Arsenic release and speciation in a degraded fen as affected by soil redox potential at varied moisture regime

H. Weigand [a,*], T. Mansfeldt [b], R. Bäumler [c], D. Schneckenburger [d,1], S. Wessel-Bothe [e], C. Marb [f]

[a] University of Applied Sciences Giessen-Friedberg, Department KMUB, 35390 Giessen, Germany
[b] Department of Geography, University of Cologne, 50923 Cologne, Germany
[c] Department of Geography, Friedrich-Alexander-University Erlangen-Nürnberg, 91054 Erlangen, Germany
[d] Institute for Geography, University of Augsburg, 86159 Augsburg, Germany
[e] ecoTech Umweltmeßsysteme GmbH, 53129 Bonn, Germany
[f] Bavarian Environment Agency, Josef-Vogl-Technology-Centre, 86167 Augsburg, Germany

ABSTRACT

Soil surveys have demonstrated arsenic (As) contents of up to 1600 mg kg^{-1} in surface horizons of degraded fens in the Bavarian Molasse basin, Germany. Ground water from the Tertiary aquifer seems to be the primary source of As. Yet, the cause of its accumulation in the topsoil is unclear. Focussing the influence of redox processes on As redistribution, we conducted soil column experiments with the A (716 mg As kg^{-1}), Ag (293 mg As kg^{-1}) and 2Ag (37 mg As kg^{-1}) horizons of a Mollic Gleysol (pH 7.2). The fixed beds were equipped with redox electrodes and suction cups and subjected to a saturation–drainage–saturation cycle. Water table fluctuations were simulated by defined pressure heads applied to the lower column boundaries via a digitally controlled vacuum system. After water saturation, the redox potential (E$_H$) dropped to minimum values of around 0 mV in the A/Ag and −400 mV in the 2Ag horizon. Soil drainage resulted in a quick return to oxidising conditions. Both in the A and Ag horizons total aqueous As concentrations were low (up to 20 µg l^{-1}) and not related to E$_H$. In contrast, aqueous As concentrations of the 2Ag horizon were between 5 and 140 µg l^{-1} and increased as the E$_H$ decreased. However, the As species distribution showed no clear trend with E$_H$ since both As(III) and As(V) were detected under reducing conditions. High release of As in the 2Ag horizon is consistent with low contents in Fe (hydr)oxides. In the A and Ag horizons, pedogenetic enrichment of sesquioxides contributes to a comparably lower sensitivity of E$_H$ to water saturation and favours As retention. Thereby, As released under saturated conditions in the 2Ag horizon may be stabilised in the topsoil following capillary rise. Thus, surface horizons may act both as historic and as recent sinks for geogenic As at the site.

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1. Introduction

In contrast to anthropogenic arsenic (As) contaminations caused by, e.g., mining activities, timber preservation, or the production of arsenical pigments (Matera and Le Hécho, 2001; Gemeinhardt et al., 2006), elevated geogenic background levels in soils may have large-scale impacts on ground water quality. The mobility, bioavailability, and toxicity of As in soil–water systems depend on its oxidation state (Ng et al., 1998; Nickson et al., 2000; ATSDR, 2007), and may thus be influenced by soil moisture conditions (Masscheleyn et al., 1991). Anoxia caused by prolonged waterlogging may shift soil redox potentials (E$_H$) towards the stability domain of the more toxic and more mobile trivalent inorganic species (Haswell et al., 1985;

McGeehan and Naylor, 1994), or promote the formation of less toxic methylated As (Huang and Matzner, 2006) as well as thioarsenic species (Beak et al., 2008). Toxicity of the latter has been reported to depend on the number of thio(SH) groups. While mono- and dithioarsenate proved much less toxic the toxicity of trithioarsenate is comparable to arsenate and arsenite (Planer-Friedrich et al., 2008).

Aqueous concentrations of As are controlled mainly by sorption and/or mineral dissolution and precipitation. In soils, As is sorbed primarily to clay minerals and sesquioxides (Jain and Loeppert, 2000; Grafe et al., 2001; Goldberg, 2002; Kinniburgh and Cooper, 2004). De Brouwere et al. (2004) reported that the content of short-range-ordered pedogenic Fe (hydr)oxides, i.e., ferrihydrite, explains up to 63% of As(V) partitioning between the solid and aqueous phase of spiked soil suspensions. Minerals controlling the solubility of As include Mn arsenates (Tournassat et al., 2002), Ca arsenates (Bothe and Brown, 1999) and sulphides (Signes-Pastor et al., 2007).

Regarding As dissolution O'Day et al. (2004) have suggested a distinction between Fe-controlled and S-controlled systems. Highest As solution concentrations are likely to occur under redox conditions

* Corresponding author. University of Applied Sciences Gießen-Friedberg, Department KMUB, Environmental Engineering, Wiesenstr. 14, 35390 Gießen, Germany. Tel.: +49 641 3092525; fax: +49 641 3092914.
E-mail address: harald.weigand@tg.fh-giessen.de (H. Weigand).
[1] Present address: Ottostr. 10, 86391 Stadtbergen, Germany.

when Fe (hydr)oxides are not stable and As sulphide phases have not yet precipitated. Reductive dissolution of Fe (hydr)oxides has been recognised as an important mobilisation pathway for sorbed As (Postma et al., 2007) and is supposed to be the cause of large-scale groundwater contaminations in the West Bengal basin (Nickson et al., 2000). Data by Polizzotto et al. (2005) indicated that Fe (hydr)oxides are not dissolved at well depth but close to the surface. This may be due to seasonal water table fluctuations inducing oxic–anoxic cycles during which As is released and subsequently introduced into the aquifer with ground water recharge.

