Groundwater derived arsenic in high carbonate wetland soils: Sources, sinks, and mobility

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ABSTRACT

Wetlands and organic soils have been recognized as important sinks for arsenic in the environment, yet sources and immobilization mechanisms of As are often unclear. To begin rectifying this deficiency, we investigated As retention and binding mechanisms at a degraded, minerotrophic wetland site in contact with groundwater rich in As and Fe. Arsenic occurred in high dissolved concentrations of up to 467 μg L⁻¹ in the groundwater, but dropped to values below 10 μg L⁻¹ towards the surface. The solid phase As content instead was high in the topsoil with up to 3400 mg kg⁻¹ and decreased with depth to 15 mg kg⁻¹. A similar pattern was observed with respect to Fe. Amorphous and crystalline iron precipitates were the main sorbents for arsenic in the soil horizons according to results from wet chemical sequential extractions. Arsenic was apparently not associated with inorganic carbon phases, but a substantial portion of up to 31% of As_{total} could be mobilized by dispersion of soil organic matter. Ratios of dissolved As(III)/As(V) decreased from the deeper As(III) dominated groundwater to the As(V) dominated soil porewaters, where As was apparently immobilized in its oxidized form. Concentrations of the organic species DMA and MMA were negligible. According to the results of simple one-dimensional estimates the vertical arsenic transport from the source in the groundwater to the topsoil was slow given an extrapolation of current conditions. These results suggest that As accumulation started before the beginning of drainage in the now degraded peatland soils and the degradation and mass loss of organic matter under oxic conditions caused the very high As concentrations found in the topsoil horizon today.

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1. Introduction

Arsenic is one of the most widespread and dangerous toxic substances in the environment, and the contamination of drinking water is especially problematic in developing countries (Mandal and Suzuki, 2002; Naidu et al., 2006; Smedley and Kinniburgh, 2002). Arsenic pollution of groundwaters can occur through natural and anthropogenic processes. In South Asia, for instance, the geogenic release of arsenic from sedimented iron phases under reducing conditions is seen as the main cause for groundwater contamination (Stuben et al., 2003). Co-deposition of organic matter with arsenic enriched iron phases in these sediments probably favours this subsequent reductive arsenic mobilization (McArthur et al., 2004; Meharg et al., 2006).

Oxidizing conditions often lead to lower As mobility because of the formation of As(V) and its subsequent adsorption to metal oxides. Arsenic binding by carbonates (Magalhães, 2002) and silicates (Goldberg, 2002) has been demonstrated but Al, Mn and especially Fe oxides are the most important As sorbents under oxic conditions due to their large surface area (Smedley and Kinniburgh, 2002). The oxygenation of Fe(II) containing water to induce iron precipitation is used to sorb and remove As during water treatment (Jessen...
et al., 2005). At circumneutral pH As(V) ($pK_{a1} = 2.2$) occurs mainly in the charged $\text{H}_2\text{AsO}_4^- \text{ or } \text{HAsO}_4^{2-}$ forms, whereas As(III) ($pK_{a1} = 9.2$) is predominantly uncharged $\text{H}_3\text{AsO}_3^-$. (Cherry et al., 1979). Nonetheless, the sorption capacity of As(V) and As(III) on positively charged ferrihydrite or goethite at neutral pH were found to be similar (Dixit and Hering, 2003). Sorption competition is known for anions, such as phosphate (Geelhoed et al., 1998), but also for dissolved organic carbon (Bauer and Blodau, 2006; Redman et al., 2002). Natural organic matter (NOM) influences arsenic mobility in several ways (Wang and Mulligan, 2006). Dissolved humics induce As redox transformation (Buschmann et al., 2005; Palmer et al., 2006; Tonesayi and Smart, 2006), form chemical bonds with aqueous As (Buschmann et al., 2006; Thanabalasingam and Pickering, 1986; Warwick et al., 2005) and influence the stability of As bearing colloids (Ritter et al., 2006). Finally, organic matter promotes microbial activity, which changes the redox conditions and may induce methylation of arsenic (Huang and Matzner, 2006; Huang et al., 2007).

The relative immobility of As in organic matter rich peat bogs was used for instance to trace the history of atmospheric immision (Shotyk et al., 1996; Ukonmaanaho et al., 2004), but retention mechanisms of As have not been sufficiently investigated yet. Arsenic was also found to accumulate in mineralotrophic peatlands and fens, which are in contact with more mineralized groundwaters (Shotyk, 1996; Steinmann and Shotyk, 1997; Szramek et al., 2004). The strong correlation of aqueous As(III) and Fe(II) concentrations during times of low redox potential, for example, suggested a binding of As and Fe in the same solid phase pool of a minerotrophic and iron rich fen (Blodau et al., in press; Huang and Matzner, 2006). Iron oxides typically precipitate in oxic surface layers or at the surfaces of oxygen conducting plant roots and may function as arsenic adsorbers. Pfeifer et al. (2004) hypothesized that Fe oxides formed in such organic rich layers are especially amorphous and have a large surface area available for sorption. Also in wetland soils influenced by geothermal waters, iron precipitates provided the main arsenic adsorption sites, even in presence of high contents of calcite, which is also a potential adsorber for As (Cornu et al., 2001). The storage of As in wetland soils may not be permanent though. Burial with ongoing decomposition and inudnation of organic soils can entail decreasing redox potentials. Such changes are expected to lead to release of arsenic by iron oxides dissolution and peat degradation, which may to some extent be balanced by As binding in sulphide minerals under sulphate reducing conditions (Gonzalez et al., 2006; Meharg et al., 2006).

