

Lysimeter and in situ investigations for the quantification of the heavy metal and As release from a floodplain soil

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Abstract

Weighable lysimeter with groundwater regulation were used to quantify groundwater recharge from a floodplain site of the Elbe River. The lysimeter experiments are linked with *in situ* investigations carried out at a semi-automated field research station situated in the floodplain area. Here, more process orientated investigation of possible migration of heavy metals and As by means of suction cups and redox probes, installed into a flood channel were carried out. The investigations revealed a substantial mobilization of As and partly Cd, Cu and Ni that exceeded the precaution values for the path soil - groundwater. While Cd, Cu and Zn were leached or immobilized, the concentration pattern of Co and Mo coincided with the increase of Mn. The release of these elements was assumed to be due to the dissolution of Mn and Fe oxides and hydroxides at lower redox potentials as dominating process. Also As showed a significant response to the dissolution of the oxides. Ni and Cr were characterized by a continuously increasing release peaking after the end of the inundation. Results of in-situ redox potential measurement indicated a delay of 4-5 weeks for the release of the redox-sensitive metals.

Introduction

The quantification of soil water balance quantities of floodplain sites close to groundwater or regularly flooded is the prerequisite for detailed determination of evapotranspiration, capillary rise, the deduction of interactions with the water course or the clarification of infiltration processes. The dynamics of soil water has a substantial impact on the concurrently proceeding processes of solute and pollutant dislocation. In the event of flooding,

the parameters which influence groundwater dynamics need to be quantified as completely as possible so that the water absorption capacity of adjacent floodplains can be predicted more accurately.

Soil hydrological measuring setups are used to gain knowledge of the water and solute balance of floodplain sites. Evapotranspiration and groundwater recharge are determined on this experimental set up indirectly on the basis of hydrological calculation approaches (SCHWARTZ, 2001; RUPP, 2000). This type of procedure is often associated with errors, due to lacking direct measurement of amounts of seepage water (only estimation from the change of water tension / water content) and the adjustment of stationary water content in the soil profile in dry and high-evapotranspiration periods (water transport through the soil profile causes no changes in water content).

The newly developed groundwater lysimeter enables us to investigate the water budget of floodplain sites by using undisturbed representative soil monoliths (MEISSNER et al., 2000). The groundwater level measured in the floodplain (inclusive inundation) can be transferred to the lysimeter. Parameters of the soil water balance, like the rate of groundwater outflow and inflow, evapotranspiration, groundwater recharge and capillary rise can be directly quantified.

Many floodplain soils in European river basins show pollution with heavy metals due to inputs of contaminated sediments particularly during flood events (JAKOVLJEVIC et al., 1997; ZHAO et al., 1999; FRIESE et al., 2000; MARTIN, 2000; MIDDELKOOP, 2000; KOOISTRA et al., 2001; KRÜGER et al., 2003). In contrast to the opinion that heavy

metals are fixed in floodplain soils, there are indications in the literature that illustrate the source function of floodplain soils for pollutants. Specific statements on the element dynamics of metal contaminated floodplain sites and the dominating processes are still lacking.

According to HILLER et al. (1988) Mn²⁺ and especially Fe²⁺ occur as soluble metal-organic complexes in soil at decreasing redox potentials as a result of a temporal inundation and can be translocated in the profile in this form. With the reduction of oxides, elements (P, Mo, Co, Cu, Zn, ...) that are fixed in them are often transformed to a more mobile and plant available form. Due to these redox sensitive processes the mobility of metals can increase considerably. MASSCHELEYN et al. (1991) reported e.g. for As an increased solubility by a factor of 13 between a redox potential of +500 and -200 mV.

The objectives of this study were (i) to quantify groundwater recharge of the investigated floodplain sites and (ii) to assess the temporal dynamics of the heavy metal and arsenic concentrations in the soil solution in respect to inundation events and redox potential modulation.

Material and methods

Site

The investigated floodplain site is located south of Wittenberge in Saxony Anhalt on the left side of the Elbe (km 435 - 440). Flood channels passing in East-West direction structure the floodplain into plateau and depression zones that are used as grassland for cattle. In one of these flood channels near to the river the suction cups were installed in a gleyic humic fluvisol that developed on Holocene sands which are covered by floodplain loam.

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The long-term annual precipitation is 508 mm. At the study site the first aquifer was detected from 70 cm down to a depth of 30 m.

The saturated water conductivity of the profile comprised a wide range and was on average quite high with 100-1000 cm/d. Excepted were the horizons between 50 and 70 cm whose saturated water conductivity was between 3 and 15 cm d⁻¹.

