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Arsenic speciation and turnover in intact organic soil mesocosms during experimental drought and rewetting

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Abstract

Wetlands are significant sources and sinks for arsenic (As), yet the geochemical conditions and processes causing a release of dissolved arsenic and its association with the solid phase of wetland soils are poorly known. Here we present experiments in which arsenic speciation was determined in peatland mesocosms in high spatiotemporal resolution over 10 months. The experiment included a drought/rewetting treatment, a permanently wet, and a defoliated treatment. Soil water content was determined by the TDR technique, and arsenic, iron and sulfate turnover from mass balancing stocks and fluxes in the peat, and solid phase contents by sequential extractions. Arsenic content ranged from 5 to 25 mg kg^{-1} and dissolved concentrations from 10 to 300 μg L^{-1}, mainly in form of As(III), and secondarily of As(V) and dimethylated arsenic (DMA). Total arsenic was mainly associated with amorphous iron hydroxides ($R^2 > 0.95$, $\alpha < 0.01$) and deeper into the peat with an unidentified residual fraction. Arsenic release was linked to ferrous iron release and primarily occurred in the intensely rooted uppermost soil. Volumetric air contents of 2–13 % during drought eliminated DMA from the porewater and suppressed its release after rewetting for >30 d. Dissolved As(III) was oxidized and immobilized as As(V) at rates of up to 0.015 mmol m^{-3} d^{-1}. Rewetting mobilized As(III) at rates of up to 0.018 mmol m^{-3} d^{-1} within days. Concurrently, Fe(II) was released at depth integrated rates of up 20 mmol m^{-3} d^{-1}. The redox half systems of arsenic, iron, and sulfur were in persistent disequilibrium, with H_2S being a thermodynamically viable reductant for As(V) to As(III). The study suggests that rewetting can lead to a rapid release of arsenic in iron-rich peatlands and that methylation is of lesser importance than co-release with iron reduction, which was largely driven by root activity.

1. INTRODUCTION

Arsenic (As) is a ubiquitous trace metalloid in sedimentary formations and ground waters and concentrations often exceed recommended drinking water standards (Smedley and Kinniburgh, 2002). The best known example in this respect are elevated arsenic concentration levels in aquifers of Bangladesh, where a population of about 57 million is threatened by consumption of high arsenic ground waters (BGS and DPHE, 2001). The mechanisms and geochemical conditions by which arsenic is mobilized in the subsurface are thus of great interest and have become increasingly a focus of geochemical research over the past years. Previous work documented that redox conditions, physicochemical surface processes, and microbial mediation are important regulators of arsenic dynamics (Masscheleyn et al., 1991; Bissen and Frimmel, 2003). Arsenic occurs mainly as inorganic arsenate, here referred to as As(V), under oxic conditions. It can be chemically and microbially reduced to arsenite, here referred to as As(III), when oxygen is depleted (Smedley and Kinniburgh, 2002). Most recently, thio-derivatives of arsenic oxyanions have been identified as a further, important group of arsenic species in sulfidic waters (Wallschäger and London, 2008). Methylation of inorganic species is also carried out by aerobic and anaerobic microorganisms, which produce monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsine oxide (TMAO); and further

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organic species of biogenic origin have been found (Cullen and Reimer, 1989). Both the toxicity and mobility of arsenic depends on its speciation. Generally inorganic species are more toxic and less mobile than the organic forms (Mandal and Suzuki, 2002). Among the inorganic species, As(III) and As(V) differ in their toxicity and adsorption characteristics depending on pH and competitors for sorption sites (Dixit and Hering, 2003).

Peat soils have often been used to trace atmospheric arsenic pollution (Shotyk, 1996) but relatively rarely been investigated with respect to arsenic biogeochemistry, although it has become evident that organic-rich soils are often highly enriched with arsenic and that pore water concentrations in these systems can be very high (Gonzalez et al., 2006). In particular, little is yet known about the mechanisms causing a phase transfer of arsenic from dissolved to solid state in organic-rich soils and the geochemical conditions and time scales involved. In less organic-rich aquifers, arsenic dynamics have been linked primarily to the redox processes of iron and sulfur. Arsenic may for example be mobilized in oxidized form through oxidation of arsenic-bearing pyrites (Zheng et al., 2004) and immobilized through formation of arsenic-sulfide minerals and adsorption to pyrite surfaces (Bostick and Fendorf, 2003). In absence of oxygen, arsenic was generally found to be released when ferric iron hydroxides are reduced, and this has been also speculated to be the case at minerotrophic wetland sites (Huang and Matzner, 2006). The mobility of arsenic is also influenced by sorption on iron, aluminum, and manganese hydroxides (Anderson et al., 1976; Dixit and Hering, 2003) and clay minerals (Manning and Goldberg, 1996). Of importance for the distribution of arsenic between dissolved and solid phase associated state are further the competition of arsenic with phosphate and dissolved organic matter (DOM) for sorption sites (Bauer and Blodau, 2006) and the binding of arsenic to organic matter, which may proceed through both covalent binding and metal bridges (Redman et al., 2002; Buschmann et al., 2006).

Most aquifer systems and wetlands differ in their biogeochemistry in important aspects, which makes extrapolation of arsenic dynamics from one to the other geochemical environment problematic. The high content of organic matter of organic soils can result in more abundant organic binding of arsenic, which may also be the direct or indirect cause for the observed accumulation of arsenic in wetlands (Gonzalez et al., 2006). Little is, however, known about the strength and stability of organic arsenic binding under changing geochemical conditions. The soils are also often intensely rooted, which leads to the development of structured microenvironments of greatly differing redox conditions and distribution of potential adsorption surfaces (Blute et al., 2004), and entails the release of easily decomposable substrates for respiration, e.g. by bacterial iron and sulfate reduction. Furthermore, most wetlands frequently undergo strong changes in redox conditions due to water table fluctuations, which typically occur during summer droughts. Such dynamics may in the future become more pronounced, as temperate and northern regions have been predicted to undergo wetter winters, and drier periods and stronger rainstorms in summer (IPCC, 2001). A number of studies have already addressed the effects of drying and rewetting on arsenic mobility in soil samples and laboratory systems (McGeehan, 1994; Reynolds et al., 1999), or in the solid phase of agricultural and mine drainage contaminated field sites (La Force et al., 2000; Fox and Doner, 2003). In contrast, the *in situ* dynamics of geogenic or airborne arsenic in intact peat soils during drought and rewetting, and the way arsenic dynamics is linked to anaerobic respiration and other redox processes is not well documented.

To improve our insight into the dynamics of arsenic in natural wetlands we conducted a mesocosm study with undisturbed soils of a northern fen, in which all boundary conditions could be controlled. Arsenic, iron, and sulfate turnover in the peat were quantified in high temporal and spatial resolution by mass balance. The impact of the vegetation was analyzed by comparing a defoliated to an intact mesocosm, and the effect of drying and rewetting by comparison to a mesocosm kept with high water level. Our specific objectives were (I) to identify the spatial distribution, speciation, and binding of arsenic in the peat, (II) to elucidate the short-term temporal dynamics of pore water arsenic concentrations and its coupling to other redox processes, and (III) to identify the potential importance of the vegetation for arsenic dynamics.

2. MATERIAL AND METHODS

2.1. Experimental setup and instrumentation

The minerotrophic Schlöppnerbrunnen II peatland is part of the Lehstenbach watershed (4.2 km^2), situated at an elevation of 700–880 m (50°08′38″N, 11°51′41″E, Fichtelgebirge, Germany). The average annual air temperature is 5 °C, and mean annual precipitation varies between 900 and 1160 mm with a maximum both in summer and winter (Huang and Matzner, 2006). The organic soils reach a depth of 40–70 cm, were classified as Fibric Histosol, and are spatially quite heterogeneous in elemental contents and vegetation patterns on the scale of meters. The vegetation is dominated by graminoid species with only few mosses. The mean *in situ* water level at the site is 13 ± 19 cm below surface, but may drop down to below 70 cm depth during summer. Especially close to the peatland surface, iron and sulfur contents in the peat may reach as much as >16 and >4 mg kg^{-1}, respectively (Paul et al., 2006). Three intact peat monoliths (60 cm diameter, 60 cm depth, 'mesocosms') were collected in September 2005 and incubated in a 15 °C climate chamber for 10 months (~60% RH, 12 h light/dark cycles, 660 μmol s^{-1} photosynthetic photon flux). To this end a waste water tube with a wall strength of 2 cm and PVC lining was manually driven into the soil and dug out on all sides. The mesocosm was then tilted, which disconnected the mineral material beneath from the peat core, and a PVC bottom mounted and fixed with screws. A cap was also mounted on top to protect the vegetation. The mesocosm were rolled out of the pit on a wooden plank and transported to the laboratory. The water table position at time of sampling was at about 30 cm below surface. Two mesocosms contained *Agrostis sp.* (bentgrass), *Nardus stricta* (mat-grass), *Molinia caerulea* (purple moor grass), *Sphagnum fallax* (flat topped bog moss), *Brachythecium rivulare* (river feather moss), *Atrichum undulatum* (common smoothcap) and *Galium hercynicum* (bedstraw). One of these, which was the only containing *Carex rostrata* (beaked sedge), was kept permanently wet ('Wet-Vegetation' or 'W-V'), and the other ('Drying/Wetting–vegetation' or 'DW-V') and a defoliated ('Drying/Rewetting–defoliated' or 'DW-D') were dried and rewetted. The vegetation had been eliminated by inhibiting vegetation growth after the winter of 2005 by covering the plot with a plastic sheet. The von Post index of peat decomposition (Stanek and Silc, 1977) increased from 3 on a scale of 1–10 at depths of 0–10 cm to 7–9 at a depth of 25–60 cm.