Wetland soils often cover large areas in valleys and lowlands, where groundwater occurs close to the land surface and promotes the transfer of arsenic rich water into the soil (Gonzalez et al., 2006; Pfeifer et al., 2004; Szramek et al., 2004). Many wetland systems are also subject to changes in the water regime such as drainage and rewetting, which may be the consequence of land use and climate change (Gotham, 1991). Little is yet known about the impact on the mobility of stored arsenic in the short- and long-term. In this study we thus focussed on arsenic dynamics in a groundwater influenced former wetland that has been subject to drainage and peat degradation for more than two centuries. The soils of this site are rich in organic and inorganic carbon, iron, and arsenic. Our specific goals were (I) to analyse the current As distribution and the main soil arsenic pools, (II) to identify current processes of As mobilisation and immobilisation, and (III) to infer potential mechanisms and time periods leading to the extraordinary high As contents found in these soils. To achieve these goals, the soil solid phase and the porewater were sampled in the most important soil horizons and in the upper aquifer of two sites differing in iron oxide content in the top soils. The samples were analyzed with chemical and spectroscopic methods to determine the distribution of As between aqueous and solid phase and As speciation. These data were related to hydrological and geochemical controls at the site. We hypothesized that the As enrichment in the topsoil was primarily a result of a flux of ferrous Fe and As(III) from the deeper ground water, leading to Fe and As oxidation and enrichment in Fe oxides and As associated with the oxides. Other possible controls, such as association of dissolved As with the organic matter and carbonates, and enrichment in the solid phase due to degradation of the peat soils were considered as well.

2. Materials and methods

2.1. Site description

The study was carried out at a field site on the quaternary gravel plain north of Munich (Germany). The quaternary aquifer consists of dolomitic, fluvioglacial material and is underlain by semipermeable marly silts of tertiary origin (Zahn and Seiler, 1992). The groundwater on the field site today is within 0.5–1 m of the land surface. Until the beginning of drainage in the 18th century minerotrophic peatlands dominated the study area, which have since then been degraded and converted into calcic or mollic gleysols (FAO). Arsenic enrichment was found with varying concentrations ($10–50 \ \mu g\ kg^{-1}$, peaks $>500 \ \mu g\ kg^{-1}$) in the topsoil on a regional scale (personal communication, Bayrisches Landesamt für Umwelt). Arsenic and iron content in quatemary aquifer material is low, and both elements are believed to be transported into the quaternary groundwater with water infiltrating from the subjacent tertiary aquifer at zones of high permeability (Rauert et al., 1993).

2.2. Field instrumentation and sampling

We selected two locations (site A and B), about 50 m apart, on an extensively used grassland for the investigation. The horizons 1 and 2 had a dark brown colour on site A, whereas ochre to red colours were prevalent at site B. The two sites differed strongly with respect to the solid phase iron content in the topsoil, and were chosen to elucidate the effect of different iron oxide content on As enrichment in the degraded wetland soil. Soil profiles were divided into 4 soil horizons (site A and B, horizon 1 to 4) above the coarse grained, dense aquifer material. The water table, averaged from measurements at all 4 sampling dates, was at 68 cm (site A) and 50 cm (site B) below the surface.

Soil samples were taken in triplicates from the four soil horizons in December 2005. To account for spatial heterogeneity three separate soil profiles about 1 m apart from one
another were sampled per site. The samples were frozen and freeze dried in the lab. Gravimetric water content was determined as the difference of field fresh and freeze dried samples. After sieving (<2 mm grain size) and removal of large roots, samples were ground for pH measurements, extractions, and spectral measurements.

The two sites were instrumented for porewater and groundwater sampling up to a depth of 130 cm below the surface. Suction cups consisting of a polyamide membrane on polyethylene film (10 cm long; 0.45 μm pore size; preconditioned with 0.1 mol L⁻¹ HCl; Ecotech) were used above the water table. Below the groundwater table polyvinylchloride tubes (diameter 4.5 cm, perforated length of 10 cm, covered by nylon mesh) were installed as piezometers. To account for spatial heterogeneity in the aquifer, piezometers were set up in triplicate in 110 cm depth and in duplicate in 130 cm depth. The hand-drilled piezometer bore holes were refilled with layers of coarse and fine quartz, followed by bentonite up to the surface to prevent preferential flow along the tube. Every piezometer was fitted with a floating diffusion barrier on the water table, thus minimizing gas exchange with the atmosphere. A permanently installed groundwater well located nearby was used to sample groundwater from a depth of 2.5 m. Long-term recordings of the groundwater table were also available for this well. Soil solution and groundwater was sampled on 4 dates between November 2005 and June 2006. Samples from the piezometers and the groundwater well were taken after pumping and exchange of at least 2 piezometer or well volumes. Aqueous samples were immediately prepared taken after pumping and exchange of at least 2 piezometer or well volumes. Aqueous samples were immediately prepared

## 2.3. Laboratory and analytical procedures

The wet chemical sequential extraction procedure consisted of four steps. As extractants we used 0.1 mol L⁻¹ NaNO₃, 1 mol L⁻¹ HCl, 6 mol L⁻¹ HCl, and 65% HNO₃. Soil samples of 0.3 g were shaken in duplicates and darkness with the extraction solution and centrifuged before sampling. Sample contained no visible particles or colloids. Between extraction steps the soil was rinsed with Millipore water. Separate assays contained no visible particles or colloids. Between extraction solution and centrifuged before sampling. Samples were shaken overhead in duplicates and darkness with the encompassed a reaction of 0.2 g sample with 1 ml HNO₃ (65%) and 0.3 ml HCl (32%) for 24 h at room temperature and in triplicate. This step was followed by a microwave extraction with an additional volume of 8 ml HNO₃ and 0.2 ml HCl for a period of 1 h. Reaction conditions, target fractions, and references are listed for all extracts in Table 1. Extractions with NaNO₃ and Na₂P₄O₇ were carried out in an oxygen free glovebox to avoid changes in arsenic speciation.

The elemental composition of the soil extracts was analysed after filtration (0.45 μm Nylon, Roth) and acid stabilisation (1% HNO₃) by ICP-OES (Varian Vista-Pro) and Graphite Furnace AAS (Analytik Jena, Zeenith 60).