Rüde and Königskötter (2009) and a soil survey carried out by the Bavarian Environment Agency suggested that a similar process, yet operating in the opposite direction, may be responsible for pedogenic accumulation of As in degraded fens of the Erdinger Moos, Upper Bavaria, Germany. The Tertiary aquifers, connected with the overlying Quaternary aquifer through hydraulic windows, have been identified as the primary As source. However, the causes of As accumulation within the unsaturated zone are unclear, as up to 1600 mg As kg^{-1} were detected in topsoil horizons.

The scope of this investigation was to gain insight into the processes involved in As redistribution within the soil profile. As a possible route of As enrichment in the surface horizons of the Erdinger Moos, we focussed on soil redox processes triggered by water table fluctuations. If redox processes were responsible for As enrichment, the transfer of dissolved As by capillary rise should greatly depend on the timescales in which the E_H of the individual horizons responds to moisture regime variations as well as the resulting changes of As concentration and species distribution. These aspects were studied in soil column experiments performed at room temperature with three horizons of a Mollic Gleysol sampled at the site. Water table fluctuations were simulated by defined pressure heads applied to the lower column boundaries. The As(III) and As(V) species were determined in suction cup samples and soil E_H was continuously monitored within the columns.

2. Materials and methods

2.1. Site and soil description

The sample site is about 35 km northeast of Munich in the Erdinger Moos and belongs to the Isar River discharge system (Fig. 1). Mean annual temperature and precipitation are 7.7 °C and 814 mm. The area represents the northern extension of the Munich Plain formed by alluvial fans during withdrawal of the glaciers of the Upper Pleistocene (Weichselian). The aquifer is built up of coarse carbonaceous sediment over fluviatile silt (Flinz) deposited in the Molasse Basin during the Upper Miocene. In the Holocene, accumulation of organic matter was favoured by high ground water levels and fens were formed as the natural soil cover of the region (Jerz, 1996). Arsenic enrichment up to 1600 mg As kg^{-1} in topsoil horizons is hypothesised to be the result of mixing of ground water from Quaternary and Tertiary aquifers (Rüde and Königskötter, 2009). To our knowledge no indications exist for further inputs of As. Arsenic
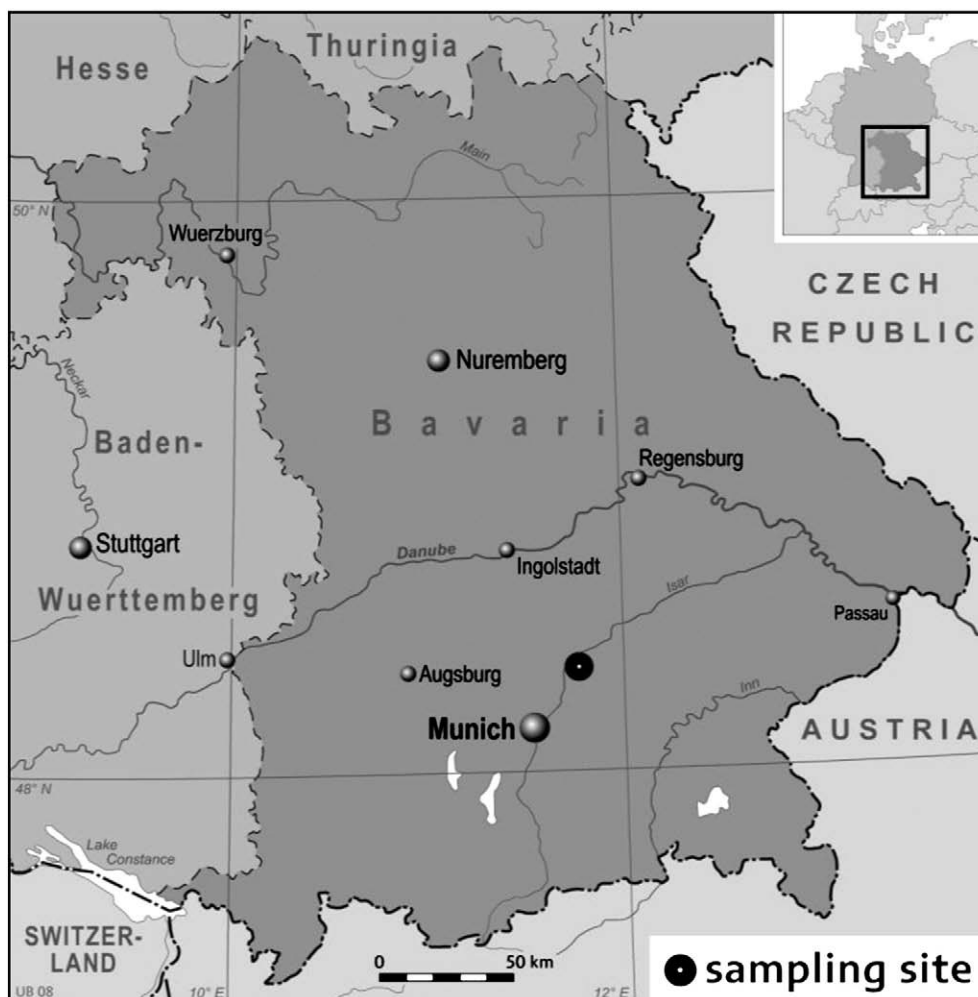

Fig. 1. Location of the sampling site in Bavaria, Germany.

maxima in the soil coincide with patchy enrichment zones of pedogenic Fe (hydr)oxides (Weigand et al., 2007).

