



Controlled variation of redox conditions in a floodplain soil: Impact on metal mobilization and biomethylation of arsenic and antimony

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ABSTRACT

An automated biogeochemical microcosm system allowing the control of redox potential (E_H) in soil suspensions was used to assess the effect of E_H on the mobility of cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), iron (Fe), and manganese (Mn) as well as on the methylation of arsenic (As) and antimony (Sb) in a contaminated and slightly acidic floodplain soil. The experiment was conducted under stepwise variation from reducing (approximately -300 mV at pH 5) to oxidizing ($+600$ mV at pH 5) conditions. The E_H was found to be an important factor controlling the dynamics of studied compounds and elements. Concentrations of Cd, Cu, Mn, Ni, and Zn in solution were low at low E_H and increased with rising E_H what might be attributed to the interaction with dissolved organic carbon (DOC), Mn, and precipitation as sulphides. Redox potential and pH correlate significantly with Cd, Ni, Cu, Zn, and Mn. Total Fe concentrations in solution were high at low E_H and dropped sharply at $E_H > 350$ mV at pH 5 to lower values due to the formation of Fe (hydr)oxides. Other metals did not adsorb to or co-precipitate with Fe, which may be attributed to the low pH (between 4.4 and 5.3) amongst other factors. Concentrations of inorganic arsenic (As_i) and antimony (Sb_i), monomethyl arsenic (MMAs), monomethyl antimony (MMSb), and dimethyl arsenic (DMAs) in solution decreased significantly with rising E_H , indicating that low E_H promotes the mobility of these compounds.

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1. Introduction

Many floodplain soils are highly contaminated both from anthropogenic (e.g., industrial, municipal and agricultural discharge of waste into the river) as well as geogenic sources (e.g., Devai et al., 2005; Rinklebe et al., 2007; Rennert and Rinklebe, 2010). Pollutants such as heavy metals and metalloids are transported with the river water and its suspended material, and accumulate in floodplain soils during flooding with low flow velocity (Rinklebe et al., 2007; Du Laing et al., 2009c). In particular, large areas of the floodplain soils along the River Wupper (Germany) are highly polluted due to discharge of waste originating from textile and metal industry during the last centuries. Thus, considerable amounts of metals are still accumulated in sediments and floodplain soils of the River Wupper (Schenk, 1994).

The mobility of metals in frequently flooded soils is determined by a range of factors, such as metal content, adsorption/desorption processes, salinity, presence of organic matter, sulphur (S), and carbonates, plant growth, pH, and redox processes (Gambrell, 1994; Du Laing et al., 2009c). Redox processes determine the redox potential (E_H), which is an

electric potential measured in millivolt [mV]. The E_H arises by the transport of electrons from the electron donor to the electron acceptor. Oxidation processes prevail at high E_H whereas reduction processes dominate at low E_H . In floodplain ecosystems, drastic changes of water table levels occur resulting in frequent changes of E_H which in turn affect pH. Oxidation processes produce protons and subsequently decrease pH, whereas reduction processes consume protons and therefore increase pH (Yu et al., 2007).

We simulated changing redox conditions in the laboratory, because E_H can be the dominating factor affecting metal fate (Kalbitz and Wennrich, 1998; Patrick and Verloo, 1998; Van den Berg et al., 2000; Vink, 2002; Du Laing et al., 2009c). Particularly at the oxic–anoxic interface and in the anoxic layers of floodplain soils, redox-sensitive processes occur which can result in metal precipitation or dissolution of metal precipitates. Kinetics of these processes are of large importance for these soils as the location of the oxic–anoxic interface is subject to change due to fluctuating water table levels (Du Laing et al., 2009c). The dynamics of trace metals in floodplain soils are particularly driven by redox chemistry of S, iron (Fe), and manganese (Mn) (Van Griethuysen et al., 2005). As a result of temporal inundations and establishment of low E_H , Fe and Mn (hydr)oxides in the solid phase are reduced to Mn^{2+} and Fe^{2+} , which occur as soluble metals and organic complexes in the liquid phase (Reddy and DeLaune, 2008). Accordingly, elements that are fixed to these (hydr)oxides, for example arsenic (As), are often

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transformed to a more mobile form. On the other hand, elements such as As can also be immobilized due to co-precipitation with or adsorption to Fe and Mn (hydr)oxides under oxic conditions. Moreover, divalent metal immobilization can be induced under anoxic conditions due to the presence of hardly soluble sulphides (Van Griethuysen et al., 2005; Du Laing et al., 2007, 2008, 2009a,b,c). Brümmer (1974) mentioned that sulphides are generated from sulphates below $E_H -50$ mV at pH 7 (corresponds to E_H 68 mV at pH 5). Such sulphate reduction can be catalysed by microorganisms (Burkhardt et al., 2010).

In addition to the reduction of Fe and Mn (hydr)oxides and concurrent release of associated As, reduction of arsenate to arsenite can lead to an increased As mobility under reducing conditions (Masscheleyn et al., 1991; Mitsunobu et al., 2006; Du Laing et al., 2009a). Antimony (Sb), another metalloid in the same periodic group like arsenic, was found to be more stable, and therefore less available, than As in soils, even under reducing conditions (Thayer, 2002; Mitsunobu et al., 2006). Both metalloids are subject to biomethylation under oxic as well as anoxic conditions (Bentley and Chasteen, 2002; Thayer, 2002). This methylation process has been found to be conducted by a broad spectrum of both microorganisms and higher organisms (Thayer, 2002) and can fundamentally change mobility, availability, and toxicity of metalloids (Craig, 2003). As a consequence, methylated As and Sb species have been detected in many different environmental and industrial compartments, in particular with high biological activity (e.g., soils, fresh water, seawater, estuarine sediments, sewage sludge, or compost) (Thayer, 2002; Bentley and Chasteen, 2002). Although the presence of methylated metalloids in the environment has been clearly documented, informations on the impact of E_H on As and Sb methylation are very scarce up to date.

Studies that specifically address redox-induced mobilization and immobilization processes of metals and metalloids under slightly

acidic conditions in frequently flooded soils are still rare as previous studies mainly focussed on neutral or alkaline soils and sediments (Buykx et al., 2000; Caetano et al., 2003; Du Laing et al., 2007; Herbel et al., 2007). Thus, a slightly acidic soil was chosen in our study. Due to the relatively low pH of the soil, precipitation of Fe oxides is induced at high E_H , whereas precipitation of Mn oxides was not found. In this study, we present a method for studying the impact of redox conditions on metals in flooded soils by using an automatic biogeochemical microcosm system allowing computer-controlled adjustment of E_H in order to study the effect of E_H mechanistically. We aimed to assess the impact of E_H , pH, sulphate (SO_4^{2-}), and dissolved organic carbon (DOC) on the mobility of cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn), Fe, Mn, As, and Sb as well as on the biomethylation of As and Sb in a heavily contaminated floodplain soil.

2. Materials and methods

2.1. Study site and soil characteristics

Soil samples were collected from a floodplain at the lower course of the Wupper River close to the confluence into the Rhine River. The study site is located near the town Leverkusen, about 20 km to the north of Cologne, Germany (RW 2570359, HW 5661521) (Fig. 1). The geological parent material is sediment of the Rhine River (“Niederrheinische Bucht”). It is dominated by shale from Devonian origin (“Rheinisches Schiefergebirge”). The long term annual precipitation is approximately 774 mm and the long term annual air temperature is 10.8 °C (Deutscher Wetterdienst, 2009). The site is used as grassland. The study site is flooded periodically by the Wupper River, usually in springtime (Wupperversand, 2009). The Wupper River is approximately 115 km long; the average gradient is 0.4%, and