X-ray powder diffraction data were collected at room temperature using a Philips X Pert Pro X-ray diffraction system operating in reflection mode, with Cu-Kα (λ=1.78897 Å) radiation selected with a focusing monochromator, a symmetrically cut curved Johansson Ge(111) crystal, and a Philips Xcelerator detector. The Kα₁ line was reduced by the monochromator to <2% of the intensity of the Kα₂ line. The samples were X-rayed with diffractometer settings step size 0.03°, scan window 0.004 °/s, spinning platform rotation 1/s, and collection range 2 theta = 7°-90°. XRD bands were identified by comparison to single mineral spectra of the mincryst database (Chichagov, 1997). FTIR spectra were measured with a Bruker Vector FTIR device (KBr pellets; transmission mode; wavelength = 2–25 μm) and analysed using the Salisbury spectral library (Salisbury, 1991).

### Table 1 – Extraction procedures applied on the soil samples

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Conditions</th>
<th>Target As phase</th>
<th>Mechanism</th>
<th>Step no.</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO₃</td>
<td>0.1 mol L⁻¹ 24 h</td>
<td>Exchangeable</td>
<td>Exchange</td>
<td>1</td>
<td>Cai et al. (2002)</td>
</tr>
<tr>
<td>HCl</td>
<td>1 mol L⁻¹, 1 h</td>
<td>Amorph metal oxide, Carbonate, Acid volatile sulfide</td>
<td>Dissolution</td>
<td>2</td>
<td>Keon et al. (2001)</td>
</tr>
<tr>
<td>HCl</td>
<td>6 mol L⁻¹, 30 min, 70 °C</td>
<td>Crystalline metal oxides</td>
<td>Dissolution</td>
<td>3</td>
<td>Regenspurg and Peiffer (2005)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>16 mol L⁻¹, 1 h, microwave</td>
<td>Alumosilicates, sulfides</td>
<td>Dissolution, oxidation</td>
<td>4</td>
<td>Keon et al. (2001)</td>
</tr>
<tr>
<td>NaH₂PO₄</td>
<td>0.1 mol L⁻¹, pH 5, 24 h</td>
<td>Specifically sorbed</td>
<td>Desorption</td>
<td>Separate</td>
<td>Cai et al. (2002)</td>
</tr>
<tr>
<td>Na₂P₄O₇</td>
<td>1 mol L⁻¹, pH 5, 24 h</td>
<td>Carbonate</td>
<td>Dissolution</td>
<td>Separate</td>
<td>Tessier et al. (1979)</td>
</tr>
<tr>
<td>HNO₃/HCl</td>
<td>Conc.HNO₃/HCl 1 h, microwave</td>
<td>Organic matter bound</td>
<td>Dispersion</td>
<td>Separate</td>
<td>Bhattacharya et al. (2001)</td>
</tr>
</tbody>
</table>
Dissolved inorganic carbon (DIC) and CH₄ in the water samples were analyzed by headspace technique after sample acidification to pH < 2 (GC-FID/TCD; HP 6890; Beer and Blodau, 2007).

The arsenic speciation was measured by HPLC-ICP-MS (PRP X100 column, Hamilton; Agilent 7500ce). The separation method of Francesconi et al. (2002) allows for the quantification of arsenite, arsenate, dimethylarsinic acid (DMA) and monomethylarsenic acid (MMA). Sample preparation required a 0.2 μm filtration step (0.2 μm, Nylon, Roth), which was carried out in the field. To address As recovery problems, i.e. discrepancies between total As determined by AAS and the sum of As species detected by HPLC-ICP-MS, different other stabilization protocols were executed. Testing included the additional measurements of unfiltered samples and the chemical stabilization of samples filtered in the field with 2 mmol L⁻¹ EDTA or 20 mmol L⁻¹ HCl.

2.4. Calculations and modeling

The contribution of aqueous transport processes to the depth distribution of As was considered separately for the saturated and the vadose zones.

The As concentration versus depth profile for the aqueous phase below the groundwater table was simulated using a simple hydraulic box-model (Figure S1 of the supporting information) implemented in a STELLA system dynamics software (Beer and Blodau, 2007). The STELLA model consisted of five boxes representing the As or Cl pool in the four aqueous sampling depths in the saturated zone of site A and the nearby groundwater well (Figure S1 of the supporting information). The pools were linked to adjacent pools above and below through bidirectional diffusion and a vertical downward advection term as shown in Eqs. (1) and (2), which results also in some vertical numerical dispersion when a simulation is run.

Fig. 1 – Aqueous concentrations of total As, the As(III)/As(V) ratio, total Fe and DOC in soil porewater and in the quaternary groundwater (left to right). Values are depicted for site A (top) and B (bottom) in winter 2005/2006 (diamonds) and spring 2006 (squares). The lowest depth represents data from a groundwater well at the site.
An aquifer porosity of 0.26 (Zahn and Seiler, 1992) and a groundwater recharge of 100 mm a\(^{-1}\) was estimated by difference between rainfall (700–800 mm a\(^{-1}\)) and evapotranspiration (500–600 mm a\(^{-1}\); Winnegge and Maurer, 2002). Due to the lateral groundwater velocity (1–3 m d\(^{-1}\), Rauert et al., 1993) and resulting Peclet numbers of >100, dispersion in vertical direction can be assumed to outweigh diffusion in this direction (Appelo and Postma, 2006). A transversal, i.e., vertically oriented, dispersion coefficient of 0.002 m\(^2\) d\(^{-1}\) used in the model was approximated according to Appelo and Postma (2006) by \(D_{\text{transversal}} = 0.1D_{\text{longitudinal}}\). Concentration in segment 5 was kept constant to account for the source in the deep groundwater. Model calculations were performed until pool concentrations in the 4 upper segments were constant. Chloride served as a conservative tracer for comparison.

\[
F_x = -D_x \frac{\partial c}{\partial x} + u_x c
\]

\[
v_x = q_x \frac{n}{\eta}
\]

\(F_x\) = flux \([\text{M L}^{-2} \text{T}^{-1}]\); \(D_x\) = transversal diffusion–dispersion coefficient \([\text{L}^2 \text{T}^{-1}]\); \(c\) = concentration \([\text{M L}^{-3}]\); \(x\) = length \([\text{L}]\); \(u_x\) = velocity \([\text{L T}^{-1}]\); \(q_x\) = flux density \([\text{L}^2 \text{T}^{-1}]\); \(n\) = porosity [%].