Soil material was sampled from a Mollic Gleysol. The mollic A horizon forms the upper 15 cm. Slight mottling of the soil was observed between 15 cm and 29 cm (Ag horizon). The 2Ag horizon between 29 cm and 43 cm overlays the gleyic 3Cr1 and 3Cr2 horizons. Since the study focussed on the temporarily waterlogged parts of the profile, the C horizons were not sampled. In view of possible alterations of the soil material including microbial activity, Fe chemistry and As speciation the collection of undisturbed soil cores would be favourable. Due to low horizon thickness and heterogeneity of As levels, however, we opted for disturbed samples.

To minimise sample heterogeneity, about 10 kg of the soil material were air-dried and passed through a 2 mm sieve. Aliquots for the column experiments and for basic soil characterisation were obtained by coning and quartering (Crosby and Patel, 1995). For analysis of total element contents, subsamples of the fraction < 2 mm were ground in an agate ball mill.

2.2. Experimental

Three parallel column experiments (duration 53 d) each involving a saturation–drainage–saturation cycle were performed with the homogenised fraction <2 mm of the A, Ag and 2Ag horizons. The column set-up is shown in Fig. 2. The soil material was poured into cylindrical polymethylmetacrylate tubes (length 30 cm) and compacted layer-wise with a plunger. Bulk densities (determined from dry mass and packed bed volume) were 0.52 g cm^{-3}, 0.33 g cm^{-3}, and 1.10 g cm^{-3} for the A, Ag, and 2Ag column, respectively. As a base for the packed beds, a porous plate (MlP2-100, ecoTech GmbH, Bonn, Germany) with a polyamide membrane (porosity 80% v/v) was used. It combines a saturated hydraulic conductivity of 2×10^{-2} m s^{-1} with a bubble point of 200 kPa.

Experiments were conducted with a computer-controlled soil column system (IPM-ISC 01, EMC GmbH, Erfurt, Germany). Given the dimensions of the soil columns (packed bed length 25 cm, diameter 9.5 cm) and homogenisation of the material we opted against replicates in favour of longer experiment duration. The sequence of experimental steps and the corresponding lower boundary conditions are given in Table 1. For saturation, the columns were upstream fed with degassed tap water until the water level was 3 cm above the soil surface. The tap water stems from a carbonaceous Quaternary aquifer and was chosen as a surrogate for the ground water at the site. Unsaturated conditions were established by equilibrating the columns at defined pressure head values based on long-term ground water table data at the site (Bavarian Environment Agency, 2010). The second saturation period was simulated by repeating the saturation procedure. Before disassembling the packed beds, soil water was freely drained from the columns, i.e., without vacuum application. Influent and effluent solutions of the saturation and drainage steps were delivered by a peristaltic pump at a flow rate of 1 cm^3 min^{-1}.

The packed beds were equipped with nylon suction cups (MacroRhizon SMS, Eijkelkamp, Giesbeek, The Netherlands) with a pore diameter of 0.15 μm and an active sampling area of 9.5 cm^2, approximately. To monitor E_H, two platinum electrodes according to Mansfeldt (2003) and an Ag/AgCl reference electrode were installed (both manufactured by ecoTech GmbH, Bonn, Germany). Redox potential was recorded every 2 min and related to the standard hydrogen electrode by adding +207 mV. Given the neutral soil reaction E_H values were not pH-corrected. All instruments were inserted horizontally at the following positions above the porous plate: 6 cm and 22 cm (suction cups), and 6.5 cm and 22.5 cm (platinum electrodes). These levels are denoted as the lower and upper column sections, respectively.

During each pressure head step between one and five pore water samples were collected from both column sections to gain insight into
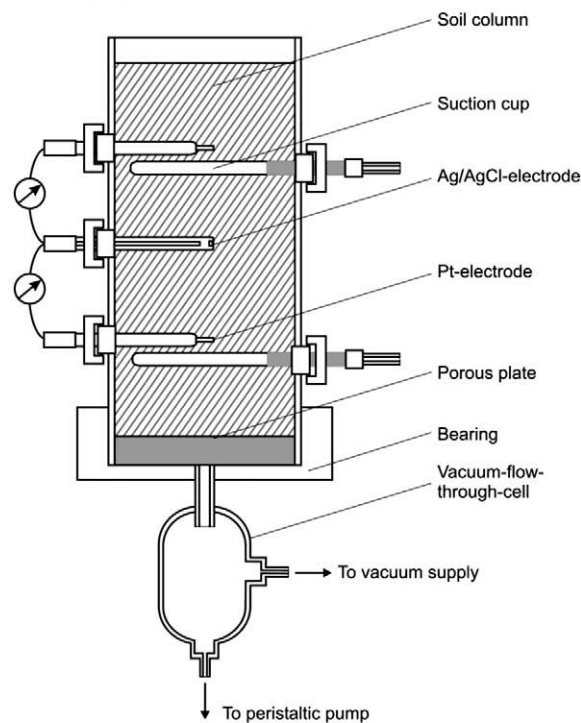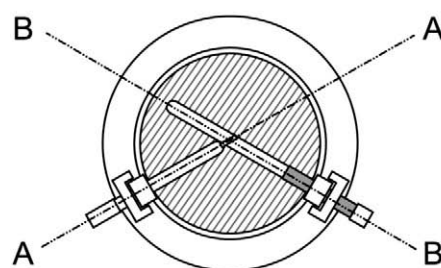

Fig. 2. Soil column set-up and packed bed instrumentation.