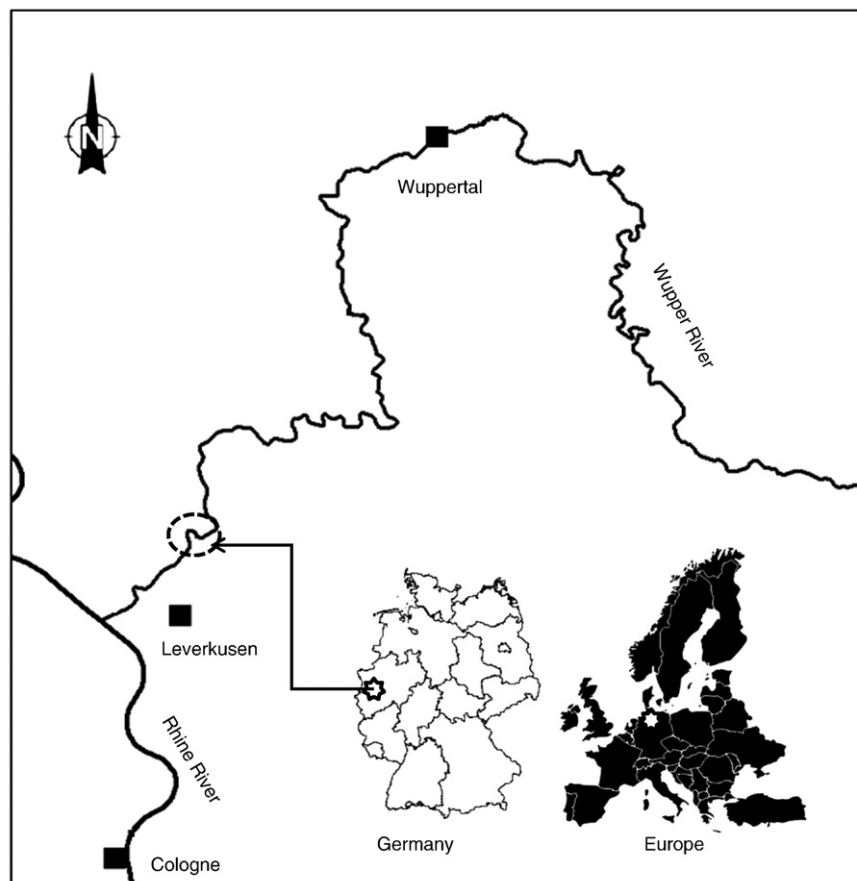


Fig. 1. Location of the study site.

Table 1

Total metal concentrations (aqua regia), dithionite (Fe_d) and oxalate (Fe_o) extractable iron (Fe) and manganese (Mn) of the bulk soil.

Depth	Al	Fe	Fe_o	Fe_d	$\text{Fe}_o/\text{Fe}_d^{-1}$	Mn	As	Cd	Cu	Ni	Zn
[cm]	[g kg ⁻¹]		[%]			[mg kg ⁻¹]					
0–32	15.2	49.7	1.83	3.1	0.59	944	56.1	7.7	2071	86.1	1133

the discharge average is 15.4 m³s⁻¹. The catchment area of the Wupper River encompasses 814 km². The soil texture is dominated by sand (55%) and silt (36%), similar to the texture of other soils sampled along the Wupper River (Schenk, 1994). The content of soil organic carbon (C_{org}) is relatively high (7.9%), total nitrogen (N_t) is 0.4% and the relation between C_{org} and N_t is 19.8. The soil is classified as Eutric Fluvisol according to IUSS-ISRIC-FAO (2006). Total metal concentrations of the bulk soil are given in Table 1. Concentrations of Cd, Ni, and Zn exceed the precaution values, whereas concentrations of As and Cu exceed the action values set by the German Soil Conservation Law (BBodSchV, 1999).

2.2. Sampling, pre-treatment and analysis of bulk soil

The soil was collected from the genetic A-horizon (0 to 32 cm). Sampling was performed in four replicates of about 1 kg which were thereafter pooled to one composite sample. Soil material was homogenized, air-dried and sieved to <2 mm. Subsamples were ground in an agate disc mill. The soil properties were determined according to standard methods (Schlichting et al., 1995) as follows: Total C (C_t) and N_t were measured with dry combustion and thermal conductivity detection using a C/N/S-Analyser (Vario EL Heraeus, Analytik Jena, Jena, Germany). Inorganic C was quantified by dry combustion and IR-Detection with a C-MAT 550 (Stroehlein). Soil organic C was calculated as the difference between C_t and inorganic C. Particle-size distribution was determined by wet sieving and sedimentation using the pipette sampling technique according to Handbuch der Bodenuntersuchung (2000). Total metal and As concentrations of the soil were quantified after digestion using aqua regia (37% HCl + 65% HNO₃, 3:1) ignoring the immobile silica-bound fraction. Oxalate soluble Fe oxide (Fe_o) was determined according to Schwertmann (1964). Dithionite soluble Fe oxide (Fe_d) was measured as described by Mehra and Jackson (1960).

2.3. Experimental setup

An automated biogeochemical microcosm system was used to simulate flooding of the soil in the laboratory (Fig. 2). Controlling redox conditions in a microcosm setup has several advantages. Redox conditions are reproducible and defined, and can be changed rapidly. Furthermore, the effect of E_H can be studied mostly independent from other parameters. This system was successfully used in a previous study for the determination of trace gas emissions from flooded soils (Yu et al., 2007; Rinklebe et al., 2010). Each microcosm (MC) consists of a glass vessel with a content of 2.88 L, which can be hermetically sealed with an air-tight lid. It is equipped with a stirrer, a platinum (Pt) electrode with a silver-silver chloride (Ag/AgCl) reference electrode (EMC 33, Meinsberger Elektroden, Ziegler-Knobeldorf, Germany), a pH electrode (EGA 153, Meinsberger Elektroden, Ziegler-Knobeldorf, Germany), and a temperature electrode (Pt 100, Meinsberger Elektroden, Ziegler-Knobeldorf, Germany). These sensors allow measuring E_H , pH, and temperature at a very high temporal resolution. Data collected by the sensors are reported by a computer via a data logger (LogTrans 16-GPRS, UJT, Dresden, Germany). The vessels were wrapped with aluminium foil to protect them against daylight, preventing algae growth, and photo-oxidation. The system is equipped with an automatic-valve gas regulation system which

allows automatic control of E_H by adding nitrogen (N_2) (to lower the E_H) or oxygen (O_2) (to increase the E_H).

Four independent biogeochemical MCs were used as replications. MCs were filled with 200 g air-dried soil and deionised water in a 1:8 ratio. The achieved slurry was continuously stirred to reach homogeneous conditions. Redox potential, pH, and temperature in each MC were automatically monitored every 10 min. The pH values of MC 4 could not be monitored due to a failure of the pH electrode. The measured E_H -values were normalized to pH 5, since the pH ranged between 4.4 and 5.3 during the experiment (Table 2). These values will be referred to as " E_H at pH 5".

At the beginning of the incubation, 5 g glucose was added to each MC to provide an additional carbon source for microorganisms. This addition was repeated after 2 days (5 g) and 4 days (5 g twice). After 13 days, another amount of 5 g glucose was added to MC 1 and MC 4, respectively. As a result, levels of E_H at pH 5 decreased to values between approximately -330 and -130 mV. This process was accelerated by continuously flushing the MCs with N_2 for a period of 5 to 7 days. Thereafter, E_H -values were increased in steps of 100 mV by adding oxygen. Redox potential was kept within E_H -windows of approximately 30–40 mV around the set E_H -values by automated supply of O_2 or N_2 . The E_H was kept for approximately 24 h within each window and subsequently set to the next value. The slurry was sampled (55 mL) approximately 24 h after reaching each new E_H -window. The soil/water ratio remained the same during the experiment. After achieving the highest E_H at pH 5 levels between approximately 450 and 600 mV, N_2 was added to decrease E_H again. The total incubation period was 22 days.

2.4. Sample preparation, subsampling and storage

The slurry samples were centrifuged for 15 min at 3000 rpm and the supernatants were immediately filtered under N_2 -atmosphere through a 0.45 μm Millipore membrane (Whatman Inc., Maidstone, UK). For the filtrate the term "soluble fraction" was used in this manuscript. The soluble fraction was thereafter aliquoted to different subsamples for subsequent analysis. First, 10 mL subsample was stabilized by addition of 400 μL 65% HNO₃ for analysis of metals and S, and stored at -20 °C until analysis. For analysis of inorganic and methylated As and Sb species, a second 1 mL subsample from MC 3 was stored at -20 °C and thawed a few minutes prior to the analysis. A third subsample (10 mL) was used for determination of DOC and SO_4^{2-} .