Transport in the unsaturated zone above the groundwater table was estimated through water balance considerations. In the vadose zone of the upper soil horizons rainwater seepage, capillary rise and evapotranspiration take place. We used an evaporation rate of 500–600 mm a\(^{-1}\) (Winnecke and Maurer, 2002) as the maximum estimate for upward water transport and calculated annual rates of mass transport with measured groundwater iron and arsenic concentrations data (Eq. (3)).

\[
q_{\text{element}} = \frac{c_{\text{element}}}{\eta} q_{\text{water}}
\]

\(q_{\text{element}}\) = flux density \([\text{M T}^{-1}]\); \(c_{\text{element}}\) = concentration \([\text{M L}^{-3}]\); \(q_{\text{water}}\) = flux density \([\text{L}^2 \text{T}^{-1}]\).

Chemical saturation indices (SI) were calculated as the quotient of ion activity product (IAP) and saturation product (K\(_{\text{sp}}\)) with PhreeQC (Parkhurst and Appelo, 1999). Aqueous data from profile A was used and calcite, ferrihydrite, and goethite were considered.

Half cell redox potentials \(E_h\) were calculated according to the Nernst equation (Eq. (4)) for the redox pairs Fe(OH)\(_2^+/\)Fe\(^{3+}\) and HAsO\(_4^{2-}/\)H\(_2\)AsO\(_2\). Standard potentials \(E_h^0\) were determined from standard energy of formation values by Eq. (5) (Pankow, 1991; Sergeyeva and Khodakovskiy, 1969).

\[
E_h = E_h^0 + \frac{RT}{nF} \ln \left( \frac{I_{\text{II}}/I_{\text{I}}}{{I_{\text{I}}}/(I_{\text{III}}/I_{\text{II}})^{n}} \right)
\]

\[
E_h^0 = -\frac{AG^0}{nF}
\]

3. Results

3.1. Water chemistry

The water samples had circumneutral pH between 8.1 in the soil porewater and 7.0 in the groundwater. Dissolved oxygen in the piezometers decreased with depth from >6 mg L\(^{-1}\) at the surface to 1.5 mg L\(^{-1}\) in the groundwater. Dissolved NO\(_3^-\) followed a similar trend from 34 mg L\(^{-1}\) in the topsoil to <1 mg L\(^{-1}\) in the aquifer. In contrast SO\(_4^{2-}\) concentrations were between 12 and 50 mg L\(^{-1}\) and increased slightly with depth. CH\(_4\) was found in low concentration of less than 3 μmol L\(^{-1}\) in the groundwater below 100 cm depth. The redox potential on the field site therefore must be expected to decrease with depth, but conditions were not strongly reducing even in the groundwater, as the CH\(_4\) concentration was low and both oxygen and nitrate were not fully depleted.

The concentrations of DIC (2–8 mmol L\(^{-1}\)), Ca (150–300 mg L\(^{-1}\)), Mg (12.5–30 mg L\(^{-1}\)), Mn (0.1–0.8 mg L\(^{-1}\)) and Al (0–0.2 mg L\(^{-1}\)) did not vary systematically along the depth profile. Because of different pH the SI of calcite was ~0 in the groundwater but increased to 1.2 in the topsoil, indicating calcite supersaturation in the topsoil horizons.

In contrast, concentrations of As, Fe, and DOC strongly varied with depth (Fig. 1). DOC concentrations were above 100 mg L\(^{-1}\) in the upper part of the profiles and peaked in the third horizon at site A, and the first and second horizon at site B. Iron concentrations were 2–10 μmol L\(^{-1}\) down to a depth of 100 cm, and increased strongly below, particularly in the form of Fe(II) contributing between 82% and 99% of total Fe. With SI well above 1, ferrihydrite formation was thermodynamically favourable at all depths, even in the groundwater. Arsenic was similarly distributed with depth. Concentrations were below 10 μg L\(^{-1}\) in the upper 100 cm but reached 50–100 μg L\(^{-1}\) in the lowest piezometer, and 250–500 μg L\(^{-1}\) in the groundwater well, mostly in form of As(III). The As(III)/As(V) ratio changed from <1 to >10. DMA was detected at both sites at levels of 0.4–3.3 μg L\(^{-1}\) only during winter. Organic species were previously shown to contribute significantly to the aqueous and mobile arsenic pool (Huang and Matzner, 2006; Huang and Matzner, 2007a; Huang and Matzner, 2007b). With DMA concentrations of 0.4–3.3 μg L\(^{-1}\) and no detectable MMA, organic species accounted for less than 5% of As(tot) including the organic

![Fig. 2 – Detail of the X-ray diffractograms recoded in material of horizons 1 to 4 of site B. Labels indicate the identified mineral phases quartz, goethite, calcite and dolomite. Clay/ feldspar/mica peaks in the center of the diagram could not be attributed to specific minerals.](image-url)
matter rich horizon, and were of minor importance on the investigated field site.

The total aqueous concentrations of As, Fe and DOC varied more strongly with depth than with sampling season or sampling site. Site B samples showed slightly higher concentrations of aqueous Fe and As in the groundwater and differences in concentrations occurred between sampling dates but clear temporal trends could not be identified. The general depth distribution pattern did not change with sampling time or site.