As species distribution. No pore water could be extracted from the A and Ag horizon columns after application of 10 kPa. In the saturation periods, the sample volumes were replaced with a syringe to maintain a ponded soil surface.

Ion chromatography for nitrate (NO_3^-) and sulphate (SO_4^{2-}) required relatively large sample volumes. Therefore these constituents could not be determined in pore water samples but were

Table 1
Sequence of experimental steps and pressure head at lower column boundary (tolerance ± 10%).

Step –	Pressure head kPa	Duration h	Cumulative time h
Upstream infiltration	f(t)[a]	9	9
Saturation	−2.8	284	293
Free drainage	0	42	335
Suction	1.0	24	359
	2.5	264	623
	5.0	96	719
	10.0	308	1027
Upstream infiltration	f(t)[a]	9	1036
Saturation	−2.8	240	1276
Free drainage	0	2	1278

[a] Pressure head at the lower column decreases with advancing saturation front.

analysed in the column effluents obtained upon pressure head application.

2.3. Analytical

Textural analysis was carried out by wet sieving (sand fraction) and dispersion/sedimentation of the fine fractions after destruction of organic matter and carbonates. Carbon and nitrogen in bulk soil were determined by dry combustion. Other elements were analysed in nitrohydrochloric digestates. Iron and Mn in pedogenic (hydr)oxides were determined after Mehra and Jackson (1960). Short-range-ordered (hydr)oxides were extracted according to Schwertmann (1964). Binding forms of As were analysed following the sequential extraction scheme of Zeien (1995). The method provides As fractions operationally defined as the mobile, exchangeable, Mn oxide, organic, amorphous Fe (hydr)oxide, crystalline Fe (hydr)oxide and residual pools. Analyses were performed by atomic absorption spectroscopy {Fe and Mn in pedogenic and short-range-ordered (hydr)oxides} and inductively coupled plasma-mass spectroscopy (As in suction cup samples and sequential extracts, Mn, and Fe in column effluents). Nitrate and SO_4^{2-} were determined by ion chromatography. Separation of tri- and pentavalent As species in suction cup samples was carried out by on-line solid phase extraction with quaternary amine as described by Weigand et al. (2007). Quantification limits of the method were $2 \mu l^{-1}$ for As(III) and $1 \mu g l^{-1}$ for As(V).

3. Results

3.1. Soil properties

Important soil properties are summarised in Table 2. The topsoil is characterised by a pH of 7.2 and a clayey texture. The 2Ag horizon shows a higher portion of the sand fraction compared to the A and Ag horizons. Organic carbon levels decrease with depth while the C/N ratios increase. The As contents are highest in the A horizon exceeding 700 mg As kg^{-1} and drop to 37 mg As kg^{-1} in the 2Ag horizon. A similar trend is observed for (i) total, (ii) oxalate-, and (iii) dithionite/ citrate/bicarbonate-extractable Fe and Mn. Sequential extraction (data not shown) revealed that As is predominantly associated with short-range-ordered (47% to 52%) and crystallised Fe (hydr)oxides (27% to 40%) followed by the residual (6% to 16%) and the organic fractions (3% to 7%). Less than 1% of total As was detected in the remaining fractions.

Table 2
Soil properties.

Horizon/– Depth/cm	A 0–15	Ag 15–29	2Ag 29–43
pH (CaCl₂)/–	7.2	7.3	7.3
Sand/%	3.4	2.8	17.1
Silt/%	34.7	41.3	35.9
Clay/%	61.9	55.9	47.0
OC/%	12.8	10.7	5.5
IC/%	0.2	1.9	0.04
C/N/–	8.6	10.1	14.3
As/mg kg⁻¹	716	293	37.0
Al/g kg⁻¹	15.8	4.36	21.3
Ca/g kg⁻¹	95.4	155	16.1
Fe/g kg⁻¹	45.8	23.6	18.5
Fe₀[a]/g kg⁻¹	7.26	4.96	2.29
Fe_dcb[b]/g kg⁻¹	22.1	9.52	4.06
Mn/g kg⁻¹	1.10	0.28	0.15
Mn₀[a]/g kg⁻¹	0.29	0.07	0.02
Mn_dcb[b]/g kg⁻¹	0.64	0.14	0.05

[a] Ammonium oxalate extract.
[b] Dithionite/citrate/bicarbonate extract.

3.2. Redox potential and arsenic in pore water

The course of soil E_H and the concentration of As species in the pore water of the A, Ag and 2Ag horizons are shown in Figs. 3–5. Stepwise changes of the pressure head are indicated as dashed vertical lines. The E_H decreased continuously during saturation and re-increased after soil drainage. The individual horizons differed with respect to the velocity of E_H change and the E_H level attained as well as the concentration and speciation of As.

An E_H value of 170 mV was reached after 290 h of saturation in the upper section of the A horizon column, (Fig. 3a). During free drainage the E_H increased sharply. In the lower column section (Fig. 3b), the E_H dropped to 50 mV during water saturation and responded slower to column drainage. Values around 600 mV were asymptotically approached by 500 h, i.e., during the 2.5 hPa pressure head step. Re-saturation caused the E_H to decrease again, matching the values of the first saturation period in both column sections.