After 40 days (first 'dry period' or 'equilibration period') the water table was raised from about 30 to 10 cm below surface by irrigation with 30 (DW-V, DW-D) and 40 mm (W-V) in two days. The water table was then kept constant at ~11.9 ± 1.3 cm (DW-V) or 9.9 ± 0.9 cm (DW-D) for 70 days ('wet period'), by irrigating up to 7 mm d^{-1}. Treatments DW-V and DW-D were subsequently dried out by reducing irrigation to 0 (DW-D) and 1 mm d^{-1} (DW-V) (second 'dry period') to a water table of 55 cm within 50 days. The mesocosms were then rewetted ('rewetted period') by irrigation with 54 (DW-V) and 53 mm (DW-D) within 2 (DW-V) and 5 (DW-D) days. During the rewetted period, the mean water table was held at 12.7 ± 1.8 (DW-V) and 9.8 ± 1.8 cm (DW-D). Time series of water table levels and volumes of irrigate applied are given in the Electronic annex (Fig. 1S). The irrigate was mixed according to precipitation chemistry at the site and contained Na^+ (5 μmol L^{-1}), Ca^{2+} (6 μmol L^{-1}), SO_4^{2-} (10 μmol L^{-1}), Cl^- (12 μmol L^{-1}), NH_4^+ and NO_3^- (40 μmol L^{-1}). The solution was equilibrated with atmospheric CO_2, yielding a DIC concentration of ~15 μmol L^{-1} and adjusted to a pH of 4.82 mixing SO_4^{2-} and H_2SO_4 for the concentration adjustment.

2.2. Sampling and analytical procedures

Volumetric gas content was derived using calibrated TDR probes at 10, 20, 30, and 40 cm depth (IMKO, Germany). All sensors had a comparable slope in the signal response of 0.22 ± 0.04 units per % volumetric water content, and we used relative changes in TDR measurements and the total porosity to calculate the gas content. Water tables were monitored in two piezometers per mesocosm, which were driven into the peat after pre-drilling and either screened from 15 to 25 cm or from 40 to 50 cm. Total porosity was measured by oven drying of 100 cm^3 samples.

Soil solution was sampled from Rhizon® samplers at depths of 5, 10, 15, 20, 30, 40, and 50 cm depth (microporous polymer, <0.2 μm pore size, fibre glass support, 10 cm sampling length). The pH and concentrations of H_2S were determined immediately on sub-samples of extracted pore water using a glass electrode, and an amperometric micro-sensor (AMT) before day 145 of the experiment, respectively. Subsequently, H_2S was measured at 665 nm using the methylene blue method (Cline, 1969). Dissolved Fe^{2+} and Fe_{tot} were determined immediately as well using the phenanthroline method (Tamura et al., 1974). Nitrate and sulfate was measured in filtered samples (0.2 μM, nylon syringe micro filter) by ion chromatography (Metrohm IC system, Metrosep Anion Dual 3 separation column at 0.8 mL min 1 flow rate, conductivity detection after chemical suppression). NH_4 was measured photometrically according to the method of Searle (1984). Concentrations of arsenic species As(III), As(V), DMA, and MMA were analyzed by High Performance Liquid Chromatography/Inductively Coupled Plasma Mass Spectrometry (HPLC-ICP/MS) according to Francesconi et al. (2002). Samples were filtered to 0.2 μM and were analyzed within two days, so that further stabilization was not necessary (McCleskey et al., 2004). The limit of detection (LOD) was 0.02 μg L^{-1}. Total dissolved arsenic was quantified using Graphite Furnace Atomic Absorption Spectroscopy (Gf-AAS, Zeenit 60, Analytik Jena) following filtration by 0.45 μm and acidification with 1 vol % HNO_3. LOD was 1.4 μg L^{-1}. Concentrations below LOD were set to 0 in calculations.

To analyze the solid phase peat we obtained subcores of 3 cm diameter at the beginning of the experiment. The resulting voids were filled with prepared PVC tubes of the same diameter. Total arsenic in the peat was analyzed in 0.2 g of dried and ground sample in three analytical replicates following digestion using 9 mL of HNO_3 (65%) and 0.3 mL HCl (32 %) in a microwave digester (Berghof Speedwave). The digest was filled up to 100 mL and filtered to 0.45 μm. Arsenic bound to reactive and total iron hydroxides was analyzed in duplicates subsequent to a sequential extraction. For the determination of operationally defined reactive iron, we extracted 0.3 g sample with 1 N HCl (30 mL) on a shaker for 24 h. This procedure dissolves amorphous and poorly crystalline iron hydroxides, acid volatile sulfur, siderite, vivianite and partly iron bound to chlorite minerals (Wallmann et al., 1993). Subsequently we extracted the residue with 6 N HCL (30 mL) at 70 °C for 30 min, which dissolves goethite and other well crystalline iron hydroxides (Cornell and Schwertmann, 1996). A precipitation of orpiment As_2S_3 in presence of As(III), H_2S, and acidic conditions has been reported (Smieja and Wilkin, 2003), which may lead to an underestimate of total arsenic concentrations in such solutions. Due to the oxic conditions during extraction, which lead to rapid oxidation of H_2S, we believe that a significant precipitation of orpiment was unlikely. The samples were centrifuged following extraction at 9800 rpm for 20 min, decanted, and the solution stored at 4 °C. Concentrations of the elements Al, Ca, Fe, K, Mn, and Al were quantified in the extracts on an ICP-AES following internal calibration accounting for matrix effects. The content of total inorganic reduced sulfur compounds (TRIS: FeS_2, FeS, S°) was determined using the method of (Fossing and Jorgensen, 1989). Frozen peat samples were freeze dried and 2 g of the material boiled with HCl ($c = 5$ mol L^{-1}) and $CrCl_2$ ($c = 0.15$ mol L^{-1}) under a constant nitrogen stream. The H_2S released into the nitrogen stream was trapped in 50 mL of NaOH ($c = 0.15$ mol L^{-1}) solution. The sulfide was precipitated by addition of zinc acetate and determined photometrically as described above.

To characterize the depth distribution of root activity, we applied a $^{13}C–CO_2$ pulse label for 1 h, filling a transparent chamber, which was tightly installed on the mesocosms, with a 63% $^{13}C–CO_2$ atmosphere of ~900 ppm total CO_2, and traced the label in soil CO_2. We extracted CO_2 from pore water and air using nitrogen-filled silicon tubes of a diameter of 10 mm, which were horizontally installed at the same depth as rhizon porewater samplers. Equilibration time of the samplers was approx. 6 h. A volume of 2 ml was extracted and thereafter replaced by nitrogen. The isotopic signature of the soil CO_2 was measured using a Trace GC 2000 gas chromatograph connected via Combustion III interface to a DELTA^{plus} isotope ratio mass spectrometer (Thermo Finnigan MAT, Bremen, Germany).

2.3. Calculations, statistics, and visualization of data

The mesocosms represent a system that is closed at the bottom and, with the exception of the unsaturated zone, transport thus proceeded by diffusion. Net turnover of ferrous iron and arsenic in the peat could thus be calculated by mass balance from Eq. (1) for individual depth layers:

$$R_{t(i)} = \underbrace{\frac{\mathrm{d}}{\mathrm{d}z}\left(-D^{\mathrm{w}} \cdot (\bar{\varphi})^2 \cdot \frac{\mathrm{d}c_{t(i)}}{\mathrm{d}x}\right)}_{\text{mean diffusive flux } \Delta J} + \underbrace{\left(\frac{\mathrm{d}c_{t(i\pm1)} \cdot \varphi}{\mathrm{d}t_{(i\pm1)}}\right)}_{\text{mean change in storage } \Delta S} \quad (1)$$

D^{w}	diffusion coefficient in water ($\mathrm{cm^2\,d^{-1}}$)
φ	porosity (–)
c	concentration ($\mathrm{nmol\,cm^{-3}}$)
$c_{\mathrm{t(i)}}$	mean of $c_{\mathrm{t(i-1)}}$ and $c_{\mathrm{t(i+1)}}$ in a depth increment
z	boundary between depth layers (cm)
x	sampling depth (cm)
t	time (d)
$t(i)$	time between sampling $t(i-1)$ and $t(i+1)$

$R_{t(i)}$ represents the sum of changes in dissolved storage ΔS within a depth layer in a time period $t(i \pm 1)$, and the mean diffusive flux ΔJ at time $t(i)$, which is calculated from the mean concentration gradients in period $t(i \pm 1)$. The diffusion coefficient of arsenic ($HASO_2^{2-}$) ($7.18 \times 10^{-6}\,\mathrm{cm^2\,d^{-1}}$) and of Fe(II) ($5.42 \times 10^{-6}\,\mathrm{cm^2\,d^{-1}}$) were calculated for water and 15 °C using a linear temperature correction according to (Lerman, 1979) and corrected for porosity φ using $D = D_0\varphi^2$. The diffusive flux at the upper and lower boundary of upper- and lowermost depth layers 1 and 7 was set to 0. To reduce noise, ΔS was calculated using the floating mean of concentrations of the two preceding and following sampling dates. For the calculation of total turnover in the peat, the turnover in individual depth layers were integrated over depth. $R > 0$ was defined as release into the dissolved phase.