2.5. Chemical analysis

Concentrations of Cd, Cu, Fe, Mn, Ni, Zn, and S were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany). A 4-point calibration was performed with standard solutions (CertiPur, Merck) diluted in deionised water. Each sample was measured in three replications. The relative standard deviation of replicate analysis was below 5% with a few exceptions.

Inorganic and methylated As and Sb species were analyzed by hydride generation followed by purge-and-trap gas chromatography and detection via inductively coupled plasma mass spectrometry (HG-P&T-GC-ICP-MS) as described previously (Diaz-Bone and Hitzke, 2008). In brief, 100 μL soluble fraction was added to 40 mL citric acid/citrate buffer (pH 7) and purged by 300 mL He min⁻¹ for 120 s in order to remove oxygen. Then, 10 mL 1 M NaBH₄ (purity >99%, in 0.1 M sodium hydroxide) and 10 mL 2 M HCl (trace analysis grade) were continuously added via automated piston pumps with ceramic head (REGLO-CPF Ismatec, Wertheim, Germany) within 420 s. The volatile derivatives were continuously purged out of the reaction solution by 300 mL He min⁻¹ and cryofocussed on a column (ID: 4 mm, length: 40 cm) packed with Supelcoport 2100 (Sigma-Aldrich, St. Louis, US) immersed in liquid N_2 . After derivatization, the purge

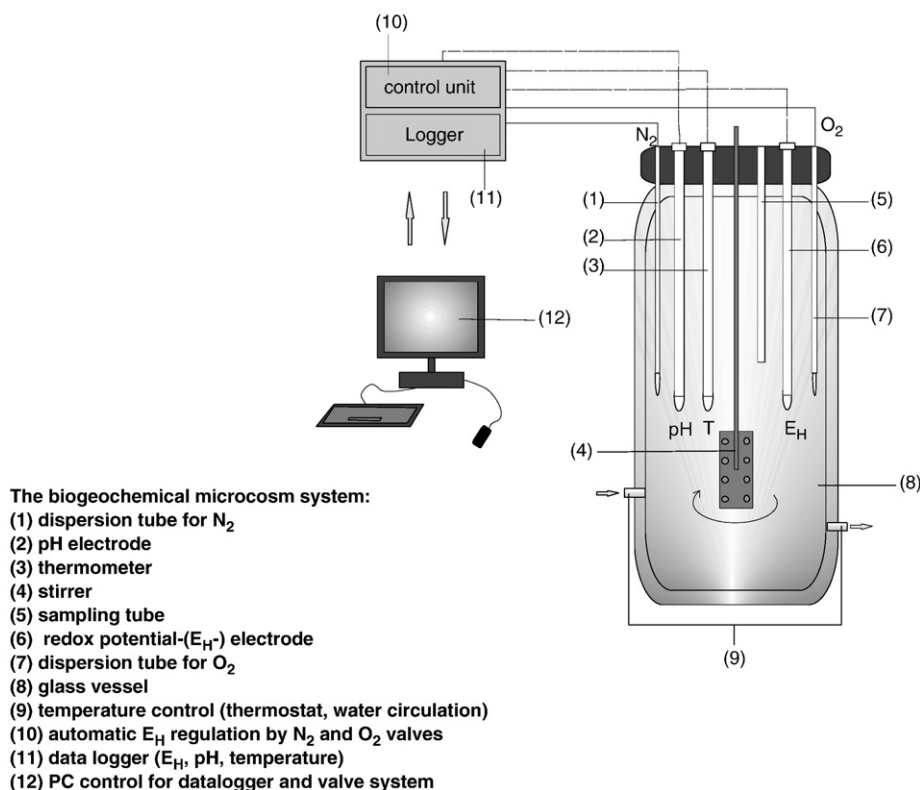


Fig. 2. Biogeochemical microcosm setup.

flow was maintained for additional 2 min. Then, the column was heated to 180 °C within 600 s for separation of the volatile hydrides according to their boiling point. Multi-element detection of organo-metal(loid) species was accomplished by online-coupling to ICP-MS (7500a, Agilent Technologies, Yokogama, Japan). Continuous internal standardization with Ga and In and post-column quantification by interaggregate calibration (IAC) was used as described by Feldmann (1997). Detection limits based on the 3 σ of blank levels were 1–10 pg for methylated species and 100 resp. 160 pg for As_i and Sb_i. Analysis was conducted in triplicate. Relative standard deviation was below 20% with a few exceptions ranging up to 40% in case of methylated species close to the detection limit.

Dissolved organic carbon was measured with a TOC-analyser (TOC-V_E, Shimadzu, Kyoto, Japan). A 2-point calibration was conducted. Measurements were carry out in two replications for each sample with a detection limit of 1 mg L⁻¹. Sulphate was determined using an ion chromatograph (Personal IC 790, Metrohm, Filderstadt, Germany) with a Metrosep A Supp 4-column (Metrohm, Filderstadt, Germany). A 2-point calibration was conducted. The detection limit was 0.03 mg L⁻¹.

2.6. Calculations and statistical analysis

Mean values of E_H and pH data originated from 3, 6, 12, and 24 h prior to sampling were calculated and thereafter correlation analyses between E_H/pH and DOC, SO₄²⁻, Cd, Cu, Fe, Mn, Ni, Zn, and S were conducted. The results 6 h before sampling revealed the highest correlation coefficients and were therefore presented here. Concentrations below the detection limit were set to the half of the detection limit for the statistical analyses. In some cases the standard deviation of the ICP-OES measurements were above 5%. These values were not included into the statistical analyses. Pearson's correlation coefficients (*r*) were calculated using PASW 18.0. ORIGIN 6.0 was used for calculating the regressions equations and creating the figures.

3. Results

Mean, median, and range for the measured parameters are provided in Table 2. A negative correlation between pH and E_H (each measured every 10 min during the experiment) was detected ($r^2 = 0.604$; $p < 0.01$; $n = 18,098$).

Concentrations of Cd, Ni, Cu, Zn, Fe, Mn, DOC, and SO₄²⁻ and versus E_H at pH 5 are presented in Fig. 3. Total Cd, Cu, Mn, Ni, and Zn

Table 2

Variations (mean, median, range) of concentrations of elements and compounds in the soluble fraction as well as pH, and redox potential (E_H) in the slurry.

	Mean	Median	Range	<i>n</i>
DOC	2637	2229	1885–4464	38
SO ₄ ²⁻	50.3	30.5	3.5–223	38
S	2.20	1.99	1.39–7.72	38
Cu	6.14	5.00	0.06–14.67	36
Fe	286	301	2.73–553	38
Mn	77.1	80.5	22.0–112	38
Ni	1.57	1.74	0.59–2.56	36
Zn	28.3	28.0	3.7–48.3	38
Cd	145	160	9.42–354	37
As _i	179	167	10.5–347	9
MMAs	0.24	0.18	0.04–0.65	9
DMAs	0.53	0.70	0.06–0.88	9
Sb _i	4.33	3.38	0.24–9.67	9
MMSb	0.35	0.42	0.09–0.61	9
DMSb	0.16	0.15	0.12–0.22	9
E _H (6 h) ^{a,c}	89	168	–332–577	38
E _H (all data) ^{b,c}	238	311	–337–601	23,735
pH (6 h) ^a	4.7	4.7	4.4–5.3	38
pH (all data) ^b	4.6	4.6	4.4–5.3	18,098

^a Means of data 6 h before sampling.

^b Data measured every 10 min during the experiment.

^c E_H corrected to pH 5 (see Materials and methods).