Weighable groundwater lysimeter

Two lysimeter monoliths were extracted from the field site. The lysimeter has a surface area of 1 m² and is 2 m deep. A layer of sand and gravel, 25 cm thick with graduated particle sizes, was placed at the bottom of the lysimeter to avoid interfacial effects underside the soil monolith and disturbances to natural water movement and perched water due to interrupted capillaries. The groundwater level data from the floodplain are transmitted once a day by modem to the lysimeter located at UFZ's field research site in Falkenberg and regarded as the target water level.

The groundwater lysimeter is weighable. Weight (changing of mass) is recorded every minute. In order to balance groundwater inflow and outflow, weight changes need to be recorded with as little delay as possible. These measurements are condensed to 15-minute average values in order to reduce effects caused for example by the wind (oscillation of the soil in the lysimeters) or brief weight increases (being trodden on by animals etc.). For further details see BETHGE-STEFFENS et al. (2004).

Chemical analyses

In December 2004 borosilicate glass suction cups were installed in the floodloam horizons at 15 and 45 cm depth and the sandy horizon at 85 cm below the floodloam. At each depth the soil solutions were sampled in triplicate after the suction cups had *in situ* equilibrated for six weeks. For the collection of the solution a low pressure of 500 mbar was applied to the suction cups 2-3 days before sampling. During the inundation the suction cups could not be sampled at the highly flooded period but more continuously in 2006 by the use of a boat. Samples were taken weekly - as far as soil solution

could be gained - from February 4th 2005 to the July 10th 2006.

In July 2005 after the flood five redox electrodes were installed at each of the three depths. The redox potential is given normalized on the hydrogen potential. Due to the very high flood in 2006 (maximum water level of 720 cm at the Elbe River gauge in Wittenberge downstream km 435) the logger for the redox electrodes were deinstalled on April 4th 2006 and re-installed on April 21st 2006.

Total organic carbon (TOC) and total inorganic carbon (TIC) were analysed with a carbon analyser (DIMA-TOC 100, Dimatec, Germany), the pH was measured by an electrode (Dr. Lange, Germany). Heavy metals and arsenic (As) were analysed, acidified with HNO₃, in unfiltered suction cup solutions (< 1 µm). Aluminium (Al), arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb) and zinc (Zn) were determined by mass spectrometry with inductively coupled plasma (ICP-MS; Agilent 7500 Series), iron (Fe) by the additional use of a collision cell.

Results and Discussion

Lysimeter experiment

The groundwater recharge for the floodplain site is presented in *Figure 1*. Based

on investigations with the weighable groundwater lysimeters it could be demonstrated that a groundwater recharge occurs on this site. The annual average amount of groundwater recharge ranges between 24 and 43 mm a⁻¹. Contrary to previous assumptions (NESTLER, 1998) and to the results of a calculation approach (DIN 4049) it was possible to prove groundwater recharge for the floodplain sites.

Redox potential

In *Figure 2* the redox potential is shown for the three depths. The redox potential reflected very well the gauge of the Elbe River. MANSFELDT (2003) suggests the grouping of redox potentials to classes for the interpretation of measured values. The redox status in soils can be classified as follows: (i) oxidizing (> 400 mV, CO₂ dominated), (ii) weakly reducing (400 to 200 mV, nitrate and Mn(III, IV) reduced), (iii) moderately reducing (200 to -100 mV, Fe(III) reduced) and (iv) strongly reducing (< -100 mV, sulphate and CO₂ reduced). The redox potential measured during inundation in a depth of 15 and 45 cm (100 mV ... -100 mV) points to moderately reductive conditions (class III) according to the above given classification scheme. An increased solubility of heavy metals and As can be expected at redox potentials measured during inundation until a soil depth