The thermodynamics of potential elemental transformations in the peat was analyzed by calculating redox potentials for the individual half redox couples $Fe(OH)_3/Fe^{2+}$, SO_4^{2-}/HS^-, and As(V)/As(III), standardized to the standard hydrogen electrode, and using the Nernst equation (Eq. (2)) (Stumm and Morgan, 1996). Standard redox potentials were calculated from standard Gibbs free energy of formation according to Eq. (3), with thermodynamic data taken from Pankow (1991) for iron and sulfur and Sergeyeva and Khodakovskiy (1969) for arsenic. For the estimate we used concentrations, as the ionic strength of solution was low (~10^{-3}).

$$E_h = E_h^o + \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\Pi_i\{\mathrm{Ox}\}^{n_i}}{\Pi_j\{\mathrm{Red}\}^{n_j}} \quad (2)$$

$$E_h^o = \frac{-\Delta G^\circ}{n \cdot F} \quad (3)$$

Statistical correlations between parameters, such as between solid phase contents of arsenic and metals, were calculated using the non-parametric Spearman method using SPSS (release 10) because not all data were normally distributed even after log-transformation, and tested for their significance. Time series of dissolved concentrations were visualized using SURFER (release 8) using natural neighbor interpolation, which is particular suited for anisotropic data (Sibson, 1981). This was the case as data varied more strongly with depth than with time. An anisotropy factor of 1.5 was implemented, which causes a stronger interpolation along the time axis. Arsenic concentrations are reported in units of $\mu g\ L^{-1}$, as this notation is more commonly used than the chemically more meaningful unit of $\mu mol\ L^{-1}$.

3. RESULTS

3.1. Solid phase contents of arsenic, metals, and sulfur

Contents of total arsenic were similar in the mesocosms, peaked at 18 to 25 $mg\ kg^{-1}$, and remained >5 $mg\ kg^{-1}$ down to a depth of 60 cm. Standardized to dry mass, contents were highest near the soil surface, at a depth of 7.5 cm in all mesocosms. In the uppermost peat of the W-V and DW-V treatment, most of the arsenic could be extracted by application of 1N HCl (Fig. 1). In treatment W-V this fraction decreased from 25 $mg\ kg^{-1}$ (90 %) to <5 $mg\ kg^{-1}$ (30%) with depth, whereas the residual fraction, consisting of the difference between total arsenic and HCl extractable arsenic, gained in relative importance up to >60% of the total arsenic. Arsenic contained in the 6N HCl extract amounted to 5–20% and peaked at a depth of 7.5 cm. A very similar depth pattern was found in the DW-V treatment. Most of the iron, whose concentrations ranged from 4 to 10 $g\ kg^{-1}$ and also peaked near the surface on a per mass basis, could be extracted by 1 N HCl (Fig. 1). Contents of 6 N HCl extractable iron were similar to the residual iron in the peat of the permanently wet treatment W-V (0.5–2 $mg\ kg^{-1}$) and became relatively less important only in the deeper peat of the DW-V treatment. Acid extractable aluminum contents were in a similar concentration range as iron contents in treatment W-V and DW-V (Table 1). Mn could only be detected in the uppermost peat of the DW-V treatment with contents of <0.2 $mg\ kg^{-1}$. Contents of analyzed metals are summarized in the Electronic annex.

Total reduced inorganic sulfur (TRIS) was present at all depths in substantial contents of 50–135 $mg\ kg^{-1}$, even in the near surface peat, which had not been water saturated at the time of sampling in fall 2005 (Table 1). TRIS had thus been formed, or not fully been reoxidized during the

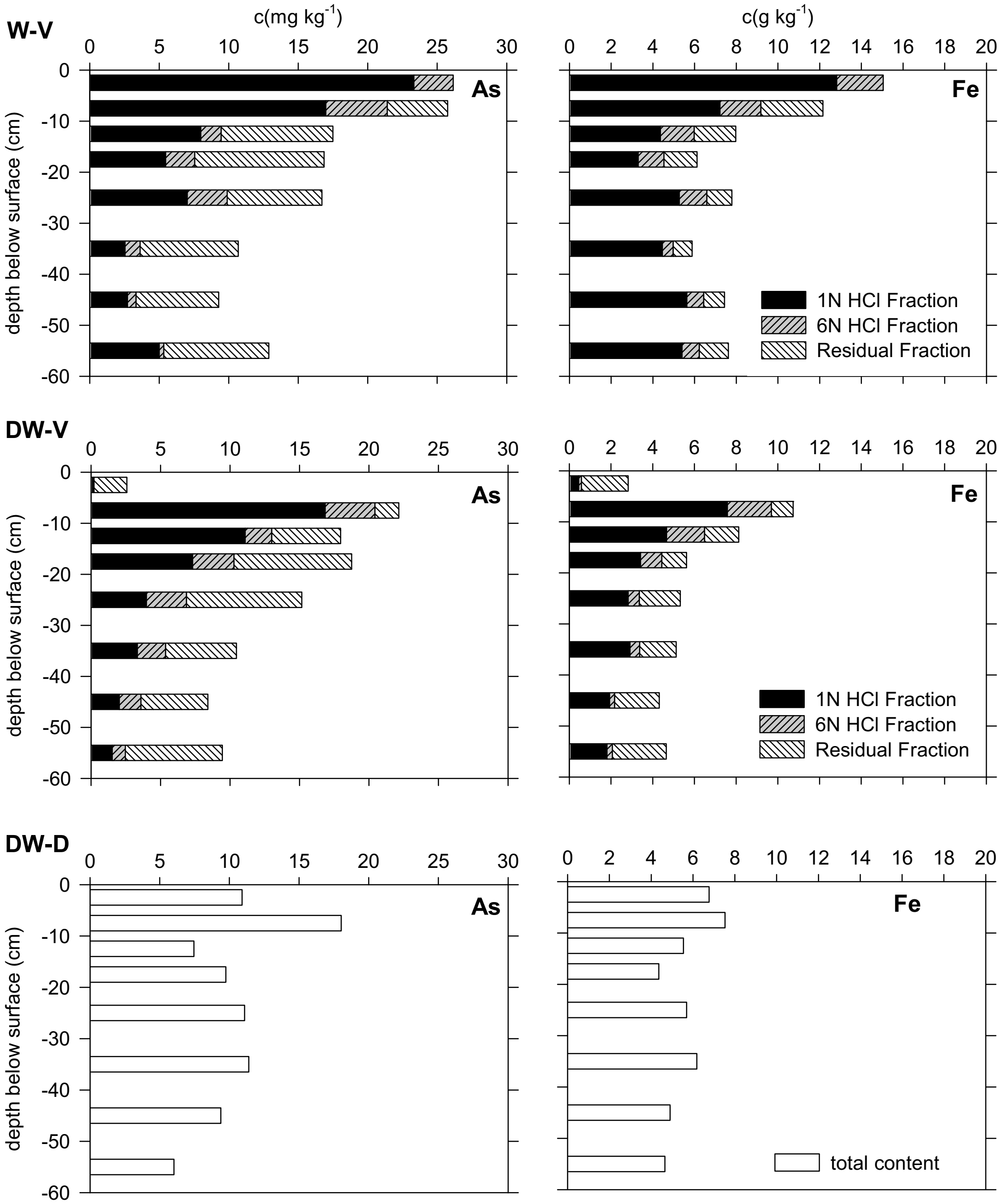

Fig. 1. Depth profiles of arsenic and iron contents in the acid dissolvable fractions and the residual fraction (residual = total content–acid dissolvable fractions) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D).

summer of 2005. Contents were largest at intermediate depths in W-V and DW-V, and near the surface in DW-D.

3.2. Correlation between solid phase contents

Statistical relationships between arsenic and contents of other metals than iron were not fully consistent, but iron and arsenic contents significantly correlated in the 6N HCl extracts in the W-V and DW-V treatment and in the 1N HCl extracts in the DW-V treatment (Table 2). Dissolution of reactive and crystalline ferric iron hydroxides by HCl thus resulted in a similar release of arsenic into solution, confirming the association of arsenic with ferric iron hydroxides in the peat. In the remaining residual fraction, arsenic and Fe were not significantly correlated. Total arsenic also significantly correlated with total iron and the iron in HCl extracts ($R^2 > 0.93$, $\alpha < 0.01$) of the DW-V, but not the W-V treatment. In the DW-D treatment we did not carry out the sequential extraction due to time constraints but total arsenic and iron were also significantly correlated ($R^2 > 0.76$, $\alpha < 0.05$). In the W-V treatment, ferric iron hydroxides were thus likely overall less important as

Table 1
Total contents of iron in the peat of aluminum in the acid extractions (g kg^{-1}) and in total reduced inorganic sulfur (TRIS) (mg kg^{-1})

Depth (cm)	Fe	Control (C)			With vegetation (V)			Without vegetation (NV)	
		Al[a]	TRIS	Fe	Al[a]	TRIS	Fe	Al[b]	TRIS
0–5	15.05	5.36	88.88	2.83	0.36	35.69	6.77	—	121.29
5–10	12.16	7.86	54.09	10.74	9.57	95.17	7.54	—	116.83
10–15	7.98	7.68	49.28	8.13	8.61	59.12	5.54	—	64.51
15–20	6.12	9.25	130.99	5.63	10.94	104.69	4.36	—	71.26
20–30	7.79	9.94	135.09	5.33	9.65	102.83	5.69	—	92.80
30–40	5.88	8.53	71.01	5.13	9.01	84.26	6.18	—	100.60
40–50	7.44	9.61	97.51	4.32	7.12	40.52	4.90	—	68.13
50–60	7.62	9.30	79.55	4.65	8.52	27.88	4.66	—	76.27

[a] Sum of 1 and 6 N HCl extractable aluminum; total contents were not determined.

[b] No extraction data available.