The sum of the concentrations of arsenic species, i.e. arsenite, arsenate, DMA and MMA, determined by HPLC-ICP-MS was up to 100 μg L⁻¹, or 70% lower than the total As concentration measured by AAS in acidified samples. Deviations were similar in unfiltered samples and samples filtered in the field, and largest deviations occurred at site B and in samples from greater depth. Addition of either EDTA or HCl to the filtered samples in the field increased As recovery in samples from greater depth. EDTA and HCl for Fe and 0 to 70% lower than the total Fe.

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>Water content (%)</th>
<th>pHKSCN</th>
<th>Corg (%)</th>
<th>Corg (%)</th>
<th>Ca (g kg⁻¹)</th>
<th>Mg (g kg⁻¹)</th>
<th>Fe (g kg⁻¹)</th>
<th>Al (g kg⁻¹)</th>
<th>As (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 1</td>
<td>0-23</td>
<td>38</td>
<td>6.97</td>
<td>6.9</td>
<td>4.0</td>
<td>112.8</td>
<td>28.8</td>
<td>45.5</td>
<td>26.8</td>
<td>605.3</td>
</tr>
<tr>
<td>A 2</td>
<td>23-48</td>
<td>58</td>
<td>6.75</td>
<td>21.6</td>
<td>1.5</td>
<td>107.1</td>
<td>7.0</td>
<td>24.6</td>
<td>28.7</td>
<td>207.4</td>
</tr>
<tr>
<td>A 3</td>
<td>48-75</td>
<td>38</td>
<td>7.00</td>
<td>3.9</td>
<td>0.1</td>
<td>12.0</td>
<td>9.6</td>
<td>28.4</td>
<td>45.3</td>
<td>67.0</td>
</tr>
<tr>
<td>A 4</td>
<td>75+</td>
<td>22</td>
<td>7.22</td>
<td>0.7</td>
<td>4.7</td>
<td>80.0</td>
<td>46.8</td>
<td>18.0</td>
<td>19.4</td>
<td>27.9</td>
</tr>
<tr>
<td>Site B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 1</td>
<td>0-18</td>
<td>48</td>
<td>6.90</td>
<td>12.4</td>
<td>3.3</td>
<td>106.4</td>
<td>6.0</td>
<td>206.8</td>
<td>12.1</td>
<td>3239.2</td>
</tr>
<tr>
<td>B 2</td>
<td>18-43</td>
<td>66</td>
<td>6.86</td>
<td>24.8</td>
<td>3.6</td>
<td>58.7</td>
<td>3.8</td>
<td>45.1</td>
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<td>B 3</td>
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<td>11.1</td>
<td>9.5</td>
<td>27.3</td>
<td>37.2</td>
<td>22.3</td>
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<tr>
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<td>70+</td>
<td>22</td>
<td>7.24</td>
<td>0.9</td>
<td>4.4</td>
<td>80.6</td>
<td>43.7</td>
<td>15.2</td>
<td>19.8</td>
<td>7.9</td>
</tr>
</tbody>
</table>

Table 3 - Calcium, iron, and arsenic content as fraction of soil dry weight in different extracts of the soil horizons on sites A and B

<table>
<thead>
<tr>
<th>Horizon</th>
<th>Depth (cm)</th>
<th>0.1 mol L⁻¹ NaNO₃</th>
<th>1 mol L⁻¹ HCl</th>
<th>6 mol L⁻¹ HCl</th>
<th>0.1 mol L⁻¹ Na₂P₄O₇</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca (%)</td>
<td>Mg (%)</td>
<td>Fe (%)</td>
<td>As (%)</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A 1</td>
<td>0-23</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>A 2</td>
<td>23-48</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.2</td>
</tr>
<tr>
<td>A 3</td>
<td>48-75</td>
<td>0.3</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>A 4</td>
<td>75+</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Site B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B 1</td>
<td>0-18</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>B 2</td>
<td>18-43</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>B 3</td>
<td>43-70</td>
<td>0.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>B 4</td>
<td>70+</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The calculated Eh of the redox couples Fe(OH)₃/Fe²⁺ and As(III)/As(V) decreased with depth from ~85 to ~300 mV for Fe and 0 to ~25 mV for As. Lowest values were reached below the groundwater table at both sites. Similarly to the As₄sed concentrations, Cl⁻ concentrations increased with depth below the groundwater table and reached 30 mg L⁻¹ in the groundwater. The concentration profiles of both As and Cl⁻ in the saturated zone could be adequately modelled with diffusion/longitudinal dispersion and advection as the only vertical transport processes (Figure S2 of the supporting information).

3.2. Solid phase

High pH values between 6.9 and 7.2 predominated in the soil and carbonates were important crystalline mineral phases at the site (Fig. 2). X-ray diffractograms showed bands for calcite (i.e. 34.4°, 2 theta, Co Ka) and dolomite (i.e. 36.2°, 2 theta, Co Ka) in the horizons B1, B2 and B4. This is in accordance with chemical extraction data, indicating largest contents of inorganic carbon, Ca and Mg in horizons 1 and 4 on sites A and B (Table 2) and high Ca and Mg extraction with 1 mol L⁻¹ HCl (Table 3). Calcite dominated in the topsoil. The prominence of the dolomite bands and the high Mg content in B4 indicates that this horizon represents the uppermost layer of the dolomite dominated aquifer (Zahn and Seiler, 1992).

Silicate minerals became more important in the two lower horizons. The X-ray diffractograms contained characteristic quartz bands (24.4°; 31.2°; 2 theta, Co Ka) throughout the profile, but highest intensities were found for B3 and B4.
Diffractograms from these two horizons also displayed bands in a range characteristic for feldspars, mica, and clay minerals (32.23–32.75°, 2 theta, Co Ka), which could not be allocated to specific mineral phase. Most Al in the soil was released only in the aqua regia extract and was associated with silicate minerals.