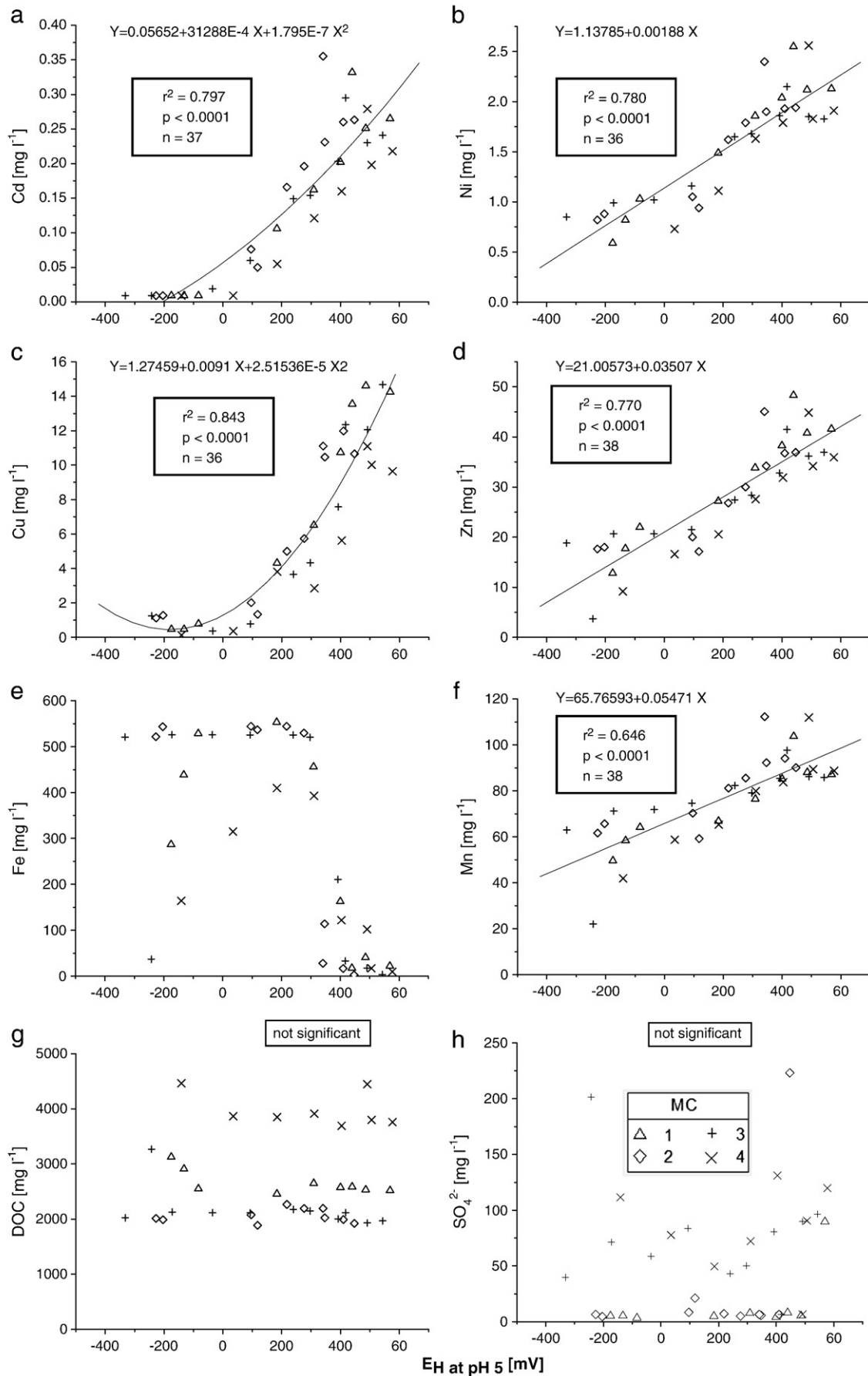


Fig. 3. Relations E_H at pH 5 in the slurry vs. total metal concentrations (Cd, Cu, Ni, Zn, Fe, and Mn), dissolved organic carbon (DOC), and sulphate (SO_4^{2-}) in the soluble fraction.

concentrations increased with rising E_H and were significantly correlated with E_H (Fig. 3). Iron concentrations were generally high at low E_H and decreased rapidly above E_H at pH 5 300 mV. The critical point was approximately E_H at pH 5 350 mV. Total S (data not shown), SO_4^{2-} , and DOC (Fig. 3) did not show a significant correlation to E_H . Total Cd, Cu, Mn, Ni, and Zn decreased with increasing pH (Fig. 4). Total Fe concentrations, DOC, and SO_4^{2-} did not show a significant correlation with pH (Fig. 4).

Methylated As and Sb species were detected with maximal concentrations ranging up to $0.88 \pm 0.06 \mu\text{g L}^{-1}$ DMAs and $0.61 \pm 0.12 \mu\text{g L}^{-1}$ DMSb (Fig. 5). Both, As and Sb showed highest levels of inorganic and methylated species at negative E_H and showed strong negative correlations (except DMSb; Fig. 5). Inorganic As, Sb_i, DMAs, and MMSb strongly correlated with concentrations of Fe (Table 3). Inorganic As, Sb_i, MMAs, DMAs, and MMSb showed a significant correlation, with highest correlation coefficients between As_i and Sb_i (0.981) as well as between As_i and DMAs (0.959) (Table 3). The proportion of methylated compounds relative to the inorganic species remained relatively constant for As. For Sb, the relative proportion of methylated species was significantly higher and increased with increasing E_H .

4. Discussion

4.1. Dissolved organic carbon, pH, and redox potential

Flooding of the soil caused a decrease of E_H in our experiment. Generally, pH decreases when E_H increases and vice versa, due to the formation of H^+ ions during oxidation process (Kaplan and Knox, 2007; Yu et al., 2007). A negative correlation between E_H and pH ($r^2=0.604$; $p<0.01$; $n=18,098$) was also found in our study. Significant relationships between DOC concentrations on one hand and E_H and pH on the other hand were not found in our study (Fig. 3g, Fig. 4g). This may be attributed to the fact that DOC concentrations were very high in our experiment due to the amendment of glucose (Table 2). However, Yu et al. (2007) who incubated soil samples with the same setup, detected decreasing DOC with increasing E_H probably due to microbial carbon consumption. Other authors also observed an enhanced mobilization of DOC under reducing conditions (DeLaune et al., 1981; Grybos et al., 2009).

4.2. Fate of Fe and Mn

Fig. 3e shows that Fe concentrations were generally high at low E_H and low at high E_H . This behaviour has been frequently described and can be attributed to the formation of Fe (hydr)oxides at high E_H (e.g. Brümmer, 1974; Rennert and Mansfeldt, 2006; Yu et al., 2007), while Fe (hydr)oxides are reduced to soluble Fe^{2+} at low E_H (Ponnamperuma, 1972; Herbel et al., 2007; Alewell et al., 2008). Total Fe concentrations at three sampling points of MCs 1, 3 and 4 were relatively low at low E_H (Fig. 3e). As these values represent the first sampling point in each of the three MCs, it is likely that the time span from the start of the incubation to the first sampling point might not have been sufficient for a complete reduction of the Fe (hydr) oxide pool. Such behaviour can be expected as the reduction of Fe (hydr)oxides is catalysed by microorganisms and a certain period of time is required to re-establish facultative anaerobe and anaerobe microbial communities after flooding soils (e.g., Rinklebe and Langer, 2006, 2008; Langer and Rinklebe, 2009). The Fe (hydr)oxide reduction process also depends on the total content of Fe in the bulk soil which is high in our case. The Fe activity level expressed as the ratio of oxalate-extractable Fe oxides to dithionite extractable Fe oxides (Fe_o/Fe_d ratio) (Table 1) is relatively high in the studied soil compared to other soils (e.g., Agbenin, 2003; Fiedler and Sommer, 2004). This indicates that amorphous, oxalate-extractable Fe oxides such as ferrihydrite are abundant in the soil of the Wupper River. Amorphous Fe oxides usually dominate hydromorphic soils (e.g., Fiedler and Sommer, 2004;

Schulz-Zunkel and Krüger, 2009); however, crystalline compounds such as goethite may also exist in parallel.