Table 2
Spearman-correlation ($N = 8$) of arsenic with major elements in extracts of treatments C and V

	1 N HCl fraction		6 N HCl fraction		Residual	
	Control	Vegetation	Control	Vegetation	Control	Vegetation
Al	—	—	—	0.762^{*}	‡	‡
Fe	—	0.976^{**}	0.738^{*}	0.833^{*}	—	—
Mn	†	†	†	†	†	†
Ca	—	—	†	†	‡	‡
Mg	0.881^{**}	—	—	—	‡	‡
K	0.881^{**}	—	—	—	‡	‡

* Correlation significant at $\alpha = 0.05$ level (two-sided), ** correlation significant at $\alpha = 0.01$ level (two-sided), ‡ not determined, † could not be calculated as value set to = 0.

binding partners for arsenic than in the DW-V and DW-D treatment. A correlation between TRIS and total arsenic was found in the DW-V and DW-D treatment ($R^2 > 0.7$, $\alpha < 0.05$).

3.3. Water table, volumetric water content, and root activity

Initially, in phase I, and during the period of drought, in phase III, volumetric gas contents (VGCs) increased from about 2% near the water table to 9–12% at a depth of 10 cm in both dried and rewetted treatments (Fig. 2). Deeper into the unsaturated zone, VGCs remained low, particularly in the DW-V treatment. In this treatment, VGCs decreased rapidly to 2–3% following rewetting. In DW-D the complete filling of VGC to <4% was delayed by 30 days. The treatments DW-V and DW-D thus primarily differed with respect to the time needed for filling of VGC and the stronger dessication of DW-D during drought (phase III). The analysis of $^{13}C–CO_2$ in pore water after application of the $^{13}C–CO_2$ tracer to the surface indicated a rapid transfer of the label into the soil by root respiration in the permanently wet treatment W-V and the vegetated treatment DW-V (Fig. 3). After 49 h, $\delta^{13}C$ of CO_2 had risen by 3 ‰ (DW-V) and 10 ‰ (W-V) in the uppermost layer and smaller amounts deeper into the peat. The respiratory activity of the roots was thus highest in the near-surface peat, particularly of the W-V treatment. In the DW-D treatment no change in $\delta^{13}C$ was detected.

3.4. Dissolved concentrations and thermodynamic data

We selected four time points for the visualization of dissolved ferrous iron, and sulfate concentrations and pH in the pore waters of the peat, representing the beginning of the first wet period (day 38), the end of this period (day 101), the end of the dry period (day 143), and the rewetting period (day 206) (Fig. 4). Ferrous iron concentrations rapidly increased after the initial irrigation during the first wet period and peaked at and above the water table at concentrations of up to 5000 μmol L^{-1} (treatment W-V), and 170 and 300 μmol L^{-1} in the other treatments. Ferrous iron concentrations stayed high in treatment W-V, particularly near the water table, throughout the duration of the experiment. In contrast, ferrous iron was effectively eliminated from the pore water in the upper 20 cm of peat in the treatments DW-V and DW-D during the dry period, as can be seen from a comparison between day 101 and day 143 in Fig. 4. This was followed by resumed release after rewetting, resulting in concentrations of 100–200 μmol L^{-1} (Fig. 4). Unsaturated conditions in the deeper peat of treatments DW-V and DW-D apparently resulted in a much slower loss of ferrous iron from the pore water than near the surface. Sulfate concentrations ranged from below LOD to 300 μmol L^{-1}, strongly varied with time as well, and followed an inversed pattern compared to ferrous iron, i.e. decreased during saturated condition and increased in the upper peat layers during experimental drought (Fig. 4). In treatment W-V sulfate was depleted after about 100 days

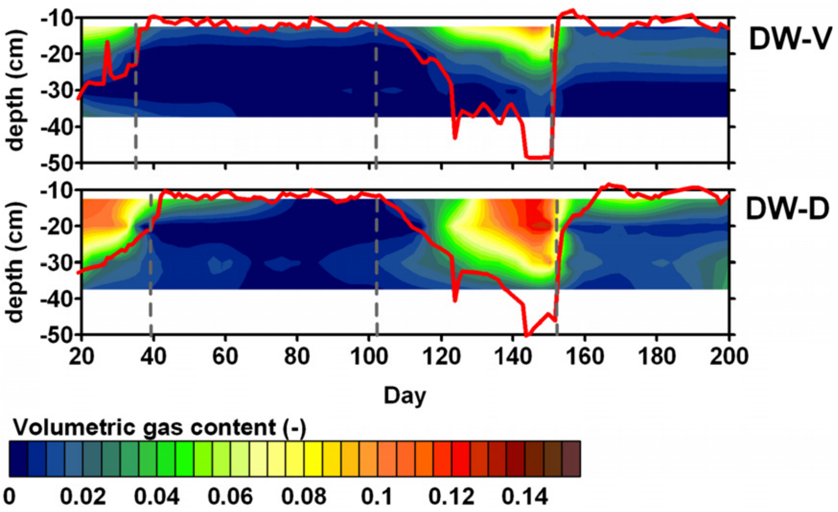

Fig. 2. Volumetric gas content in $m^3\ m^{-3}$ and water table depth (red solid line) in DW-V (top) and DW-D (bottom). Gas content was calculated from total porosity and changes in TDR soil volumetric water content. Note that the time scale in Fig. 1 ends at 200 days. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

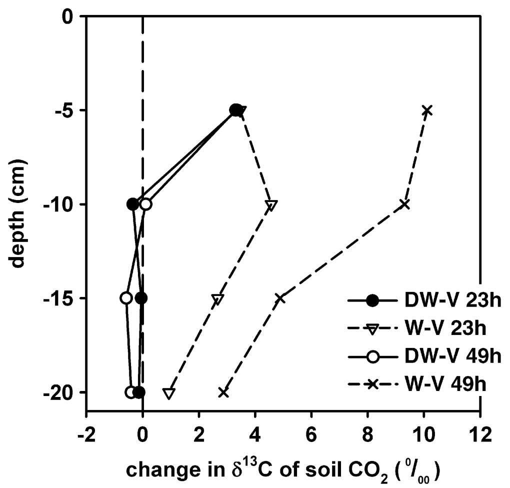

Fig. 3. Root activity as determined from $\delta\ ^{13}C$ of the soil CO_2, 23 and 49 h after the ^{13}C–CO_2 pulse label in treatments W-V and DW-V. A transparent chamber containing a ~900 ppm CO_2 atmosphere with ~63% ^{13}C–CO_2 was placed on top of the mesocosms for 1 h and changes of $\delta^{13}C$ of soil CO_2 were monitored for the following 100 h. Positive $\delta^{13}C$ shifts indicate transfer of the labeled CO_2 into the soil atmosphere by root respiration or heterotrophic respiration of root exudates.

throughout the profile. H_2S concentrations generally ranged from 3 to 12 μmol L^{-1} in all treatments during the first wet period and decreased with sulfate depletion in treatment W-V and drying in treatments DW-V and DW-D to concentrations of LOD to 5 μmol L^{-1}.

Rewetting of the peat was followed by increasing H_2S concentration. Only in the DW-D treatment, however, did H_2S concentrations increase to levels determined before the drought. H_2S remained mostly detectable also in the unsaturated peat (data not shown). Nitrate was detected in all treatments during the first dry and wet periods for about 50 days before concentrations dropped to <5 μmol L^{-1}. Unsaturated conditions resulted in the accumulation of nitrate and ammonium to concentrations >150 and >200 μmol L^{-1}, respectively, in the DW-D and a smaller accumulation of ~40 and ~30 μmol L^{-1}, respectively, in the DW-V treatment. DOC concentrations were highest in the W-V treatment at levels of 50 to >400 mg L^{-1}, and peaked in 5–15 cm and 50 cm depth (data not shown). In the other treatments concentrations were highest in the surface layer as well, but concentrations remained below 100 mg L^{-1}. Drying resulted in lowered DOC concentrations. The pore water pH ranged from 4 to 6 and often co-varied with ferrous iron concentrations (Fig. 4).

Total dissolved arsenic concentrations were strongly affected by the treatments as well (Fig. 5). In treatment W-V, arsenic accumulated to levels of up to 300 μg L^{-1} in the unsaturated zone just above the water table. Also ferrous iron concentrations peaked at this depth. A second maximum of concentrations developed in deeper layers. After about 100 days, concentrations began to decrease in these zones, whereas in intermediate depths concentration did not change. Concentrations also increased in the other treatments during the first wet period, albeit to lower levels of 20 and 70 μg L^{-1}. The development of air-filled pore space during drying resulted in a concentration decrease to LOD within a few days to two weeks, with a larger time lag and smaller response at greater depths (Fig. 5). At depths of 40–50 cm the impact of drying was small, and at depths of 20 to 40 cm arsenic release following rewetting faster and more intensive than in the near surface peat, especially in DW-V. Rewetting resulted in almost immediate release of arsenic, and previous concentration levels were reattained after about 20–40 days, with the exception of the uppermost peat layer.

During the first wet period, the depth distribution of As(III), As(V), and DMA was highly correlated (Fig. 6).