Iron content was highest in the topsoil. Site B contained more than 4 times greater quantities of Fe in horizon 1 than site A. Due to a strong decline with depth the Fe content was similar at both sites in horizons 3 and 4. Between 7 and 30% of Fe$_{\text{tot}}$ was extracted by 1 mol L$^{-1}$ HCl and therefore in the operationally defined amorphous iron oxide fraction (Table 3, Fig. 3). But despite high Fe content at all depths, the low and broad goethite band (24.9°, 2 theta, Co Ka) was the only observed XRD signal representing an iron phase. Most iron was apparently found in non-crystalline phases, which were not detected by X-ray diffraction and predominantly extracted by 6 mol L$^{-1}$ HCl (48–55% of Fe$_{\text{tot}}$).

The abundance of mineral solid phases was lowest in the organic carbon rich horizon B2, with up to 24.8% C$_{\text{org}}$. The high soil organic matter content apparently also lead to a high gravimetric water content of 50–60%. With the exception of total Fe and C$_{\text{org}}$ content, the chemical composition of the different horizons at site A was very similar to site B. The FTIR spectra confirmed a similar mineral composition at both sites, with common FTIR spectral bands of calcite (7 μm; 11.4 μm), quartz (9.2 μm), and clay minerals (6 μm; 9.6 μm).

The soil arsenic content was between 7.9 mg kg$^{-1}$ and more than 3 g kg$^{-1}$, decreased strongly with depth and was about 5 times higher in horizon 1 at site B than at site A. Despite the high total content, the exchangeable arsenic fraction in the soils was low, ranging from 0.13 to 0.82 mg kg$^{-1}$ and thus accounting for <2% of the total arsenic present. Most arsenic could be extracted using 1 mol L$^{-1}$ and 6 mol L$^{-1}$ HCl together accounting for 77 to 96% of As in all horizons. The higher total As content at the iron rich site B suggests association of Fe and

![Fig. 3 – Solid phase content of As and Fe in extracts representative of amorphous metal oxides and carbonates (diamonds; 1 mol L$^{-1}$ HCl), crystalline metal oxides (squares; 6 mol L$^{-1}$ HCl) and a residual fraction (triangles; conc. HNO$_3$). Also shown is the content of organic (diamonds) and inorganic (triangles) carbon based on soil dry weight in the horizons of sites A (top) and B (bottom).](image-url)
As. This is supported by the statistical correlation found for soil As_{tot} and Fe_{tot} content ($R = 0.885$) using the ranking method by Spearman and a significance level of $p = 0.01$.

The content of C_{org} in the soil was also correlated to As_{tot} ($R = 0.776$) and in fact a substantial As fraction, representing 10–30% of As_{tot}, was released by dispersion of organic matter with pyrophosphate (Table 3). The largest fraction was extracted from the horizons at site A and in the second horizon of site B (Fig. 4). Between 5 and 25% of the soil organic carbon was released, particularly from the organic matter dominated horizons A2 and B2, but the mobilization of Ca, Mg, Fe or Al was negligible. More arsenic was extracted by pyrophosphate than with phosphate (5 to 10%) at all depths. Phosphate has a similar molecular structure as arsenate and can therefore be used to account for possible desorption reactions.

4. Discussion

Wetlands represent retention and enrichment zones for trace metals and metalloids including As (Gonzalez et al., 2006; Meharg et al., 2006; Pfeifer et al., 2004; Steinmann and Shotyk, 1997). Inspite of this well known fact, the importance of different As binding forms and As sorbents in these soils, i.e. oxides, sulfides and organic matter, has not yet been fully understood. Moreover, information about As sources and transport to wetland soils and the conditions and processes leading to As enrichment is often lacking. Our field site is characterized by a flat topography, a groundwater table close to the land surface, and a groundwater rich in As and thus provided ideal conditions to study As transport and retention processes in an organic matter rich soil.

4.1. Distribution and binding mechanisms of As in the solid phase

Iron oxides typically have a positive surface charge at circumneutral and slightly acidic pH, as the pH of zero charge ($pH_{ZPC}$) of ferrihydrite ranges from 7.8 to 7.9 and of goethite from 7.5–9.4 (Cornell and Schwertmann, 1996), which promotes an electrostatic association with negatively charged As (V). The minerals furthermore efficiently adsorb arsenic in specific surface complexes (Dixit and Hering, 2003; Fendorf et al., 1997). The soils at the studied field site were rich in amorphous and crystalline iron oxides. Contents decreased with depth and were greater at site B than at site A, which allows for comparisons regarding the role of iron hydroxides for As retention. The As content in the solid phase at all depths and both sites followed a similar trend and the total content of As and Fe in the amorphous and crystalline metal oxide fractions were correlated. Iron oxides were the most important As scavengers at our site at all depths, including the shallow aquifer. Previous studies already indicated that As was associated with iron in organic matter rich soils (Gonzalez et al., 2006; Pfeifer et al., 2004). Our new findings show that iron oxides are the predominant As sorbing phase in the degraded peatland studied. The As content in the soils amounted to between 10 and 200 μmol (g Fe)^{−1}. The reported sorption capacities for iron oxides depend on surface area and are higher with respect to ferrihydrite (1500 μmol (g Fe)^{−1}) than to goethite (120 μmol (g Fe)^{−1}; (Dixit and Hering, 2003). Especially owing to the substantial fraction of amorphous iron oxides, the sorption capacity of iron phases was sufficient to explain As binding at all depths.

Apart from an association of As with Fe, we also found As and organic carbon content to be correlated in the different soil samples. A considerable fraction of As could further be mobilized by dispersion of organic matter especially in the second soil horizon. Arsenic was thus apparently also associated with the organic soil phase. The importance of this As fraction increased with decreasing iron content and was larger in horizon 2 compared to horizon 1 and also larger at site A than site B. Bhattacharya et al. (2001) reported As association with organic phases in lake sediments as well, but information about binding mechanisms and capacities are lacking.