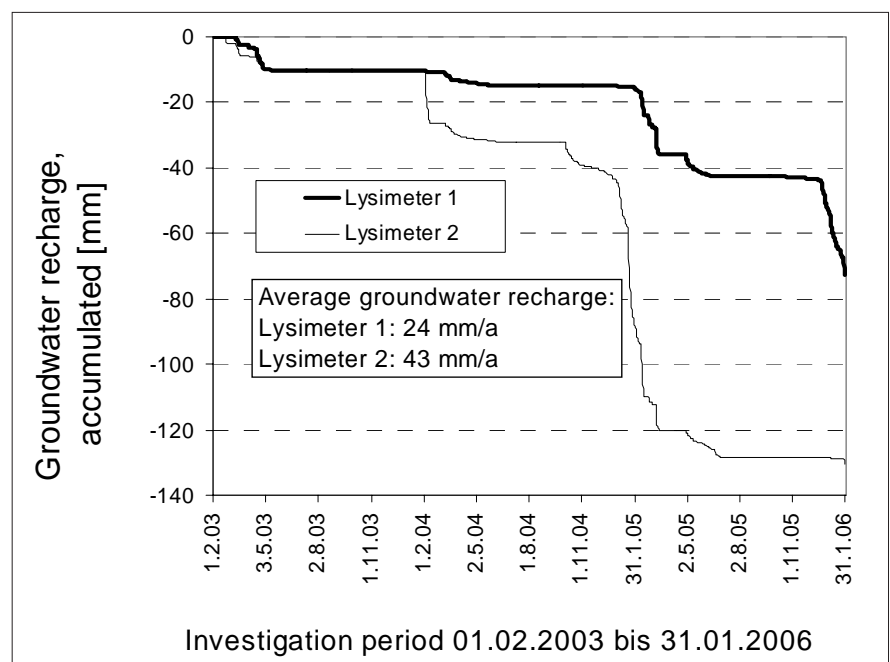


Figure 1: Groundwater recharge

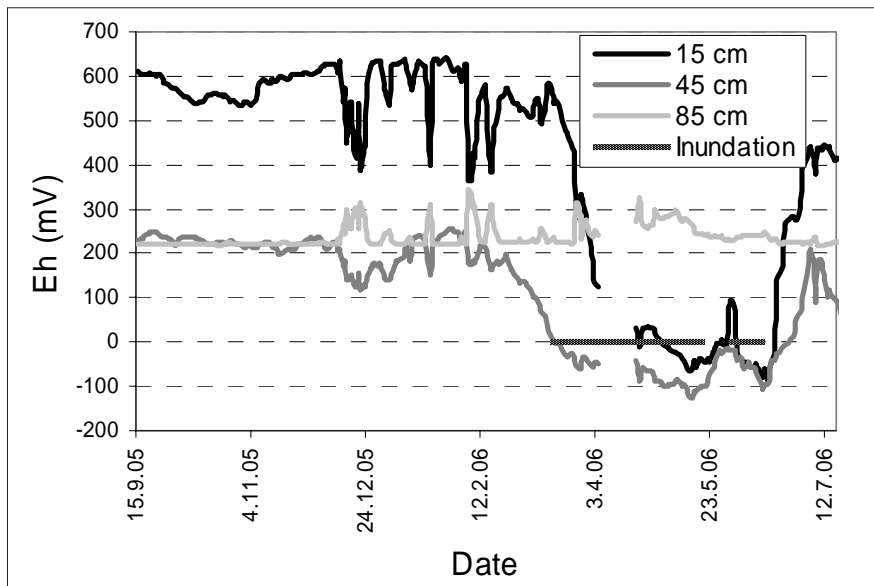


Figure 2: Median of soil redox potential in 15, 45 and 85 cm depth

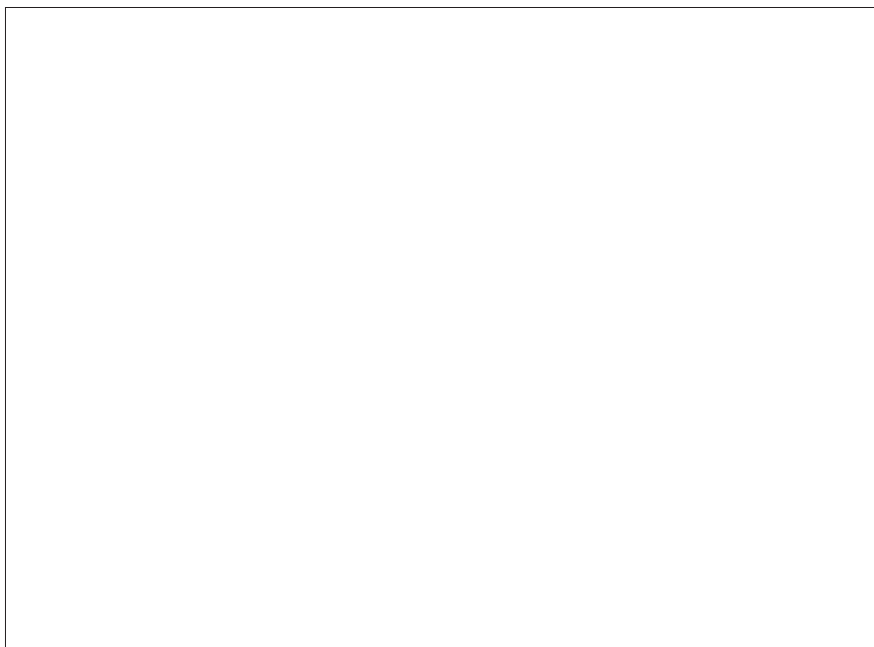


Figure 3: Median of the Mn concentrations at the three depths (The 25 and 75 % quartiles are given as error bars)

