content, sulphur (S) and carbonates, plant growth, pH and redox potential (E_H). Redox processes are central to the mobility of many metals and metalloids (Patrick and Verloo, 1998; van den Berg et al., 2000; Vink, 2002; Du Laing et al., 2009c). Whereas the mobilization of cadmium (Cd) and zinc (Zn) primarily depends on soil pH and mobile element content (Kalbitz and Wennrich, 1998), van Griethuysen et al. (2005) pointed out that the dynamics of many trace metals in floodplain soils is driven by seasonal redox cycles of S, iron (Fe) and manganese (Mn). At the oxic–anoxic interface and in the anoxic layers of floodplain soils, specific redox-sensitive processes occur which often involve the precipitation and dissolution of metals. The kinetics of these processes are of large importance for these soils as the location of the oxic–anoxic interface is subject to change due to fluctuating water table levels (Du Laing et al., 2009c). As a result of temporal inundations, Mn^{2+} and especially Fe^{2+} occur as soluble metal-organic complexes in soil at low E_H and can be translocated in the soil profile in this form (Hiller et al., 1988). With the reduction of oxides elements that are fixed in them such as phosphorus (P), molybdenum (Mo), cobalt (Co), copper (Cu), Zn are often transformed to a more mobile and plant available form.

According to the state-of-the-art of soil science in floodplains we raised the following working hypothesis: the periodic inundation of floodplain soils affect the dynamics of heavy metals and As due to changes of E_H/pH-values and the chemistry of Fe and Mn. An adverse impact on the mobilization or leaching of heavy metals and As might be also possible.

In spite of the scientific progress, our knowledge regarding the specific mechanisms prevailing in floodplain soils and the resulting approaches for controlling the contaminant mobility is still incomplete. We are in need of detailed knowledge on the behaviour of metals under alternating hydrological conditions as a precondition for the development of innovative technologies to manage and to restore large contaminated floodplain areas. Consequently, the scientific basics for practical solutions such as phytoremediation approaches (Fellet et al., 2007; Lesage et al., 2007; Suchkova et al., 2010) should comprise studies at different scales in order to reach a comprehensive understanding of the most relevant processes (Odum and Odum, 2003).

Our objectives were twofold; first, to evaluate the major biogeochemical processes that underpin the dynamics of trace elements at the lab scale and, secondly, to verify the processes at the lysimeter and field scales. The combination of biogeochemical microcosm set-up (lab scale), groundwater lysimeter (lysimeter scale) and soil hydrological measurement facilities (field scale) provides a valuable experimental hierarchy to monitor and study pollution control processes.

2. Materials and methods

2.1. Biogeochemical microcosm set-up

In the laboratory, we simulated flooding with the aim to elucidate the fate of trace metals and their relationship to E_H and dissolved organic carbon (DOC) in frequently flooded soils. For this purpose, we developed an automatical biogeochemical microcosm system based on the technique of Patrick et al. (1973). This biogeochemical microcosm set-up was successfully used for measuring trace gaseous emissions from soils (Yu et al., 2007) and for study-

ing the dynamics of mercury fluxes and their controlling factors in polluted floodplain areas (Rinklebe et al., 2010).

For this study, soil (0–15 cm depth) was sampled from the Elbe River floodplain (km 290, German mileage; 51°57′15″N, 11°54′57″E); this soil has served as a reference site in several previous studies (Böhme et al., 2005; Devai et al., 2005; During et al., 2009; Rinklebe et al., 2009, 2010). The soil has the following properties: 35% sand, 44% silt, and 20% clay; pH ($CaCl_2$): 5.8; C_{org}: 6.58%. The metal concentrations of the bulk soil in aqua regia extracts [$mg\,kg^{-1}$] were as follows: As: 123; Fe: 46611; Mn: 1236; Cr: 116. The soil was classified as Mollic Gleysol (GLm) according to IUSS/ISRIC/FAO (2006).

Four replicates of the soil were incubated (soil–water ratio: 1:8 in the biogeochemical microcosms), which allowed continuous control of soil E_H, pH, and temperature in soil slurries (Fig. 1a). A platinum (Pt) electrode with a silver–silver chloride (Ag/AgCl) reference electrode was used for the E_H measurement whereas a pH electrode was utilized for the pH measurement. The E_H, pH, and temperature in the soil slurry of each microcosm were automatically monitored every 10 min. Data recorded by the sensors were collected by a data logger.

Soil E_H was maintained within a specific range by adding N_2 (to reach lower E_H) and O_2 (to raise E_H) through an automatic valve-gas regulation system. At defined E_H levels, soil suspension was withdrawn (20 mL each time) from each microcosm, and was immediately filtered in an N_2-atmosphere through a 0.45 μm Millipore membrane (Whatman Inc., USA) into two 10-mL test tubes. One sub-sample was used to monitor concentrations of DOC. To the other sub-sample, 3 drops of 2 M nitric acid were added to preserve the solution for later analysis of metals. Changes in soil mass and water in the microcosm were considered in calculations while soil/water ratio remained the same in the microcosms.

2.2. Small groundwater lysimeter

In January 2009, two lysimeter vessels were used to remove soil monoliths *in situ* from the experimental site at Schönberg-Deich (Saxony Anhalt, Germany), which is located in the middle course of the Elbe River (km 435–440, German mileage; q.v. section 2.3). For the monolith extractions, a rotary milling tool was used (Meissner et al., 2005). This procedure avoids soil structural damage and reduces equipment needs. In our study we used two identical lysimeters. Both lysimeters have a diameter of 30 cm and a total height of 90 cm (Fig. 1b). The soil column inside the lysimeters is 70 cm high. At the bottom, there is a 15 cm filter layer which consists of three classified filter sand sub-layers each of 5 cm thickness (grain size: 0.1–0.5, 0.71–1.25 and 3.15–5.6 mm, respectively). The coarsest sub-layer is situated at the bottom of the lysimeter vessel followed by the medium and fine material, which represent the transition to the soil monolith. Above the soil, there is a 5-cm column of space to permit flooding.

The water table inside the lysimeter is regulated by an integrated tube at the bottom of each lysimeter vessel. The lysimeter is equipped with suction cups to sample soil solution, redox probes and frequency domain (FD)-probes to measure the soil temperature, the E_H, the soil moisture content and the temperature in depths of 10 and 30 cm below soil surface level, respectively. Soil solution was collected twice a week by applying a vacuum of approximately −50 kPa which is comparable to the field studies. The measured data (E_H, volumetric soil moisture content and temperature) were monitored with data loggers continuously in 15 min intervals from June 2009.

During the experiment different water levels were adopted. At the beginning of the study, the water level was 30 cm below the surface (May 20, 2009–June 10, 2009). Subsequently, it was raised