Arsenic pore water concentrations of the upper section of the A horizon were between $5 \mu g l^{-1}$ and $16 \mu g l^{-1}$ during the initial saturation period. In the lower section, the average As concentration was slightly higher. No clear trend could be discerned for total As and As species in response to the moisture regime. In the upper section, As (III) dominated over As(V) in the first three samples collected under saturation. Further on, only pentavalent As was detected. In the lower part of the column As(III) persisted as the dominant species in the drained soil, but disappeared after rewetting. Contrasting the E_H, As levels attained during the initial saturation were not reproduced in the second saturation period.

Results of the Ag horizon are shown in Fig. 4. Except for a faster E_H decline during initial saturation the overall behaviour was similar to the A horizon. This holds for (i) the quick E_H increase in the upper column section during free drainage, (ii) the delayed return to
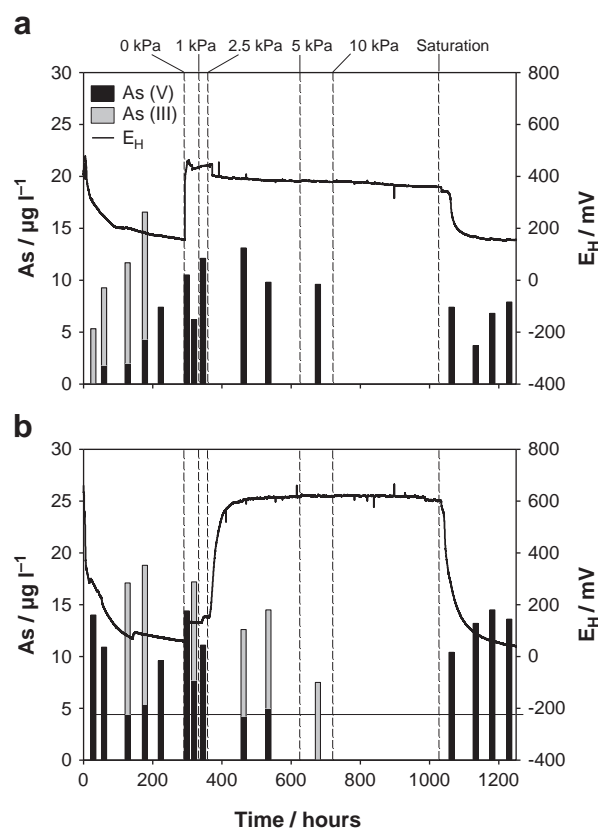
Fig. 3. Redox potential (E_H) and inorganic arsenic species in pore water of the A horizon under varied moisture regime. Graphs a and b represent the upper and lower column section, respectively. Dashed lines indicate pressure head changes.

Fig. 4. Redox potential (E_H) and inorganic arsenic species in pore water of the Ag horizon column under varied moisture regime. Graphs a and b represent the upper and lower column section, respectively. Dashed lines indicate pressure head changes.

Fig. 5. Redox potential (E_H) and inorganic arsenic species in pore water of the 2Ag horizon column under varied moisture regime. Graphs a and b represent the upper and lower column section, respectively. Dashed lines indicate pressure head changes.
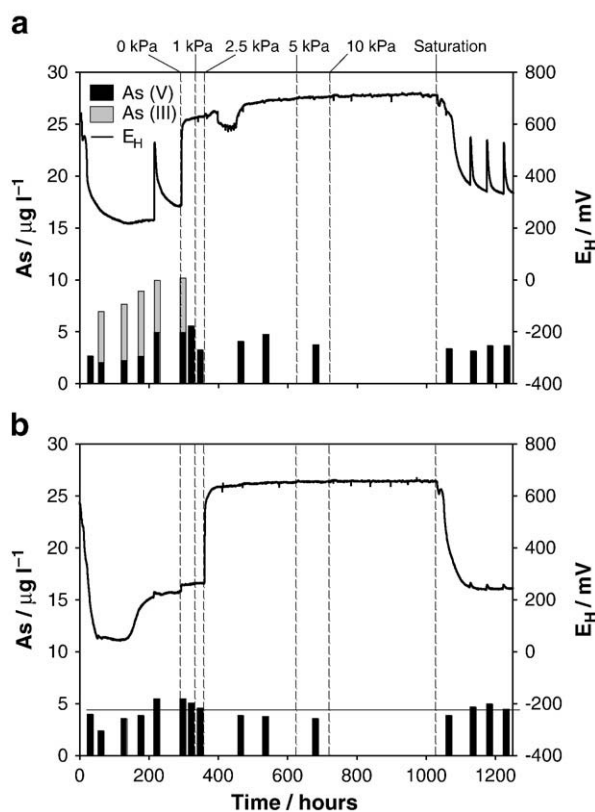
oxidising conditions in the lower section, and (iii) the consistency of E_H values between both saturation periods.

Total dissolved As concentrations of the upper column section ranged from 2 µg l^{-1} to 10 µg l^{-1} in the first saturation period, with up to 2/3 trivalent As. Upon drainage, the As concentration decreased and was dominated by As(V). Pore water samples of the lower columns section were free of As(III) and total As levels changed only moderately.

In the 2Ag horizon (Fig. 5), E_H values responded fastest to initial saturation and reached lowest values. In the upper section, the E_H dropped to around −300 mV. After free drainage, the E_H first sharply increased to 400 mV and slowly continued to rise to 600 mV. During the second saturation period, strongly reducing conditions were not reproduced. In the lower part of the column, the E_H dropped to −400 mV within 100 h (Fig. 5b). Free drainage caused a minor E_H increase to about −300 mV. As the 10 kPa pressure head step was applied, the E_H gradually returned to oxidising conditions. During the second saturation period the E_H established close to 0 mV.