of 45 cm. Higher redox potentials in 85 cm than in 45 cm depth especially during summer and autumn were probably the result of a lower water storage capacity or content in the sandy horizon at 85 cm depth.

Metal concentrations in the soil solution

The Cd concentrations ranged between 1.5 and 5.5 $\mu\text{g L}^{-1}$ in 15 cm depth while the concentrations in 45 and 85 cm were rather constant throughout the year (data not shown). Nevertheless, they reflected the course in 15 cm but damped. During

the floods 2005 the Cd concentrations in 15 cm depth reached their peak quickly at the first sampling after the site was no longer inundated and decreased rapidly thereafter. The same fast response was observed during the flood 2006. The elevated concentrations reflected the peaks of the gauge of the Elbe River and showed a very fast decrease. This indicates that Cd was released into the soil solution very quickly obviously due to desorption processes. Also in the subsoil this pattern was detected to a lower extent. However, an immobilisation of Cd as a result of slightly increasing pH va-

lues instead of a release into the soil solution can not be excluded.

The Cu concentrations (data not shown) showed distinct effects in 15 cm depth. After the inundation in 2005 the Cu concentrations are characterised by a period of increased values. This period could be explained more distinctive at elements that are redox sensitive like Mn (Figure 3), which might indicate that Cu was released from the oxides. In contrast to the flood 2005 the Cu concentrations decreased constantly during the inundation period in 2006 pointing to a constant leaching or immobilisation of Cu.

The concentrations of Co and Mo (data not shown), Ni (Figure 4) and Mn showed a similar response to the inundation of the site. When the site started to be inundated in spring 2006 and the redox potential decreased in 15 cm depth the concentrations of Co, Mo, Ni and Mn in 15 cm also started to increase. Between four and five weeks after the inundation the concentrations increased rapidly. The release of these metals reached the overall maximum at the end of the second inundation or 3 days after the inundation, like Ni. In contrast to Co, Mo and Mn, Ni showed a continuous increase of the concentrations. In 2005 the pattern of the Ni concentrations followed the pattern of Mn.

The Cr concentrations (data not shown) are characterized by a release pattern rather similar to that of Ni. The mass available in the soil solution was especially high during the flood events. After the inundation 2005 the Cr concentrations increased constantly until it decreased five weeks after the end of the inundation like Ni. During the inundation 2006 the Cr concentrations decreased at first before they followed the pattern of Ni. The flood 2006 revealed that Ni and Cr were released constantly until one to two weeks after the inundation ended.

The As concentrations (Figure 5) remained relatively constant between 1 and 5 $\mu\text{g L}^{-1}$ in the investigated period. At the end of the inundation in 2005 the As concentrations reached their maximum of 15 $\mu\text{g L}^{-1}$ in 15 cm depth and showed the a fast decrease thereafter. During the inundation in 2006 the As concentrations reached also a maximum.