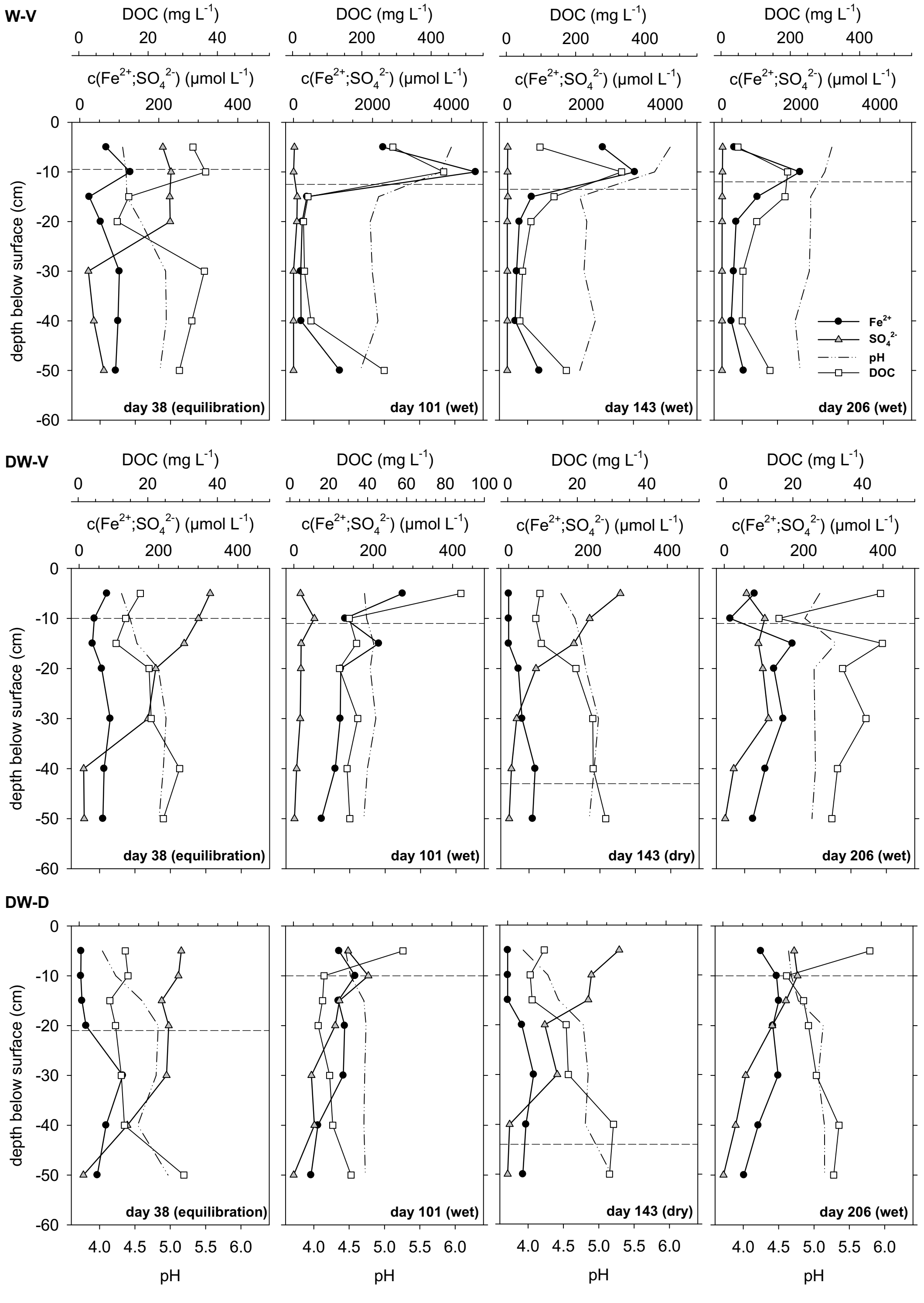

Fig. 4. Concentrations of dissolved ferrous iron, sulfate and dissolved organic carbon (DOC), and pH towards the end of the initial dry equilibration period (day 38), the first wet (day 101), the second dry (day 143) and the middle of the rewetted period (day 206) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Note the change in scale of ferrous iron and the dotted lines which represent the water table. The DOC concentrations during the wet period were determined at day 66 due to missing data.

As(III) dominated (> 85%) and smaller concentrations of As(V) (<10%) and DMA (<5%) were present. MMA was only detected in treatment W-V down to a depth of 20 cm where concentrations ranged from 0.1 to 4 µg L^{-1}. Drying and rewetting had a large impact on arsenic speciation (Fig. 7). The development of air filled pore space during the dry

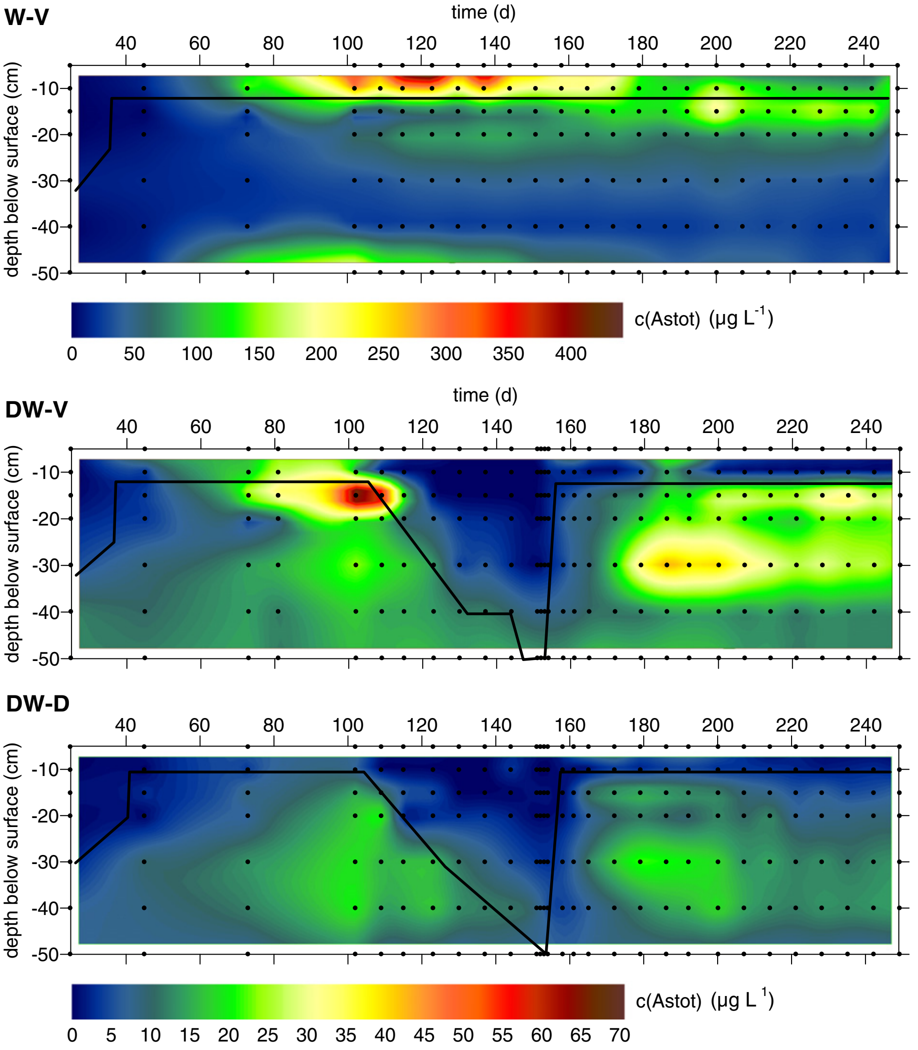

Fig. 5. Temporal dynamics of dissolved arsenic (µg L^{-1}) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Black dots indicate sampling points in time and space. The line represents the average water table. Note the scale differences.

period resulted in a strong decrease of As(III)/As(V) ratios from 4–12 to <0.25 in the uppermost 5–15 cm. Below, impacts were small and in one sample even reversed. After rewetting, As(III) began to dominate and As(V) contributed more to the total dissolved arsenic only near the water table. DMA concentrations ranged from <0.4 to 2.8 µg L^{-1} and reacted similarly as As_{tot} to the development of unsaturated conditions (Fig. 8). DMA was eliminated more effectively deeper into the peat, though, and production did not resume within 30 days after rewetting. Presence of oxygen thus inhibited DMA release strongly and in a sustained way, even after the reestablishment of anaerobic conditions.

The calculated *in situ* E_h values of the half redox couples $Fe(OH)_3/Fe^{2+}$, SO_4^{2-}/HS^-, and As(V)/As(III) varied both with depth and time and ranged from 0 to 270 mV for As(V)/As(III), −150 to 90 mV for SO_4^{2-}/HS^-, and −210 to 290 mV for $Fe(OH)_3/Fe^{2+}$ (Fig. 9). The redox couples were generally in strong thermodynamic disequilibrium. The ΔE_h was always positive for a reaction of HS^- with As(V), confirming that HS^- could be utilized to reduce As(V) under release of free energy. This was not always the case for potential reactions between iron and arsenic, whose E_h strongly overlapped. Averaged over the whole period, conditions in the W-V treatment were on average more reducing than in the other treatments, particularly in the uppermost peat layers where lowest E_h values were recorded for all redox couples.

3.5. Turnover rates of arsenic and ferrous iron

Arsenic was mobilized in treatment W-V for about 100 days (Fig. 10) at rates of up to 0.01 mmol m^{-3} d^{-1} and later on mostly immobilized at rates of 0 to 0.15 mmol m^{-3} d^{-1}. During the initial dry and wet period, the same pattern also occurred in the DW-V and DW-D treatment at lower rates, but arsenic was not yet immobilized. Drying resulted in immediate net arsenic loss from solution, when integrated over depth, in DW-V and DW-D mesocosms

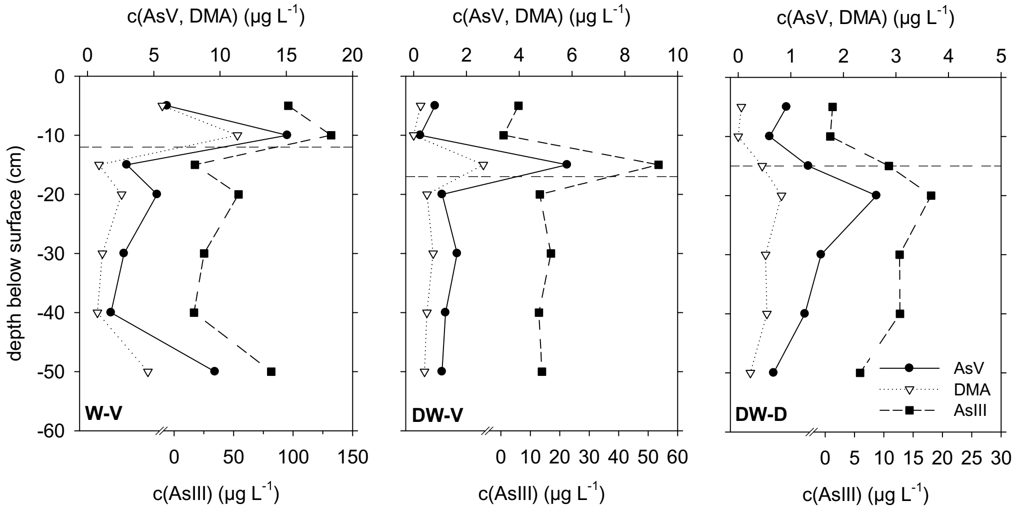

Fig. 6. Speciation of dissolved arsenic at the beginning of the drying period (day 109) in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). The interrupted line indicates the position of the water table.