Arsenic pore water concentrations were substantially higher than in the A and Ag horizons. Maxima of the upper and lower parts of the column were 115 µg l^{-1} and 140 µg l^{-1}, respectively, with trivalent As as the dominant species. After a pressure head of 2.5 kPa was applied As(III) of the upper column section dropped below the limit of quantification. The remaining samples had pentavalent As concentrations between 5 µg l^{-1} and 10 µg l^{-1}. In the lower section, total As concentrations decreased more moderately having values between 50 µg l^{-1} and 110 µg l^{-1}. Again, As(III) concentrations dropped strongly, while As(V) levels remained relatively constant until application of 10 kPa. Unlike the upper column section, As concentrations increased again upon rewetting, predominantly as trivalent species.
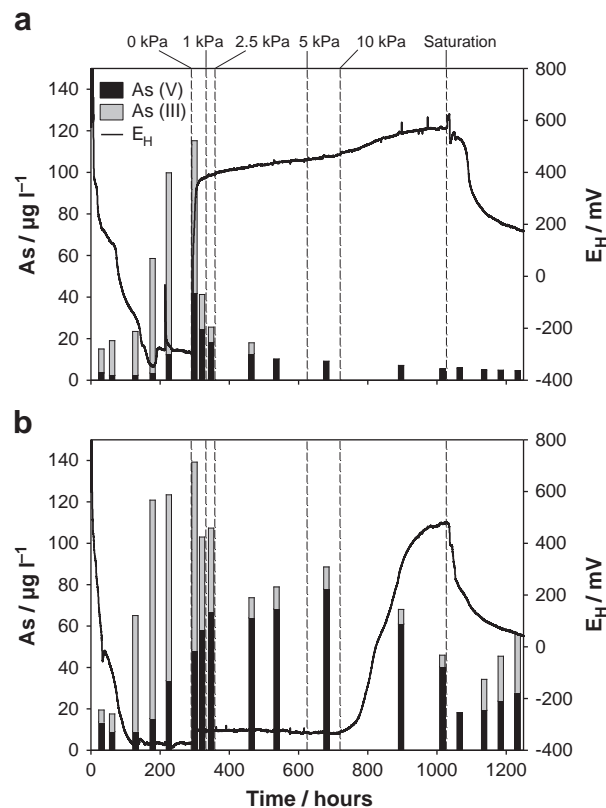
Soil E_H and the corresponding concentrations of total As are summarised in Fig. 6. In the A and Ag horizons (Fig. 6a) total As was not related to E_H and scattered in a narrow band with slightly higher levels in the A horizon. Arsenic in the pore water of the 2Ag horizon (Fig. 6b) varied much stronger. High concentrations of As coincided with low E_H and vice versa.

3.3. Column effluent chemistry

To further characterise redox conditions the column effluents were analysed for NO$_3^-$ and SO$_4^{2-}$ as well as for dissolved Mn and Fe (Table 3). Sample volumes collected from the 2Ag horizon at 5 kPa and 10 kPa were insufficient for analysis.

Nitrate concentrations decreased in the order A horizon>Ag horizon>2Ag horizon. A value of about 1100 mg l^{-1} was observed in the A horizon at maximum suction. Under saturation NO$_3^-$ levels were considerably lower as noted in the effluents collected at 0 kPa. Similar, yet more moderate trends were observed for SO$_4^{2-}$. Effluent concentrations of the A horizon were between 140 mg l^{-1} and 40 mg l^{-1} at 0 and 10 kPa, respectively. Contrasting NO$_3^-$ and SO$_4^{2-}$, dissolved Mn of the A and Ag horizons was highest in the effluents of the saturated periods (0 kPa pressure head) and decreased markedly with increasing suction. Dissolved Fe was below the quantification limit of 100 µg l^{-1}, throughout.

4. Discussion

4.1. Trends of redox potential and arsenic in response to moisture regime

It should be noted that for the Pt electrode to respond to a specific redox couple (i) electron transfer reactions need to be fast and
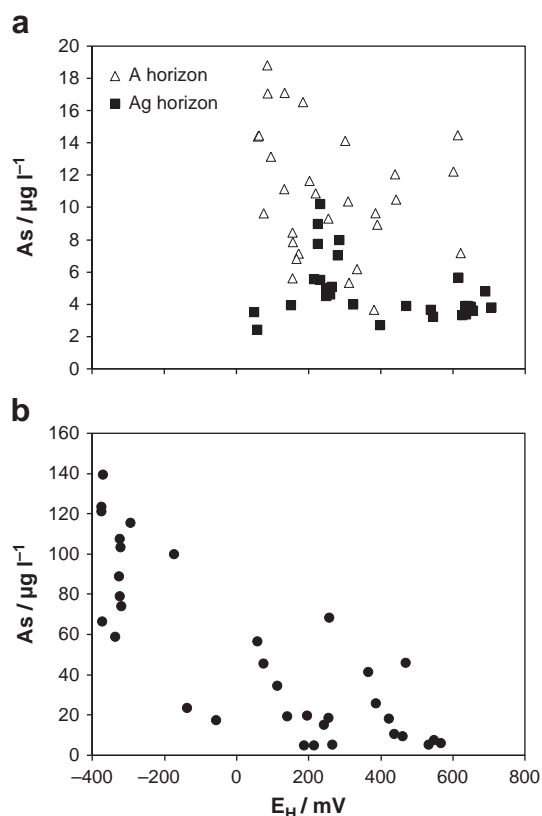
Fig. 6. Relationship between total aqueous arsenic concentrations and soil redox potentials (E_H). Graphs a and b show the data of the A/Ag and the 2Ag horizons, respectively.