Total Fe concentrations in solution increased considerably with a pH of above 4.6 (Fig. 4e). Miller et al. (2010) treated soils with leachants of different pH. In contrast to our study, they found that Fe concentrations in the leachate decreased with increasing pH in a range from pH 2.1–5.5. Generally, Fe is soluble as Fe^{2+} at low pH. At neutral pH, Fe is only soluble at low E_H (Du Laing et al., 2009c). At pH 5, Fe exists as Fe^{2+} in a large range from reducing conditions to approximately E_H 400–500 mV (Takeno, 2005). As with the other metals, E_H rather than pH might have had a strong impact on the variability of Fe concentrations in the solution, which might be attributed to the relatively small pH range in our study.

As opposed to many other studies (e.g., Tack et al., 1998; Massmann et al., 2004; Knox et al., 2006; Du Laing et al., 2007; Yu et al., 2007), concentrations of Mn increased with rising E_H in our study (Fig. 3f). Reduced Mn^{2+} is more soluble than its oxidized counterpart (Chadwick and Chorover, 2001). When the oxygen level increases, Mn ions precipitate and form secondary Mn compounds such as Mn (hydr)oxides at neutral to alkaline pH (Knox et al., 2006; Koretsky et al., 2007), which are important binding agents for heavy metals (Du Laing et al., 2009c; Borch et al., 2010). Mn (hydr)oxides were obviously not generated in a considerable amount in this study. The highest overall E_H at pH 5 value measured in our study was 601 mV (corresponds to E_H 459 mV at pH 7). It seems that the E_H was too low for the generation of Mn (hydr)oxides in this study, because their formation requires very strong oxidic conditions (approximately 900–1000 mV at pH 5) (Takeno, 2005) and is in addition pH-dependent. The pH was slightly acidic in our study, which might have inhibited the formation of Mn (hydr)oxides. Total Mn contents were high and generally declined with increasing pH (Fig. 4f), which is consistent with other studies. Carbonell et al. (1999) compared pH 5 with pH 7, and Miller et al. (2010) worked in a range between pH 2.1 to 5.5. The pH range was too low (4.4 to 5.3) to explain the variability of Mn within the soluble fraction. Furthermore, the correlation between Mn and pH is weaker than between Mn and E_H . Although Mn oxide reduction does not seem to be the main process affecting Mn mobility, E_H might be an important factor influencing the behaviour of Mn under our experimental conditions. This points towards the presence of Mn sulphides, which may explain the low Mn concentrations at low E_H and increasing Mn concentrations upon oxidation with increasing E_H (see discussion later).

4.3. Fate of Cd, Cu, Ni, and Zn

In this study, the solubility of Cd, Cu, Ni, and Zn increased with rising E_H (Fig. 3a, b, c, d). Accordingly, several authors (e.g., Cappuyns and Swennen, 2005; Du Laing et al., 2009c) reported the release of trace metals from soils due to changes in their speciation as a consequence of changed redox conditions. Some metal ions are reduced under anaerobic conditions which can lead to changed solubilities of these metals compared to their oxidized counterparts. For example, solubility of Cu can be reduced by reduction from Cu (II) to Cu (I) under anaerobic conditions with the help of electron donors (e.g., Fe (II)) and bacteria. However, for many metals (e.g., Cd and Zn), changes of the valence state as a consequence of E_H changes have not been observed in natural sediments and soils (Du Laing et al., 2009c). Instead, the solubility of these metals is often indirectly affected by E_H , e.g. through E_H -dependent pH changes, complexation with organic material, co-precipitation with Fe and Mn (hydr)oxides or precipitation as sulphides (Du Laing et al., 2009c). Therefore, we can assume that high concentrations of some heavy metals in the soluble fraction under oxidizing conditions might be related to other processes in our study.

Oxidizing conditions can affect the mobility of metals indirectly through decreasing pH in the soluble fraction as also reported by

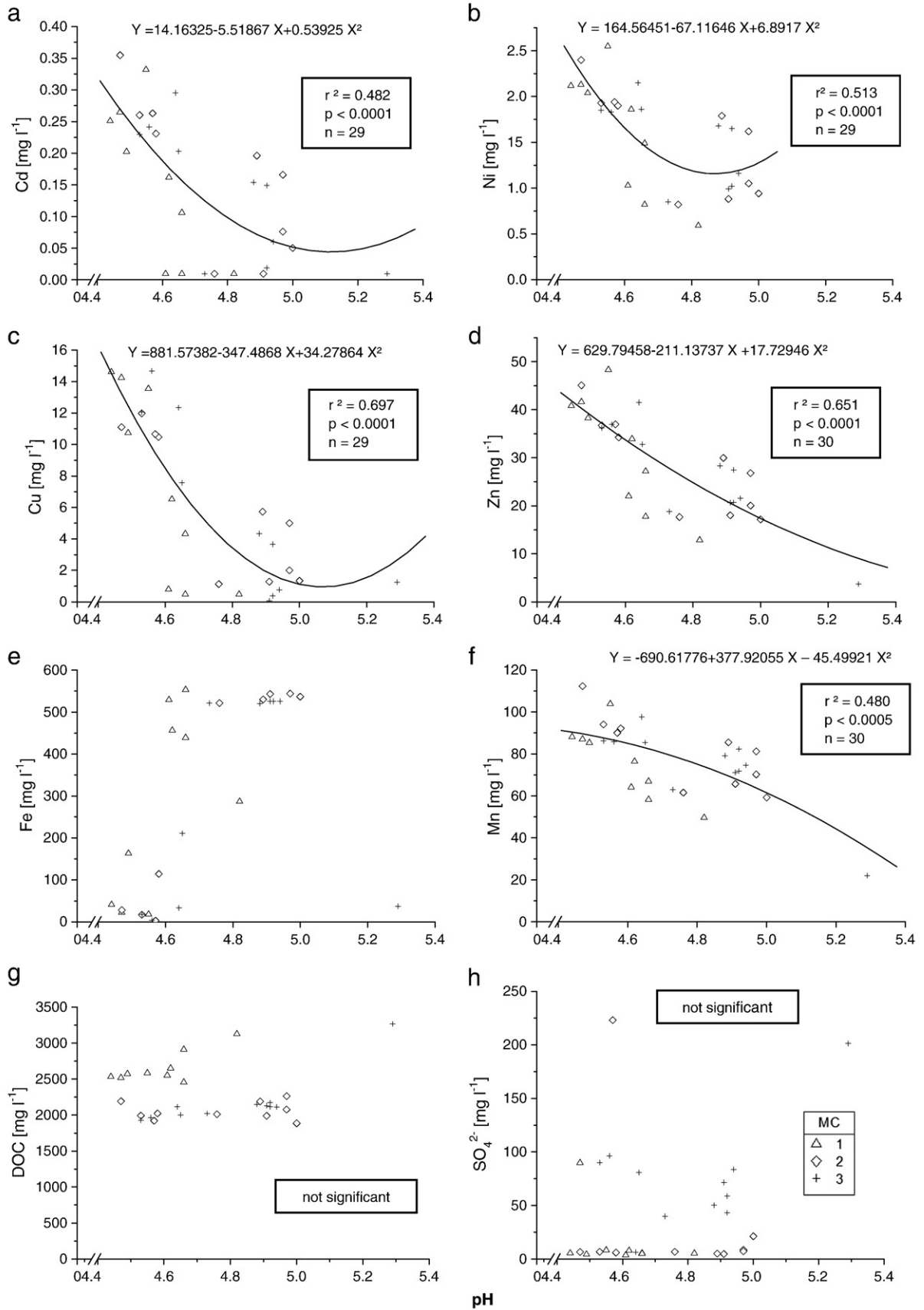


Fig. 4. Relations pH in the slurry vs. total metal concentrations (Cd, Cu, Ni, Zn, Fe, and Mn), dissolved organic carbon (DOC), and sulphate (SO_4^{2-}) in the soluble fraction.