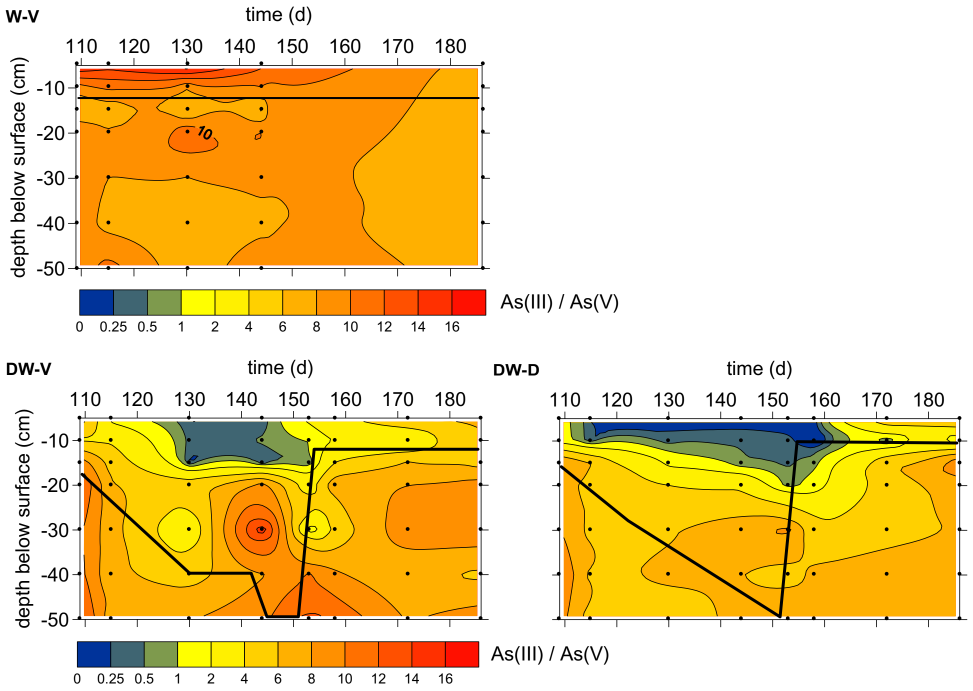

Fig. 7. As(III)/As(V) quotient in vegetation treatment DW-V and defoliated treatent DW-D during drying and rewetting periods. Black dots indicate sampling points in time and space. The line represents the position of the water table.

at rates of up to −0.01 mmol m^{-3} d^{-1} (DW-V) and −0.004 mmol m^{-3} d^{-1} (DW-D). Rewetting resulted in a short-term pulse of dissolved arsenic release of 0.05 mmol m^{-3} d^{-1} (DW-V) and 0.02 mmol m^{-3} d^{-1} (DW-D) before arsenic was lost from the pore water at low rates about 40 days after rewetting. The temporal dynamics of dissolved arsenic release and loss was coupled to ferrous iron dynamics, although at times a decoupling occurred (Fig. 10). This was for example the case during the first wet period in W-V and at the beginning of the dry period in DW-V and DW-D, when ferrous iron loss from the pore water preceded the loss of arsenic. Rates of ferrous iron loss and release ranged from −20 to 18 mmol m^{-3} d^{-1} and were thus about 3 orders of magnitude larger than net turnover rates of arsenic. Ferrous iron and arsenic release were lower in the DW-D treatment by 24% (Fe) and 55% (As) compared to the DW-V treatment and integrated over the wet periods. These differences were mainly caused by the strong release of arsenic and ferrous iron in the intensely rooted near-surface peat of the DW-V treatment.

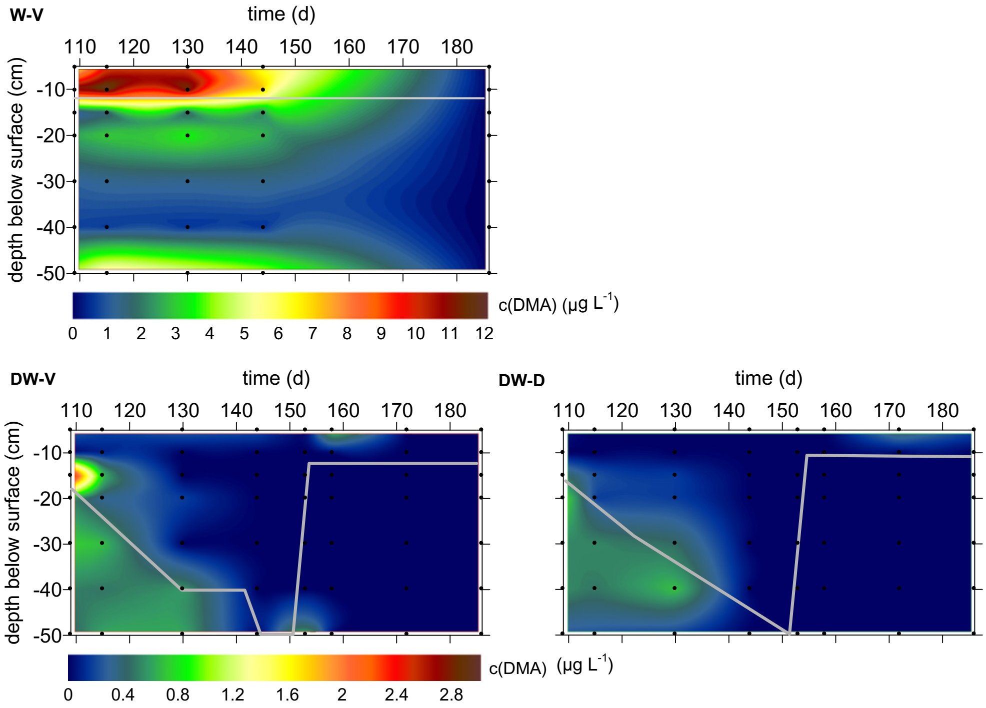

Fig. 8. Temporal dynamics of DMA concentrations (µg L^{-1}) in in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Black dots indicate sampling points in time and space. The line represents the position of the water table. Note the scale differences.

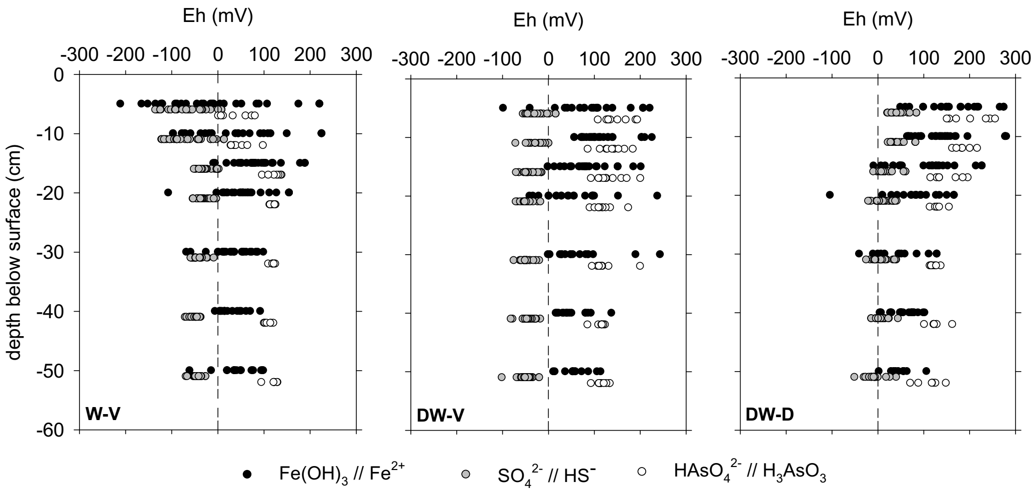

Fig. 9. Variation of redox potentials E_h for iron, sulfur and arsenic redox couples, recalculated for *in situ* geochemical conditions in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). Data for redox couples are slightly displaced for better legibility.