Fig. 4–Solid phase content of organic carbon (diamonds) and As (squares) as mobilized by 0.1 mol L^{−1} Na_{2}P_{4}O_{7} and of specifically sorbed As (triangles; 0.1 mol L^{−1} NaH_{2}PO_{4}). Results refer to soil dry weight in the horizons of site A (left) and the iron enriched site B (right).
Covalent binding mechanisms and cation bridging complexes have been proposed to facilitate As binding reactions to dissolved organic matter molecules (Buschmann et al., 2006; Ritter et al., 2006; Thanabalasingam and Pickering, 1986) and it has been suggested that binding capacities reach up to 1000 μmol As (g C)\(^{-1}\) (Warwick et al., 2005). Such a number well exceeds the measured As content of 8–180 μmol As (g C)\(^{-1}\) in the organic matter rich two topsoil horizons. Moreover, the presence of organic matter was hypothesized to cause a more amorphous structure of iron precipitates (Pfeifer et al., 2004). In similarity to the formation of iron colloids in organic matter rich solutions (Bauer and Blodau, submitted for publication), this might lead to smaller mineral particles and a higher surface area, increasing the overall quantity of sites available for As binding.

Alternative sorbents at the studied field site, such as calcite, dolomite, and silicates, were not found to considerably contribute to As binding in the solid phase. Despite the high contents of calcite in the topsoil and dolomite in the fourth soil horizon, the results from Na-Acetate extractions and correlation analysis did not indicate any association of arsenic with these carbonate minerals. This is in accordance with findings of Cornu et al. (2001), who documented that in the presence of iron phases As binding to calcite precipitates was negligible. A substantial contribution of silicate minerals to As binding was unlikely due to their low pH\(_{pzc}\) of 3–4.5 and a low As sorption capacity of 0.2 to 0.5 μmol g\(^{-1}\) on clay (Goldberg, 2002) and 2 to 5 μmol g\(^{-1}\) on mica (Chakraborty et al., 2007). No correlation between As and AI was found in the extraction solutions, suggesting that As association with AI containing minerals was negligible (Dousova et al., 2003). Our dataset provided no indication for arsenic binding to reduced iron sulphide minerals. XRD spectra showed no pyrite or arsenopyrite bands, redox conditions were only mildly reducing, and As content in the residual fraction was mostly low.

### 4.2. As source and aqueous transport in the saturated zone

Arsenic accumulation in soils and minerotrophic peatlands has previously been attributed to high As input stemming from streams or groundwater (Gonzalez et al., 2006; Steinmann and Shotyk, 1997; Szramek et al., 2004). Often, however, the source of As and its transport to the enrichment zones were not investigated and documented. The highest aqueous As concentrations at our site were found in the deepest groundwater samples and, therefore, groundwater presumably represented the source of As present in the top soil. High dissolved As concentrations are known to occur in tertiary sediment layers of southern Germany (Heinrichs and Udluft, 1996; Heinrichs, 1998). The occurrence of locally high concentrations of As in the quaternary aquifer water close to the surface was attributed to zones of a locally high permeability of the aquitard and water exchange between quaternary and tertiary sediment layers.

Along the concentration gradient towards the groundwater table, the strongest decrease in aqueous As concentration occurred in the saturated zone at a depth of 100 to 250 cm. The applied hydraulic transport model was able to adequately explain the measured As depth profile in the saturated zone with vertical advection and diffusion/dispersion processes. Alternatively, also the presence of an As sink in the solid phase might have been responsible for declining As concentrations at these depths. Inspite of this current apparent sink for arsenic, soil material from the deepest soil horizons A4 and B4 had the lowest measured total As content of all solid phases. This is in agreement with the mineralogy of these horizons, which was similar as in the aquifer material below and dominated by dolomite (Zahn and Seiler, 1992). These horizons thus had a low capacity to bind As in the solid phase (Thornburg and Sahai, 2004). A substantial sequestration of As in the lowest soil horizons, where the apparent sink occurred, thus seems unlikely also from a mechanistic point of view. The discrepancy between current apparent As sinks and contents of As in the solid phase cannot be resolved conclusively. Models of the type used were previously applied at field sites with less lateral water flux (Beer and Blodau, 2007), but due to the flat regional topography and low inclination of the groundwater table we expected effects of lateral flow on the vertical distribution of arsenic to be low at this site as well. We cannot exclude a solid phase sink as the reason for the decrease of aqueous As in the groundwater, because of an inadequate representation of reality in the model. It may also be that dilution of groundwater rich in As by infiltrating precipitation did cause the observed aqueous As profile in the saturated zone.