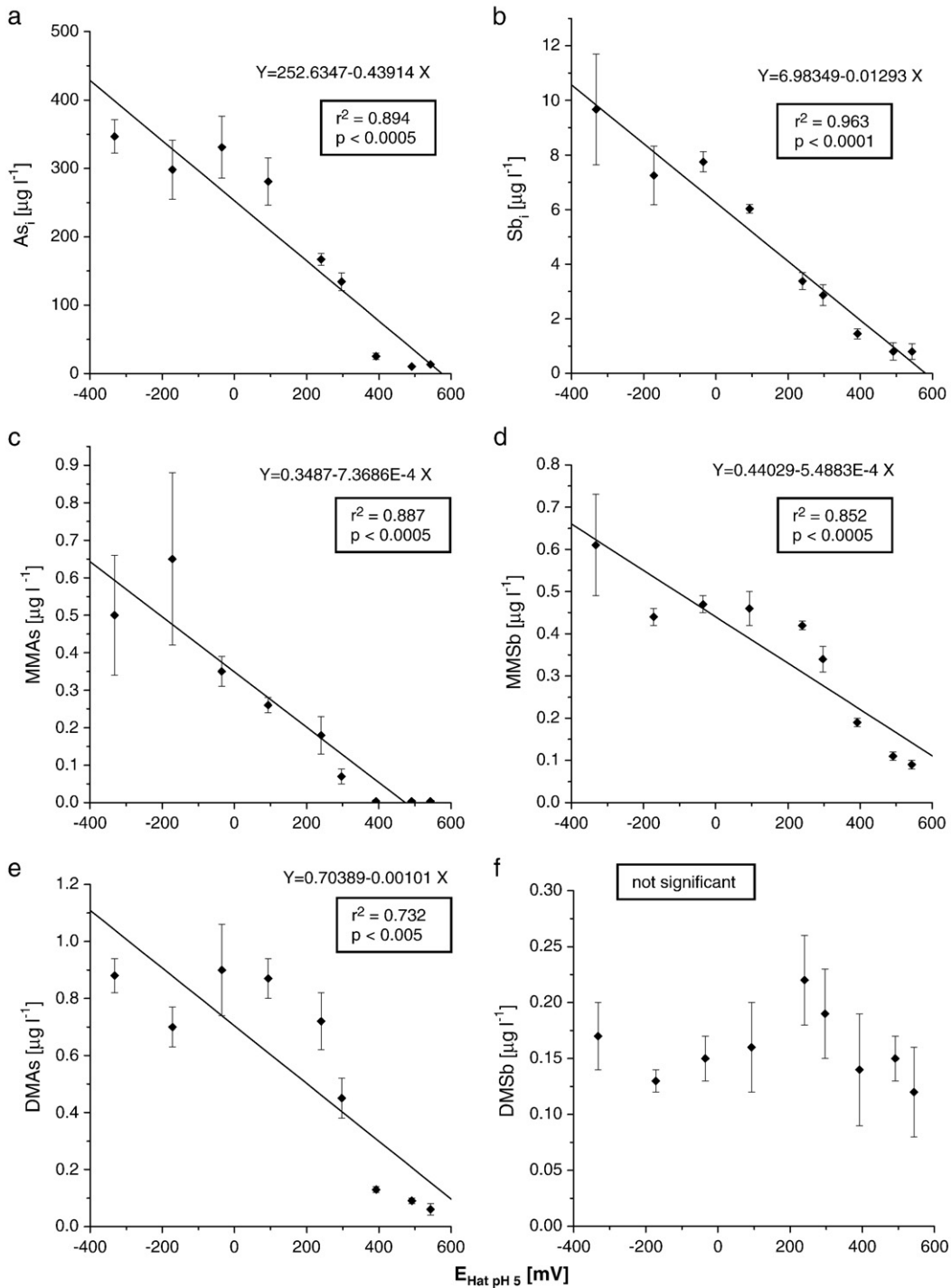


Fig. 5. Relations inorganic arsenic (As_i), monomethyl arsenic (MMAs), dimethyl arsenic (DMAs), inorganic antimony (Sb_i), monomethyl antimony (MMSb), and dimethyl antimony (DMSb) in the soluble fraction vs. $E_{H\text{ at pH } 5}$ in the slurry of microcosm No. 3 ($n = 9$).

Kumpiene et al. (2009). Accordingly, Cd, Cu, Ni, and Zn were soluble at low pH, while higher pH values decreased the solubility of these metals (Fig. 4). One reason for that can be the desorption of metal cations from organic matter or the surface of clay minerals and other sorbents at low pH (Bourg and Gustav Loch, 1995; Du Laing et al., 2009c). Several authors also proved that acidic conditions mobilize Cd, Zn, and Ni (Wiegand et al., 2009; Müller et al., 2010). For example, Chuan et al. (1996) detected that Cd and Zn solubilities were significantly higher at pH 5 in comparison to pH 8 and increased drastically at pH 3.3. Lair et al. (2008) found that the amounts of desorbable and weakly bound Cd were higher in floodplain soils with low pH compared to floodplain soils

with higher pH. Furthermore, Cu is reported to be mobile at low pH (Kumpiene et al., 2009) with a mobility threshold of pH 5.5 (Graf et al., 2007). Thus, the acidic pH in the slurry seemed to enhance the mobility of the metals in our study. Nevertheless, with regard to the small range of pH variations (Table 2), other factors can also be considered as important to explain the variability of the observed metal concentrations. This is confirmed by the closer relations between E_H and metals (Fig. 3) in comparison to the correlations between pH and metals (Fig. 4).

Iron (hydr)oxides are assumed to be important binding agents for heavy metals under oxic conditions. Metal concentrations can decrease with rising E_H and decreasing Fe concentrations since they co-

Table 3
Relations between inorganic arsenic (As_i), monomethyl arsenic (MMAs), dimethyl arsenic (DMAs), inorganic antimony (Sb_i), monomethyl antimony (MMSb), dimethyl antimony (DMSb), and total iron (Fe) in the soluble fraction of microcosm No. 3 expressed by Pearson's correlation coefficient r ($n = 9$; *significance level <0.05; **significance level <0.01).

	Fe	As _i	MMAs	DMAs	Sb _i	MMSb	DMSb
As _i	0.847(**)	1	0.865(**)	0.959(**)	0.981(**)	0.950(**)	0.169
MMAs	0.64	0.865(**)	1	0.739(*)	0.888(**)	0.776(*)	−0.1
DMAs	0.907(**)	0.959(**)	0.739(*)	1	0.908(**)	0.963(**)	0.394
Sb _i	0.792(*)	0.981(**)	0.888(**)	0.908(**)	1	0.942(**)	0.104
MMSb	0.917(**)	0.950(**)	0.776(*)	0.963(**)	0.942(**)	1	0.417
DMSb	0.534	0.169	−0.1	0.394	0.104	0.417	1

precipitate with Fe (hydr)oxides (e.g., Du Laing et al., 2009c; Borch et al., 2010). However, Cd, Cu, Ni, and Zn did not decrease when Fe concentrations decreased at increasing E_H in our study (Fig. 3). This might indicate that these elements may not directly co-precipitate with Fe (hydr)oxides under our experimental conditions, which is in agreement with results reported by some other authors. Kumpiene et al. (2009) who also worked under acidic pH conditions, detected high Ni solubilities in soils amended with Fe which they attributed to the low affinity of Ni to Fe oxides. Similar to our results, Cappuyns and Swennen (2005) and Caetano et al. (2003) did not observe a co-precipitation of Cd with Fe (hydr)oxides, whereas Cu was not affected by the dissolution of Fe oxides in the study of Tack et al. (1998). However, other studies reported contrasting results. According to Graf et al. (2007) who worked with different soils in the pH range from 5 to 8, Fe (hydr)oxides were able to retain Cu, while Chuan et al. (1996) observed low Cd and Zn solubilities at high E_H at pH 5. They attributed this to adsorption of metals on Fe (hydr)oxides at high E_H . Differences between our data and those reported in literature may be explained by several factors.

First, the relatively low pH in our study might have prevented heavy metals from co-precipitating with or adsorbing to Fe oxides. Generally, the adsorption capacity of Fe (hydr)oxides for metals is low at low pH (Schulz-Zunkel and Krüger, 2009). For example, the adsorption of metals on goethite is reported to be low around pH 6 and lower and increases with rising pH (Spark et al., 1995; Mustafa et al., 2006).