reversible so that equilibrium is attained and (ii) both members of the couple must be present at concentrations greater than about 10^{-5} M (Bohn, 1971; Whitfield, 1974; Stumm and Morgan, 1981). With respect to the redox couples considered here, condition (i) is not met for N(0, I)/N(V) and S(–II)/S(VI), and condition (ii) is not met for $Mn^{4+}(aq)$ and $Fe^{3+}(aq)$. Therefore, the linkage between measured E_H and the concentration of species should be primarily qualitative.

Under oxygen depletion microbial degradation processes rely on alternative terminal electron acceptors and the redox potential drops (Zhi-Guang, 1985; Patrick and Jugsujinda, 1992; Fiedler, 2000). In our experiments, the steep increase of E_H induced by drainage contrasts the delayed decline of E_H during saturation. This indicates that the soil E_H was buffered by reduction kinetics under saturated conditions while aerobic degradation of organic matter occurred immediately once the soil was sufficiently drained.

Column effluents (cf. Table 3) largely matched the dynamics of soil E_H. Coherence of NO_3^- and Mn concentrations with E_H agrees with data reported by Meek et al. (1970) and Mansfeldt (2004). The results indicate that NO_3^- was reduced to N_2O, N_2 or ammonia and Mn oxides were dissolved under moderately reducing conditions (200 mV to

Table 3
Redox sensitive components in column effluents. Concentrations in mg l^{-1}.

Pressure head kPa	A horizon			Ag horizon			2Ag horizon		
	Mn	NO_3^-	SO_4^{2-}	Mn	NO_3^-	SO_4^{2-}	Mn	NO_3^-	SO_4^{2-}
0	1.74	37	43	0.20	1	24	0.09	1	8
1	0.43	70	40	0.12	14	28	0.14	8	4
2.5	0.37	146	64	0.05	26	33	0.17	8	27
5	0.05	550	86	0.01	380	93	–[a]	–[a]	–[a]
10	0.02	1120	142	0.02	460	110	–[a]	–[a]	–[a]
0	0.67	2	26	0.10	4	21	0.04	5	19

[a] Not determined due to insufficient sample volume.

400 mV at pH 7). Conversely, during column drainage NO_3^- concentrations increased by nitrification while dissolved Mn decreased by oxidation and precipitation as Mn oxides. The exceptionally high NO_3^- concentrations observed in the A and Ag horizons at the end of the unsaturated period (10 kPa pressure head step) may be the result of sample pre-treatment. Homogenization and air drying of the soil are likely to have promoted mineralization of organic N sources and caused the NO_3^- peak under unsaturated conditions. Redox control of SO_4^{2-} is unlikely in view of the measured E_H of the A and Ag columns. Iron reduction might be expected at the low E_H of the saturated 2Ag horizon (Zhi-Guang, 1985). However, no Fe was found in the column effluents. Thus, either the dissolution of Fe (hydr)oxides was very slow or Fe^{2+} was instantaneously sorbed or precipitated as secondary mineral phases, e.g., siderite (Kocar et al., 2006).

Pore water samples collected immediately after column saturation showed low As concentrations. These may point to a small pool of readily available As released under moderately oxidising conditions (Jang and Dempsey, 2008). Especially in the 2Ag horizon As concentrations increased markedly during the first saturation period. The dissolution of host phases, e.g., Fe (hydr)oxides, under reducing conditions has been recognised as an important pathway of As transfer from the solid phase into pore water (Dixit and Hering, 2003; Ravenscroft et al., 2009). Therewith, aqueous phase concentrations of As and Fe should both increase with time. This could not be shown in our experiments since Fe concentrations remained below the quantification limit. Whether or not the dissolution of host phases is responsible for the increase of As concentrations may be deduced from the content of water-soluble As. Since this fraction was not addressed by our sequential extraction, results of Rüde and Königskötter (2009) on water-soluble As in soils from the same site were used for comparison. On the basis of the packed bed mass of the A, Ag, and 2Ag columns and the saturation volumes, water-soluble As was determined as 380 µg l^{-1}, 130 µg l^{-1}, and 1600 µg l^{-1}, respectively. These values are substantially higher than the maximum pore water concentrations observed in our column experiments. Hence, no additional As release from the dissolution of Fe (hydr)oxides is required to explain the temporal trends during the first saturation period. More likely, reduction of As(V) may have enhanced the desorption of As. This is supported by the remarkable contribution of As(III) to the increase of total As and by the results of Kocar and Fendorf (2009) who showed that As(V) reduction is thermodynamically favoured over the dissolution of Fe (hydr)oxides within a wide range of field conditions.

After soil drainage the E_H as well as NO_3^- and SO_4^{2-} concentrations increased while Mn and dissolved As levels decreased. In the 2Ag horizon As(III) levels dropped fast compared to a moderate response of As(V). This may indicate that sorption of As(V) towards soil surfaces controlled total aqueous As rather than the oxidation of As (III).