4. DISCUSSION

4.1. Distribution, binding, and speciation of Arsenic

Arsenic can be sequestered in soils under different redox regimes. Arsenic is generally removed from pore water by adsorption to iron, manganese, and aluminum hydroxides (Pierce and Moore, 1980; Bowell, 1994; Dixit and Hering, 2003) and clay minerals (Manning and Goldberg, 1997) under oxic conditions. Under anoxia, association with the solid phase may primarily occur by binding to sulfides or the formation of arsenic containing sulfide minerals (Rochette et al., 2000; Meng et al., 2003; O'Day et al., 2004). A binding to organic matter may also occur. Binding of arsenic to dissolved organic matter (DOM), in particular humic substances, has been documented. The binding of arsenate

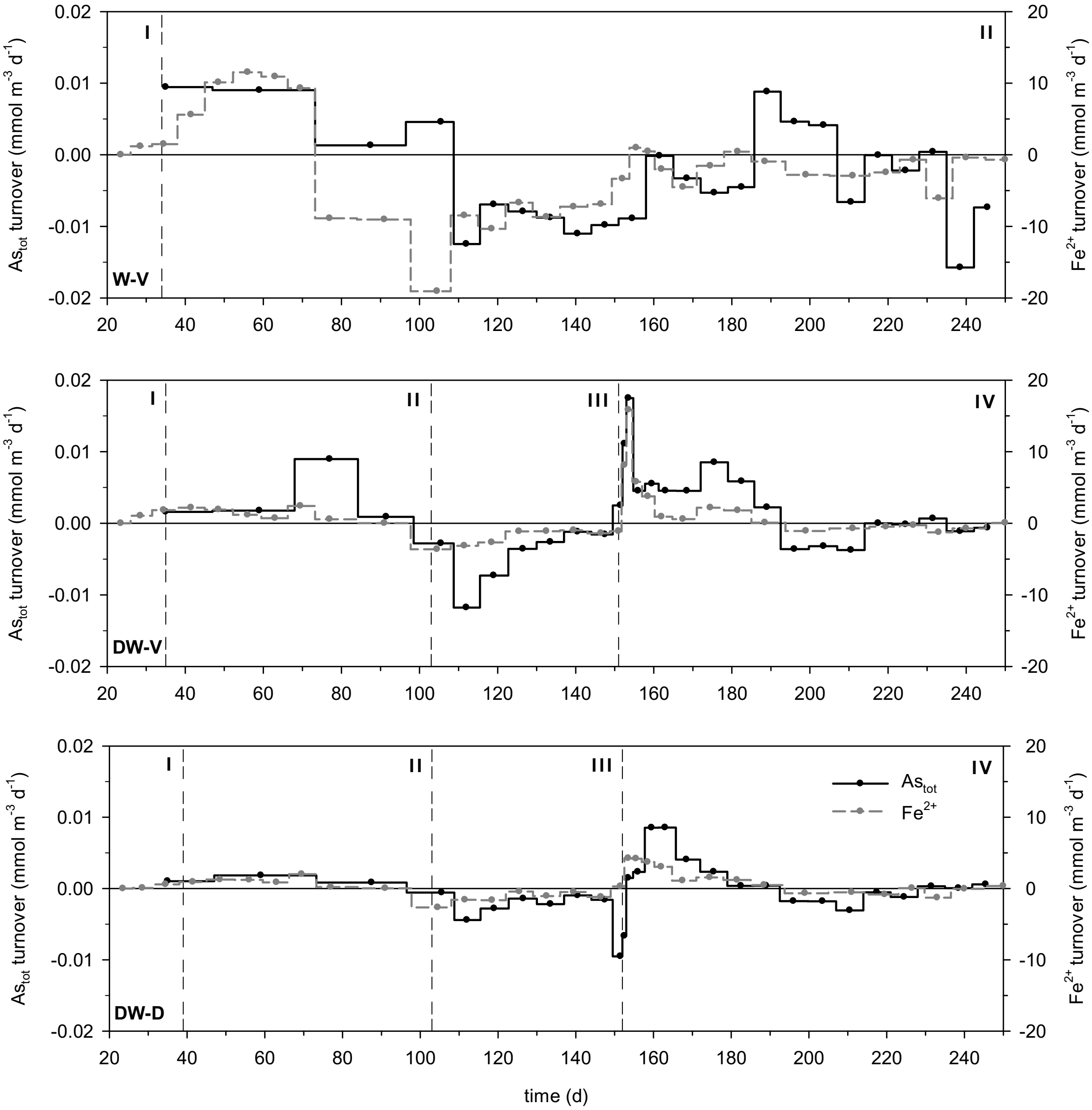

Fig. 10. Depth integrated turnover of arsenic and ferrous iron during the experiments in the permanently wet treatment (W-V), the dried and wetted vegetation treatment (DW-V) and the dried and wetted defoliated treatment (DW-D). In treatment W-V depth integration was only carried out for depth at and below the water table. Values >0 indicate release into the pore water.

and arsenite to negatively charged DOM has been linked to complexation and metal bridges (Redman et al., 2002; Lin et al., 2004) and binding by covalent mechanism and moieties such as phenolic, carboxylic, sulfhydryl and amino groups may also occur (Thanabalasingam and Pickering, 1986; Buschmann et al., 2006).

In the peats investigated, arsenic was obviously mostly bound to the solid phase over the full range of redox conditions that occur with depth and seasonally. The binding mechanisms were apparently altered depending on average redox conditions. Arsenic contents contained in the solid phase decreased with depth but varied only moderately between 5 and 25 mg kg^{-1} and were within the range of arsenic contents found in the soils of the Lehstenbach watershed, albeit higher than previously documented for an adjacent peatland by Huang and Matzner, 2006). In the unsaturated uppermost peat, arsenic was primarily found in acid extracts, which dissolve metal hydroxides, acid volatile sulfides, and carbonates (Wallmann et al., 1993). The correlation analysis further suggested that among the hydroxides, iron hydroxides were most important as binding sites (Table 2). Sorption moreover primarily occurred on the reactive hydroxide fraction, which was also most abundant in the peat and typically provides a larger sorption capacity than the crystalline fraction due to its hydrated structure and larger surface area (Pierce and Moore, 1982; Dixit and Hering, 2003). The residual fraction, which may contain organically bound and stable sulfidic arsenic, gained only in relative importance in the deeper, mostly anoxic, and strongly reduced peat.

The exact nature of the binding mechanism in the residual fraction cannot be clarified by the acquired data. We assume that both sorption by iron hydroxides and association with organic matter and sulfides occurred. Rochette et al., 2000) showed experimentally that at low pH and with S/As ratios <20, arsenous sulfide precipitates can form under anoxia. Such conditions were present in the peats. Total reduced inorganic sulfur, primarily in form of iron sulfides had formed prior to the experiments in substantial quantities throughout, albeit at contents that were about two orders of magnitude lower than total ferric iron contents (Table 1). Some insight regarding the significance of arsenic association with iron sulfides can further be gained from the concentration dynamics of arsenic, ferrous iron, and sulfate during the experiments. Although sulfate was actively reduced and iron sulfides formed during the wet periods, at least initially less arsenic associated with the solid phase than was released coupled to iron reduction, and dissolved arsenic concentrations in the pore water consequently increased. Similar findings were reported by Huang and Matzner (2006) under field conditions in an adjacent peatland. Paul et al. (2006)) further showed that the formation of iron sulfides at the site occurs only on a temporary basis due to reoxidation during dry periods. A release of arsenic bound to sulfides during reoxidation and subsequent association with iron hydroxides thus likely occurs on a seasonal basis. Binding to organic matter was not explicitly investigated in this study. A substantial binding to organic matter seems likely in view of the large residual arsenic fraction and previous work on binding of arsenic to organic moieties (Thanabalasingam and Pickering, 1986; Buschmann et al., 2006).

Arsenic concentrations in the solid phase were far lower than in naturally more enriched minerotrophic peatlands (Gonzalez et al., 2006), and relatively evenly distributed within the peats and between the three mesocosms. In spite of this fact, dissolved arsenic concentrations reached locally very high values of 300 $\mu g\ L^{-1}$, and always exceeded common drinking water standards of 10 $\mu g L^{-1}$ when the peat was saturated. Arsenic concentrations exceeded previously reported values from a field investigation conducted by Huang and Matzner (2006) by an order of magnitude. These results confirm that moderately arsenic bearing organic soil have a large potential to remobilize bound arsenic under reducing conditions. As(III) was the predominant species in soil solution, with the exception of highly unsaturated, near-surface peat during the dry period (Fig. 7). In the DW-V and DW-D treatment, As(III) further gained in importance with depth (Fig. 7), which is in agreement with more reducing conditions as indicated by the E_h values of the SO_4^{2-}/HS^- and the $Fe(OH)_3/Fe^{2+}$ redox couples. The difference in E_h values SO_4^{2-}/HS^- and As(V)/As(III) further implied a considerable free energy available for electron transfer from HS^- to As(V) that could potentially also be utilized by microorganisms mediating this process (Oremland and Stolz, 2003), thus contributing to the predominance of dissolved As(III) deeper into the peat.

The occurrence of hot spots of arsenic release near the water table in the W-V and DW-V treatments was likely related to the activity of roots. The application of the ^{13}C–CO_2 tracer showed that the arsenic hot spots were located in layers of highest root density and respiratory activity, particularly in the W-V treatment (Fig. 3). The comparison between the DW-V and DW-D treatment moreover indicated lower rates of arsenic and Fe release in absence of vegetation and smaller As(III)/As(V) ratios, which may—giving the pH of <5—enhance re-adsorption of released arsenic (Dixit and Hering, 2003). Furthermore, the presence of vegetation slowed the elimination of arsenic from the porewater and As(III)/As(V) quotients decreased in the drained peat during drought (Fig. 7). A statistical confirmation of these findings is not possible due to the lack of replication of the treatments but the results qualitatively indicate that the activity of vascular plants can contribute to the release of dissolved arsenic in wetlands during wet periods and to slow association with the solid phase during dry periods. The likely reason for this phenomenon is the exudation of easily decomposable substrates by roots, which lowers the oxygen concentrations in poorly aerated peat and enhances rates of bacterial iron reduction.