The role of organic material should be considered as a second possible explanation. Organic matter has a high capacity to complex and adsorb cations due to the presence of many negatively charged groups (Laveuf and Cornu, 2009). Grybos et al. (2007) showed that the dominant factor affecting metal fate is organic matter release. Complexation with dissolved organic matter is especially important for Cu due to its high affinity to organic ligands (Schröder et al., 2008; Du Laing et al., 2009c), but Cd and Ni can also be mobilized by dissolved organic material (Koretsky et al., 2007; Schröder et al., 2008; Schulz-Zunkel and Krüger, 2009), whereas Zn is rarely associated with DOC (Kalbitz and Wennrich, 1998; Schröder et al., 2008; Beesley et al., 2010). Thus, considering the high amounts of DOC in our study (Table 2), it is possible that the formation of mobile metal–DOC complexes under oxidizing conditions prevented heavy metals (especially Cu) from co-precipitating with or adsorbing to Fe (hydr)oxides.

Thirdly, Ni, Cu, Zn, and Cd could be assumed to be rather associated with Mn oxides than with Fe oxides, which have previously also been reported by other authors (Palumbo et al., 2001; Liu et al., 2002; Schulz-Zunkel and Krüger, 2009). As discussed in Section 4.2, due to the low pH Mn (hydr)oxides did not precipitate in a considerable amount in our study, whereas close correlations between Fe and Mn (hydr)oxides were often found in other studies (e.g., Knox et al., 2006; Du Laing et al., 2007).

The low Cd, Cu, Mn, Ni, and Zn concentrations at low E_H in our experiment (Fig. 3) could be caused by sulphide precipitation, as also found by other authors (Carbonell et al., 1999; Koretsky et al., 2007; Schröder et al., 2008; Van der Geest and Paumen, 2008; Du Laing et al., 2007, 2008, 2009a,b). The dark colour and the typical odour suggest that sulphides were formed in the MCs at reducing conditions in our experiment. Nevertheless, a significant relation between SO_4^{2-} contents

and E_H could not be detected. This might be due to the fact that total SO_4^{2-} concentrations are often poor indicators of SO_4^{2-} reduction rates due to rapid internal cycling of sulphur in wetlands (Koretsky et al., 2007). Moreover, only a very small amount of sulphides is needed to precipitate all Cd, Cu, Ni, and Zn. This amount may even not be detectable with common titration-based procedures for sulphide determination (Du Laing et al., 2007, 2008).

In contrast, total Fe was generally soluble under reducing conditions (Fig. 3e), although Fe is also expected to precipitate as sulphides (Yu et al., 2007). On the one hand, the relatively low pH in our experiment might have inhibited the precipitation of FeS under reducing conditions, since FeS is reported to be soluble in acidic solutions (Liu et al., 2009). On the other hand, sulphides will preferentially precipitate with Cd, Cu, Ni, and Zn because the solubility of CdS, CuS, NiS, and ZnS is lower in comparison to FeS (Du Laing et al., 2007). As Fe availability is also higher than Cd, Cu, Ni, and Zn availabilities, a higher amount of sulphides is needed to precipitate more Fe. If this amount is lacking in a sulphide-poor soil, Fe will stay in solution, whereas Cd, Cu, Ni, and Zn are precipitated as sulphides (Du Laing et al., 2008).

Elements which are bound to sulphides can be released during the oxidation of the soil due to the oxidation of sulphides to sulphates (Du Laing et al., 2009a,b,c). This might be one reason for the increasing solubility of the metals with increasing E_H (Fig. 3). The fact that Cd and Cu started to be mobilized at higher E_H in comparison to Ni, Mn, and Zn (Fig. 3) also confirms the role of sulphide precipitation. On the one hand, fewer sulphides are needed to precipitate the available Cd and Cu in comparison to the more available Ni, Mn, and Zn. On the other hand, the stability of sulphides of Cd and Cu is higher in comparison to the stability of sulphides of Ni, Mn, and Zn (Du Laing et al., 2008). This implies that Cd and Cu will stay longer in the solid soil phase when the amount of sulphides gradually decreases during gradual oxidation.

4.4. Impact of E_H on the mobility and methylation of As and Sb

Concentrations of As_i and Sb_i showed a similar behaviour in our experiment. Mobility of both As_i and Sb_i was significantly lower under oxic than under anoxic conditions (Fig. 5), which is in agreement with previous studies (Masscheleyn et al., 1991; Mitsunobu et al., 2006). First, increased As_i and Sb_i mobility under reducing conditions can be attributed to the reduction of Fe (hydr)oxides and concurrent release of associated As and Sb (Mitsunobu et al., 2006). This is confirmed by the positive correlation between As_i and Sb_i with Fe (Table 3). Second, reduction of arsenate to arsenite can enhance As mobility under reducing conditions (Masscheleyn et al., 1991; Mitsunobu et al., 2006; Du Laing et al., 2009a). The behaviour of Sb is less studied compared to As. In contrast to As (V), Sb (V) was found to be a stable oxidation state even under reducing conditions. Thus, dissolved Sb concentrations are reported not to increase under reducing conditions at pH 8 (Mitsunobu et al., 2006). Conditions were slightly acidic in our experiment, which might have led to a different behaviour of Sb.

Concerning the formation of methylated species, we found a significant relation between E_H and MMAs, MMSb, and DMAs. These relations give a strong indication that the degree of methylation

increased under reducing conditions resp. decreased under oxidizing conditions. There are different studies about the methylation of As and Sb in the human body (e.g., Kojima et al., 2009; Diaz-Bone and Van der Wiele, 2010). In contrast to that, studies about methylation of As and Sb in soils are very scarce. Both As and Sb are subject to biomethylation (i.e. addition of CH₃ through biological activity) under oxic as well as anoxic conditions (Bentley and Chasteen, 2002; Thayer, 2002). This methylation process has been proven to be conducted by a broad spectrum of both microorganisms and higher organisms. Whereas metals are primarily methylated by bacteria, metalloids are preferably methylated by fungi (e.g., *Scopulariopsis brevicaulis*), yeasts and algae (Thayer, 2002). Arsenic is also methylated by a wide range of bacteria (e.g., members of the genera *Enterobacter*, *Pseudomonas*, *Methanobacterium* and *Bacillus*; Cullen and Reimer, 1989). Methylantimony compounds are almost exclusively generated by fungi and bacteria (Thayer, 2002). Since fungi have been very rarely detected in long term inundated floodplain soils (Rinklebe and Langer, 2006, 2008; Langer and Rinklebe, 2009) we can assume that bacteria might be more important for the process of biomethylation than fungi in those soils. In biological systems, arsenate is reduced to arsenite which can be methylated according to the Challenger mechanism (Challenger, 1978). Introduction of methyl groups onto atoms can enhance the solubility in lipids which might increase their toxicity for organisms (Thayer, 2002; Craig, 2003).

Reducing conditions seem to enhance the mobility of As and Sb in our study. While in our study a relation between E_H and methylated As and Sb was found, a similar relationship was not observed by Düster et al. (2008) when studying an undisturbed sediment core in a laboratory incubation experiment, presumably because the effects of redox conditions were superseded by the complex effects of time and depth in this setup. Similar to Düster et al. (2008) the relative proportion of methylated species to their inorganic counterparts was higher for Sb than for As (data not shown). However, due to the high total As concentration, absolute levels for methylated As species were higher than those of methylated Sb species, at least under reducing conditions.

The high relative proportion of DMSb under oxic conditions is surprising, but can likely be explained by the conduction of the experiments in consecutive row starting from anoxic to oxic conditions. As biotransformation of Sb is slower in comparison to As (Thayer, 2002; Düster et al., 2008) it can be suggested that DMSb is kinetically stable enough to remain relatively constant during the experimental time. Overall, our data show that methylation of As and Sb occurred under changing redox conditions.