Species distribution in the upper section of the 2Ag horizon during the unsaturated period agrees with a direct oxidation of As(III) caused by soil aeration. However, in the lower section, As(V) is the predominant species in spite low redox potential. Amstaetter et al. (2010) suggested that in Fe(II)–goethite systems an intermediate reactive Fe(III) species may form and serve as an oxidant for As(III). The authors concluded that this mechanism may be responsible for the presence of As(V) in reducing environments. Our results on species distribution in the lower part of the 2Ag column may thus point to an As(V) reduction/re-oxidation cycle at low redox potential.

Compared to the first saturation period, rewetting the soil caused a more moderate release of total As. In the 2Ag horizon this observation fits with E_H. Prior to column packing the soil was homogenized by sieving. Breakdown of aggregates and improved accessibility of degradable organic matter may thus have stimulated microbial activity causing lower E_H values during the first saturation period. In the A and Ag horizons E_H values were consistent with the initial

saturation period. The apparent mismatch of As levels, however, is unexplained.

4.2. Within-column differences of redox potential and arsenic concentration

The E_H values attained during water saturation decreased with column depth. This points towards diffusive oxygen transport across the ponded surface which is also supported by the observation that in all horizons the E_H decreased more slowly in the upper column sections.

The reverse was the case when the columns were drained reflecting the water content distribution within the columns. Since in drained porous media the water content increases with depth oxygenation of the lower column sections is shifted towards higher pressure heads. Disparity of E_H between column sections was most pronounced in the 2Ag horizon where oxidising conditions were only attained after application of 10 kPa. This is in accordance with the higher bulk density of the material compared to the A and Ag horizons.

Pore water As concentrations reflected the pronounced E_H gradients of the 2Ag column under unsaturated conditions. In the upper column section, As levels dropped sharply as the E_H increased in response to soil drainage. Conversely, the prevalence of reducing conditions in the lower section is consistent with exceptionally high As pore water concentrations even at increased suction.

Our experiment was designed to simulate a falling and rising water table by stepwise changes of the pressure head. This is a simplified approach to the field situation where water table fluctuations are gradual with a sawtooth characteristic. Long-term monitoring data of investigation site show that the water table rises quickly after storm events followed by a tailing decline (Bayerisches Landesamt für Umwelt, 2010). This means that the return to oxidising conditions should be slower than in our experiments. Hence, under field conditions high As concentrations may persist in the pore water of the 2Ag horizon over comparably long periods. According to our experimental findings these can be expected to be primarily due to the more toxic and potentially more mobile As(III) thereby promoting capillary rise of dissolved As.

4.3. Pedogenetic control of arsenic distribution within the soil profile

In terms of E_H levels and their response to varied soil moisture, the A and Ag horizons behaved similarly strongly contrasting the findings for the 2Ag horizon. The latter is nearest to mean ground water table and is low in Mn and Fe (hydr)oxides due to frequent waterlogging. Takahashi et al. (2004) suggested that the depth-dependence of E_H during flooding of a paddy field was related to the distribution of Fe and Mn (hydr)oxides. Pedogenetic depletion of oxidised species in the 2Ag horizon may thus be responsible for the fast decline of soil E_H under saturated conditions. Conversely, accumulation of sesquioxides in the A and Ag horizons may represent a reservoir of electron acceptors large enough to buffer E_H during prolonged waterlogging.

While As contents of the bulk soil follow the order $2Ag \ll Ag < A$ (Table 2), average solution concentrations increased in the order $Ag < A \ll 2Ag$ (Fig. 6). Hence, As in the topsoil is present in comparably unavailable fractions.

Pedogenetically, the distribution of Fe and Mn (hydr)oxides within the Mollic Gleysol is related to ascending Fe and Mn rich pore water in the capillary fringe. Regarding As redistribution, Fe enrichment in the topsoil may play a double role. Firstly, it involves a depletion of important As sorbents in the groundwater fluctuation zone, secondly it provides a large sorbent pool in parts of the profile that are less frequently saturated.

Due to the fast decline of E_H and the concomitant release of As into pore water, the 2Ag horizon may be regarded as an As source within the unsaturated zone and probably a transition horizon within the whole profile. Arsenic may easily mobilised and transported towards the soil surface with rising water tables. Soil E_H of the A and Ag horizons proved far less susceptible to moisture conditions. Thus, the Fe (hydr)oxides provide an active sink for dissolved As explaining the exceptionally high As contents of the topsoil.

5. Conclusions

This study focussed on redox processes induced by water table fluctuations as a possible route of As enrichment in the topsoil of a Mollic Gleysol in Upper Bavaria, Germany.

Our experimental data show substantial differences among the individual horizons both with respect to soil E_H and pore water concentration of As attained during saturation and drainage. Lowest E_H values and highest dissolved As concentrations were observed under water saturated conditions in the most frequently waterlogged 2Ag horizon. In contrast, the E_H of the A and Ag horizons was higher and dissolved As concentrations were low in spite of high As contents in bulk soil. This was the case even during prolonged waterlogging. We attribute these findings to the pedogenetic enrichment of Fe (hydr)oxides in the topsoil. These lower the susceptibility of E_H to water saturation and at the same time constitute an important sink for As.

Our results strongly corroborate the hypothesis that As accumulation in the topsoil is driven by water table fluctuations at the site. Persistence of reductive conditions in the 2Ag horizon favours As mobility during falling water tables independent of As speciation and is likely to promote As transport towards the soil surface by capillary rise. In the A and Ag horizons oxidising conditions are quickly attained promoting As partitioning towards the solid phase.

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