Previously, a sequestration of arsenic in the rhizosphere of plants has also been reported due to the formation or iron hydroxide coatings along roots and subsequent arsenic sequestration (Otte et al., 1995; Doyle and Otte, 1997). In the W-V treatment, the grass *C. rostrata* dominated, which is capable of aerenchymatic oyxgen transport into the rhizosphere. A visual examination also revealed iron coatings in the peats of the W-V treatment, which may also explain the high iron enrichment in this treatment. The comparison of total arsenic contents between mesocosms accordingly illustrates that the presence of *C. rostrata* in the W-V treatment coincided with increased arsenic accumulation in the uppermost peat (Fig. 1). Integrated over depth and in the short-term the net effect of root activity was an enhanced release of dissolved arsenic following rewetting, however. This effect was particularly pronounced in the uppermost horizon of the W-V treatment, which was characterized by the highest root activity (Fig. 3) and the largest content in reactive iron and arsenic associated with reactive iron (Fig. 1). Given the large differences in dissolved arsenic concentration between this and the other treatments, a combination of these factors obviously is of great importance regarding arsenic release.

The previous observation by Huang and Matzner (2006) that dissolved arsenic primarily occurs in organic form in adjacent peatland Schlöppnerbrunnen I, mainly as MMA, could not be substantiated in this study. The methylation of arsenic is believed to be microbially mediated and to proceed under anaerobic conditions (Bentley and Chasteen, 2002; Bolan et al., 2006). The contrasting findings may be related to more persistent anaerobic conditions in the soils of Schlöppnerbrunnen I compared to Schlöppnerbrunnen II (Paul et al., 2006). Continuous anoxia may facilitate methylation of arsenic by methanogenic and sulfidogenic populations (Bolan et al., 2006). An inhibition of MMA and DMA formation by temporarily oxic conditions would also be in agreement with the lack of DMA formation in the DW-V and DW-D treatment after rewetting (Fig. 8). Regardless of the exact causes for the smaller importance of methylation in the investigated Schlöppnerbrunnen II peat, the process was of little relevance and may hence not be an important mechanism for the release of arsenic into the soil water in all peatlands, if the results of this mesocosms study can be extrapolated to the field. In this respect it has to be considered that the temperature in the mesocosms reflected mid-summer conditions instead of yearly averages and that vertical and lateral flow in the mesosocosms were eliminated. Both factors may have altered relative concentration levels of individual arsenic species and lead to a build up of total dissolved arsenic in the soil.

4.2. Impact of drying and rewetting on arsenic speciation and phase transfer

The temporal and spatial patterns of dissolved arsenic concentrations and the associated turnover was connected to ferric iron release during the wet periods and removal of ferrous iron from the pore water during drought (Fig. 10). This finding supports the hypothesis that dissolved arsenic release is mainly driven by bacterial iron reduction in iron rich peat soils, in analogy to less organic-rich anoxic aquifers. Likewise, oxic conditions resulted in co-precipitation of arsenic with ferric iron hydroxides. This pattern is plausible giving the intense association of arsenic with reactive ferric iron hydroxides, which are generally also more readily used than crystalline iron hydroxides by ferric iron reducing bacteria under neutral and weakly acidic conditions (Lovley and Phillips, 1988). A similar coupling of arsenic and iron dynamics has already been demonstrated or inferred from several field studies and laboratory experiments, but not been verified for natural peatlands with natural arsenic background (Masscheleyn et al., 1991; La Force et al., 2000; Fox and Doner, 2003). The dissolved arsenic dynamics furthermore suggests that adsorption on sulfides or precipitation of arsenic with sulfides was of little importance for the total arsenic turnover. A similar finding was recently reported based on analyses of solid phase materials in a near-neutral, iron-rich and mine drainage impacted wetland (Beauchemin and Kwong, 2006).

During the dry period, gas filled porosity in the peat increased from <2% to 2–13%. Oxygen penetrated deeper into the peat resulting in release of sulfate, likely by reoxidation of reduced inorganic and organic sulfur, and elimination of ferrous iron by oxidation and subsequent precipitation as reactive iron hydroxide phase (Reynolds et al., 1999). Arsenic was not only co-precipitated in its reduced form with the forming iron hydroxide precipitates, as can be expected due to its affinity for iron hydroxides (Dixit and Hering, 2003), but apparently also effectively and rapidly reoxidized: As(III)/As(V) ratios dropped below 1 within days in the uppermost peat layers of the DW-D treatment and more slowly in the DW-V treatment. The transformation of As(III) to As(V) and the decreasing pH (Fig. 4) contributed to the subsequent association of dissolved arsenic with solid phase soil material, since sorption of As(V) to ferric iron hydroxides increases with acidification (Dixit and Hering, 2003). Arsenite oxidation was probably in some way mediated by microorganisms because the chemical oxidation of As(III) by oxygen is slow, with a reported half-life of 4–9 days in natural waters (Kim and Nriagu, 2000). Arsenate oxidation as a detoxification mechanism and dissimilatory microbial respiration coupled to oxygen and nitrate reduction are both known to occur (Oremland and Stolz, 2003) and are in agreement with elevated concentrations of nitrate and oxygen during this period. The rapid oxidation of arsenic in the DW-D treatment, which contained less As(III) relative to As(V) even before the dry period, was likely caused by a lower respiratory oxygen demand and thus higher oxygen availability in the peat (Knorr et al., 2008).

Initial wetting and rewetting resulted in iron reduction in all treatments, either by iron reducing bacteria or by reaction of H_2S with ferric iron hydroxides, and entailed the release of arsenic associated with the solid phase, as previously described by McGeehan and Naylor (1994) and Reynolds et al. (1999). Changes in concentration were particularly strong in the uppermost, reactive iron and arsenic-rich, and intensively rooted horizon of the W-V treatment, which was at or above the water table. Smaller changes in soil moisture in this horizon, as they occurred on a regular basis due to the irrigation regime (Electronic annex, Fig. 1S) apparently also lead to local release and removal of arsenic from the pore water (Fig. 5, treatment W-V, e.g. day 180–200), which strongly influenced the depth integrated arsenic turnover in the mesocosm (Fig. 10, treatment W-V, e.g. day 180–200). We did not analyze the speciation of arsenic in the solid phase and the nature of As(V) reduction in the peats and a discussion about the mechanism of the phase transfer of arsenic following rewetting can only be speculative. It is possible that in the near surface peat arsenic was primarily remobilized as arsenate from exchange sites and subsequently slowly reduced in the pore water as described for example by Cummings et al. (1999); an *in situ* reduction of sorbed arsenate has previously also been inferred based on sediment depth profiles and XANES and EXAFS spectroscopic characterization of arsenic adsorbed to iron hydroxides (Kneebone et al., 2002; Beauchemin and Kwong, 2006). Arsenate may have been reduced in solution by dissimilatory respiration, as described for example by Campbell et al., 2006), although concentrations were low compared to environments where this process has been documented to be important, such as at contaminated sites and hypersaline lakes. A microbial detoxification process leading to excretion of As(III) from heterotrophic bacteria (Oremland and Stolz, 2003) may have occurred as well. A chemical reduction of As(V) by hydrogen sulfide, which is rapid under acidic conditions (Rochette et al., 2000) and was thermodynamically possible (Fig. 9), cannot be ruled out either.

The rapid release of dissolved arsenic coupled to iron reduction was possibly assisted by the production and accumulation of DOM. Concentrations of up to 400 mg L^{-1} DOC were attained in treatment W-V (Fig. 4) where the maximum of dissolved arsenic concentrations occurred. With the exception of these hot spots, concentrations were in the range of 10–100 mg L^{-1} DOC that is typical for peat soils and organic-rich soil horizons (Blodau, 2002; Michalzik and Matzner, 1999). Negatively charged DOM is a competitor for exchange sites on iron hydroxides, and concentrations of 10–50 mg L^{-1} have been demonstrated to mobilize arsenic in batch experiments with synthetic iron hydroxides and materials from soils and sediments (Bauer and Blodau, 2006). An effective re-adsorption of desorbed arsenic to newly available iron hydroxide surfaces may have been impeded to some extent. Re-adsorption of As(V) following chemical iron reduction of ferrihydrite by ascorbic acid has been previously described (Pedersen et al., 2006). Both re-adsorption and competition of arsenic with DOM for adsorption sites potentially contributed to the observed temporal decoupling of iron and arsenic turnover in the peat.

5. CONCLUSIONS

The study demonstrates the strong impact of drying and rewetting events on arsenic concentrations in wetland soils and the potential of uncontaminated and moderately arsenic bearing peat to mobilize arsenic in form of arsenite after rewetting. Methylated arsenic species were, in contrast, of subordinate importance for arsenic release, and their formation was inhibited by temporary intrusion of oxygen even after rewetting and development of anoxia. The dynamics of arsenic and iron were essentially coupled. Arsenic and iron were immobilized following oxidation during dry periods and rapidly mobilized by iron reduction and the associated release of arsenic after rewetting, leading to arsenic concentrations of up to 300 $\mu g\ L^{-1}$ and release of up to 0.02 $mmol\ m^{-3}\ d^{-1}$. A combination of factors apparently contributed to this dynamics. In the near-surface peat, arsenic was primarily adsorbed on ferric iron hydroxides, which were also most rapidly reduced in the uppermost intensely rooted and iron-rich soil horizons, where electron donors were abundant. Microbial activity also lead to very high DOC concentrations, which may have promoted arsenic release by impeding a re-adsorption. Aerenchymatic transport of oxygen by *C. rostrata* roots was apparently of little significance for the arsenic dynamics in the short-term, as were interactions between arsenic, organic matter, and iron sulfides. On the time scale of years to millennia, minerotrophic wetlands such as the Schlöppnerbrunnen II site seem to serve as effective sinks for arsenic due to the abundance of reactive iron hydroxides in the peat. Temporarily, however, arsenic can be mobilized at high concentration levels when water saturated and anoxic conditions are established in the uppermost biologically active peat layer.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2008.04.040.

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