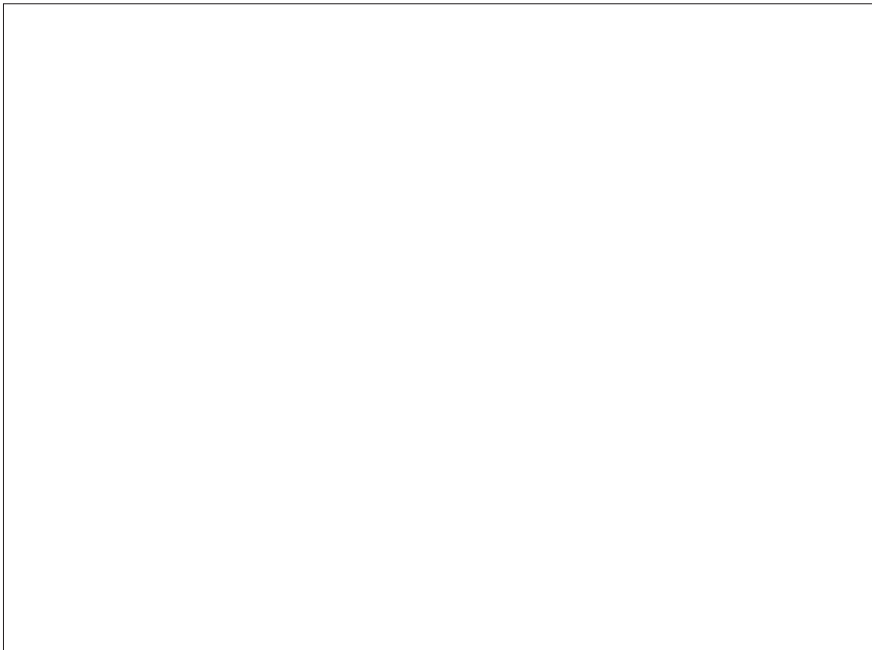


Figure 4: Median of the Ni concentrations at the three depths (The 25 and 75 % quartiles are given as error bars)

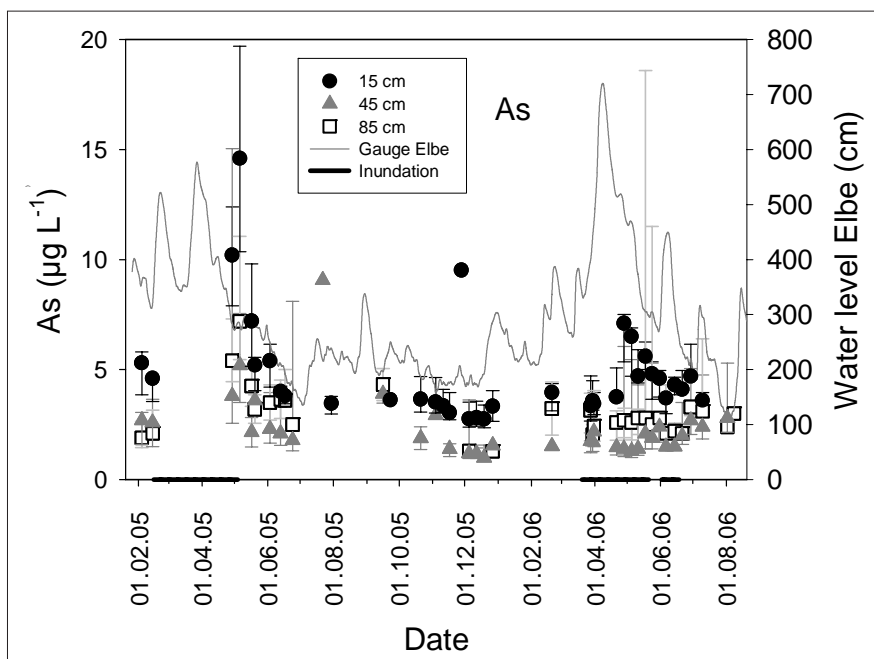


Figure 5: Median of the As concentration at the three depths (The 25 and 75 % quartiles are given as error bars)

In accordance with Mn the As concentrations increased five weeks after the inundation indicating that the decreased redox conditions are responsible for the release of As. The observed shift in the release compared to the redox potential might indicate that As is released from precipitates of Fe and Mn oxides. The higher mobility of As in its reduced species (BISSSEN and FRIMMEL, 2003) might explain the faster decrease of the

As concentrations than it was detected for the other redox-sensitive heavy metals. This suggests that also desorption processes contributed to the release of As.

The concentrations of Zn followed the pattern of Cd and Cu, those of Pb were very low at the detection limit, and those of iron (data not presented) showed despite strong variations a reaction on the flooding regime of the site and the clo-

sely connected redox potential variation.

Conclusions

The lysimeter results revealed a downward directed water movement in the soil profile which is also relevant to the transport of trace elements with the seepage water. The translocation of these pollutants from the soil into the groundwater still has to be demonstrated by lysimeter experiments. The field investigations showed that due to inundation during flooding events an appreciable mobilisation of heavy metals and As occurred. Especially the reduction of Mn and Fe oxides revealed to be a significant process in the release of Co, Mo and to a certain extent Cr and Ni. Also As showed a distinct correlation to the redox conditions. These changes in the heavy metal and As concentrations caused by the inundation exceeded the precaution values for the transfer path soil to groundwater of the German soil protection directive for As and partly Cd, Cu and Ni. The increased concentrations turned out to be a potential risk for the quality of the groundwater and underline the source function for pollutants of the contaminated floodplains. The effect of TOC on the release and translocation of the heavy metals and As should be analysed in future.

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