### 4.3. Transport and enrichment in the vadose zone

The dissolved concentrations of As and Fe above a depth of 100 cm were low and more or less uniform. Ferric iron was the predominant iron species in contrast to ferrous iron which predominated in the deeper groundwater. The supersaturation of the solution with respect to dissolved Fe and the precipitation of ferrihydrite likely caused the low total dissolved iron concentration. Dissolved As concentrations are strongly affected by sorption and coprecipitation with ferrihydrite phases, explaining the low fraction of As being in a dissolved state (Dixit and Hering, 2003; Jessen et al., 2005). The coupling of Fe and As dynamics was exemplified by the similar concentration profiles of both elements and the correlation of As and Fe content in the solid phase. The sorption capacities of ferrihydrite for As(III) and As(V) were found to be similar at neutral pH, even though As(V) species are negatively charged due to acidity constants of pK\(_{a1}\) = 2.2 and pK\(_{a2}\) = 6.8 and thus should have a higher affinity for positively charged iron phases than the uncharged As(III) species, which has a pK\(_{a1}\) of 9.2 (Cherry et al., 1979; Dixit and Hering, 2003). If this finding holds true also for the field site investigated, the change in redox speciation, from As(III) predominant in the groundwater to mainly As(V) in the topsoil, supposedly had only a minor effect on As binding by the solid phase. The sorption or incorporation of As in the water-unsatuated soil horizons was apparently not decisively impeded by high concentration of dissolved organic matter, which may lead to desorption of As from soil materials (Bauer and Blodau, 2006; Grafe et al., 2002). This finding may be a consequence of the high total iron content at the site. The total surface area available in the soils obviously provided a sufficient capacity of sorption sites for both organic and As anions.
The highest As accumulation was found in the topsoil horizons and measured As contents were high compared to literature values for soils (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). Under current conditions, capillary water movement was the only possibility for transport of As and Fe through the vadose zone to the highly enriched surface horizon. The small grain size and high organic matter content in horizons A2 and B2 most likely caused the high capillary water content in these horizons and allowed water transport into the topsoil horizon (Hoeting, 1996). Using the local evaporation rate of 500–600 mm a\(^{-1}\) as maximum estimate for upward water flux and water concentrations at the groundwater table, transport rates of 2 mg m\(^{-2}\) a\(^{-1}\) As and 60–80 mg m\(^{-2}\) a\(^{-1}\) Fe can be reached. To accumulate the amount of Fe and As found in the A1 and B1 horizons under current conditions by this process alone, time periods of more than 10,000 years would be required. We know that water regime at the site changed substantially with the beginning of drainage for agricultural purposes two centuries ago, and this supposedly lead to a substantial change in the water fluxes and geochemical conditions. Our assessment of the As accumulation time scale is therefore restricted to the conclusion that As enrichment must have started more than 200 years ago and probably considerably before this time.

Assessing the reasons for arsenic accumulation in the originally undrained, minerotrophic peatland is speculative. We assume that the process proceeded analogously to other peatland sites where As accumulated in soils with high organic matter content, high water table and under partly reducing conditions (Blodau et al., in press; Gonzalez et al., 2006; Meharga et al., 2006; Pfeifer et al., 2004). Arsenic binding to metal oxides phases in these systems primarily occurred in surface layers with at least temporarily oxic conditions or in the partly oxic rhizosphere of plants capable of oxygen transport into the soil (Blodau et al., in press; Keon-Blute et al., 2004). At another site pyrite minerals or organic phases have been conjectured to be more important as As sorbents but the authors did not provide data about As associated with different solid phases (Gonzalez et al., 2006). We thus assume that a higher groundwater table improved As transport from the groundwater into the soil at our site (Szramek et al., 2004). With the beginning of drainage As released by oxidation of iron sulphide minerals and organic matter probably was efficiently readsorbed on present or freshly forming iron oxide phases (Thornburg and Sahai, 2004). The soil mass loss due to the decomposition of the organic peat material under oxic conditions likely intensified the enrichment and accumulation of inorganic soil constituents in the topsoil layer. Even though this is speculative, this scenario outlines another explanation for the very high As enrichment found in the topsoil at the studied field site, which is more difficult to explain alone by an extrapolation of current conditions backward in time.

The solid phase content of As and Fe was substantially different at sites A and B (Table 2), confirming our original hypothesis. Site B contained up to four times more As and Fe in the topsoil horizons than site A. Given that crystalline Fe oxides were the primary sorbent for As according to the results of the sequential extraction (Table 3) the additional enrichment of As at the more iron rich site B is not surprising and again highlights the importance of iron oxide content for arsenic retention in these wetland soils. The exact reasons why Fe and As contents were so much higher at site B cannot be clarified conclusively. It may be that the As enrichment reflects an effect of more sorption sites being available during degradation of the wetland soils and the resulting potential As release from sulfides and organic matter. In this case only the historic flux of dissolved ferrous Fe and associated formation of iron oxides into the topsoil of site B was higher. Alternatively both the As and Fe flux were elevated and As co-precipitated with ferric iron oxides, which were subsequently diagenetically transformed in well crystalline iron oxides and incorporated the As. Differences in the flux of both elements into the soils could be attributed to local differences in water flux from subjacent, more As and Fe rich, tertiary aquifer (Rauert et al., 1993).

5. Conclusions

Dissolved As concentrations were in the low range of reported groundwater data up to 1 m depth and below the WHO guideline value of 10 \(\mu\)g L\(^{-1}\) (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). The very large solid phase arsenic pool in the oxic topsoil was not exchangeable and strongly sorbed mainly to crystalline iron oxide phases (Mandal and Suzuki, 2002; Smedley and Kinniburgh, 2002). This indicates a high stability of the present As pool in the soil under current conditions. A change of the redox regime to more reducing conditions, however, would probably initiate a slow release of As due to As reduction, As desorption and reductive dissolution of the iron oxides, which might be balanced by readsorption on remaining iron phases and binding in reduced solid phases like sulfides (Blodau et al., in press; Kocar et al., 2006; O’Day et al., 2004; Tadanie et al., 2005). Arsenic was primarily associated with iron oxide phases and no binding to calcite precipitates was found. Instead a considerable association was found between As and humics in the most organic matter rich horizons.

The primary As source at the field site was in the groundwater but current vertical transport towards the surface was low in the vadose zone. This implies that As accumulation at the site started already in the peatland soil before the beginning of drainage. Even though we can only speculate about conditions in the peat prior to drainage, the occurrence of As binding to metal oxide phases at the surface or reduced mineral and organic matter in greater depth can be inferred from previous studies (Blodau et al., in press; Gonzalez et al., 2006; Keon-Blute et al., 2004). Arsenic enrichment in the surface layer was possibly amplified by soil mass loss due to peat degradation under the oxic conditions after drainage. Secondly low As transport to the surface also shows that under current conditions only a small fraction of groundwater derived As is retained in the soil surface layer. The fate of the large As pool remaining in the solute phase of the groundwater is unknown and As monitoring downstream of the sampling site and on the regional scale should be the concern of future studies.

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