5. Conclusions

The E_H was found to be an important factor controlling the mobility of metals in an acidic floodplain soil (pH between 4.4 and 5.3). Oxidizing conditions facilitate the mobility of Cd, Cu, Mn, Ni, and Zn to a great extent in the studied soil, which may be attributed to dissolution of sulphides and the resulted release of metals. The solubility of Fe is mainly controlled by the formation of Fe (hydr)oxides under oxidizing conditions and their dissolution under reducing conditions. However, the adsorption of Cd, Cu, Mn, Ni, and Zn on Fe and/or a co-precipitation with Fe seem to be hindered in our experiment. Manganese does not precipitate as Mn (hydr)oxides at high E_H due to the low pH. Low E_H promotes the formation of MMAs, MMSb, and DMAs. Our results suggest that the mobility of Cd, Cu, Ni, and Zn should decrease when this acid soil is flooded whereas the mobility of As and Sb should increase under flooding conditions.

However, although the metal concentrations measured in the solution might be considered as levels close to field conditions a verification of the detected dynamics and processes at various scales (e.g., Rennert et al., 2010; Rupp et al., 2010) including field conditions is recommended in future. Moreover, similar studies should be conducted with further acid soils from the Wupper River and various frequently flooded soils world-wide.

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References

- Agbenin, J.O., 2003. Extractable iron and aluminium effects on phosphate sorption in a Savannah alfisol. *Soil Sci. Soc. Am. J.* 67, 589–595.
- Alewel, C., Paul, S., Lischeid, G., Storck, F.R., 2008. Co-regulation of redox processes in freshwater wetlands as a function of organic matter availability. *Sci. Total Environ.* 404, 335–342.
- BBodSchV, 1999. Directive of the execution of the federal protection act (Federal soil protection and hazardous waste directive – BBodSchV) (in German). *Bundesgesetzblatt* 1554–1582.
- Beesley, L., Moreno-Jimenez, E., Clemente, R., Lepp, N., Dickson, N., 2010. Mobility of arsenic, cadmium and zinc in a multi-element contaminated soil profile assessed by in-situ soil pore water sampling, column leaching and sequential extraction. *Environ. Pollut.* 158, 155–160.
- Bentley, R., Chasteen, T.G., 2002. Microbial methylation of metalloids: arsenic, antimony, and bismuth. *Microbiol. Mol. Biol. R.* 66, 250–271.
- Borch, T., Kretzschmar, R., Kapper, A., Van Cappellen, P., Ginder-Vogel, M., Voegelin, A., Campbell, K., 2010. Biogeochemical redox processes and their impact on contaminant dynamics. *Environ. Sci. Technol.* 44, 15–23.
- Bourg, A.C.M., Gustav Loch, J.P., 1995. Mobilization of heavy metals as affected by pH and redox conditions. In: Salomons, W., Stigliani, W.M. (Eds.), *Biogeochemistry of Pollutants in Soils and Sediments*. Springer, Berlin.
- Brümmer, G., 1974. Redoxpotentiale und Redoxprozesse von Mangan-, Eisen- und Schwefelverbindungen in hydromorphen Böden und Sedimenten. *Geoderma* 12, 207–222.
- Burkhardt, E.-M., Akob, D.M., Bischoff, S., Sitte, J., Kostka, J.E., Banerjee, D., Scheinost, A.C., Küsel, K., 2010. Impact of biostimulated redox processes on metal dynamics in an iron-rich creek soil of a former uranium mining area. *Environ. Sci. Technol.* 44, 177–183.
- Buykx, S.E.J., Bleijenberg, M., van den Hoop, A.G.T., Gustav Loch, J.P., 2000. The effect of oxidation and acidification on the speciation of heavy metals in sulfide-rich freshwater sediments using a sequential extraction procedure. *J. Environ. Mon.* 2, 23–27.
- Caetano, M., Madureira, M.-J., Vale, C., 2003. Metal remobilization during resuspension of anoxic contaminated sediment: short-term laboratory study. *Water Air Soil Poll.* 143, 23–40.
- Cappuyns, V., Swennen, R., 2005. Kinetics of element release during combined oxidation and pH_{stat} leaching of anoxic river sediments. *Appl. Geochem.* 20, 1169–1179.
- Carbonell, A.A., Porthouse, J.D., Mulbah, C.K., DeLaune, R.D., Patrick, W.H., 1999. Metal solubility in phosphogypsum-amended sediment under controlled pH and redox conditions. *J. Environ. Qual.* 28, 232–242.
- Chadwick, O.A., Chorover, J., 2001. The chemistry of pedogenic thresholds. *Geoderma* 100, 321–353.
- Challenger, F., 1978. Biosynthesis of organometallic and organometalloid compounds. In: Brinckman, F.E., Bellama, J.M. (Eds.), *Organometals and Organometalloids: Occurrence and Fate in the Environment*, ACS Symposium Series 82. American Chemical Society, Washington DC.
- Chuan, M.C., Shu, G.Y., Liu, J.C., 1996. Solubility of heavy metals in a contaminated soil: effects of redox potential and pH. *Water Air Soil Poll.* 90, 543–556.
- Craig, P.J., 2003. *Organometallic Compounds in the Environment: Principles and Reactions*. John Wiley & Sons Inc., New York.
- Cullen, W.R., Reimer, K.J., 1989. Arsenic speciation in the environment. *Chem. Rev.* 89, 713–764.
- DeLaune, R.D., Reddy, C.N., Patrick Jr., W.H., 1981. Organic matter decomposition in soils as influenced by pH and redox conditions. *Soil Biol. Biochem.* 13, 533–534.
- Handbuch der Bodenuntersuchung, 2000. Und Ergänzungslieferungen Bd. 1 bis 7. DIN Vorschriften. Wiley-VCH Beuth, Berlin, Wien, Zürich.
- Devai, I., Patrick, W.H., Neue, H.-U., DeLaune, R.D., Kongchum, M., Rinklebe, J., 2005. Methyl mercury and heavy metal content in soils of rivers Saale and Elbe (Germany). *Anal. Lett.* 38, 1037–1048.
- Diaz-Bone, R.A., Hitzke, M., 2008. Multi-element organometal(loid) speciation by hydride generation-GC-ICP-MS: overcoming the problem of species-specific optima by using a pH-gradient during derivatization. *J. Anal. Atom. Spectrom.* 23, 861–870.
- Diaz-Bone, R.A., Van der Wiele, T.R., 2010. Biotransformation of metal(loid)s by intestinal microorganisms. *J. Macromol. Sci. A Pure Appl. Chem.* 82, 409–427.
- Du Laing, G., Vanthuyne, D.R.J., Vandecasteele, B., Tack, F.M.G., Verloo, M.G., 2007. Influence of hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil. *Environ. Pollut.* 147, 615–625.
- Du Laing, G., De Meyer, B., Meers, E., Lesage, E., Van de Moortel, A., Tack, F.M.G., Verloo, M.G., 2008. Metal accumulation in intertidal marshes: role of sulphide precipitation. *Wetlands* 28, 735–746.
- Du Laing, G., Meers, E., Dewispelaere, M., Rinklebe, J., Vandecasteele, B., Verloo, M.G., Tack, F.M.G., 2009a. Effect of water table level on metal mobility at different depths in wetland soils of the Scheldt Estuary (Belgium). *Water Air Soil Poll.* 202, 353–367.
- Du Laing, G., Meers, E., Dewispelaere, M., Vandecasteele, B., Rinklebe, J., Tack, F.M.G., Verloo, M.G., 2009b. Heavy metal mobility in intertidal sediments of the Scheldt estuary: field monitoring. *Sci. Total Environ.* 407, 2919–2930.

- Du Laing, G., Rinklebe, J., Vandecasteele, B., Tack, F.M.G., 2009c. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: a review. *Sci. Total Environ.* 407, 3972–3985.
- Düster, L., Vink, J.P.M., Hirner, A.V., 2008. Methylantimony and -arsenic species in sediment pore water tested with the sediment or fauna incubation experiment. *Environ. Sci. Technol.* 42, 5866–5871.
- Feldmann, J., 1997. Summary of a calibration method for the determination of volatile metal(loid) compounds in environmental gas samples by using gas chromatography inductively coupled plasma mass spectrometry. *J. Anal. Atom. Spectrom.* 12, 1069–1076.
- Fiedler, S., Sommer, M., 2004. Water and redox conditions in wetland soils – their influence on pedogenic oxides and morphology. *Soil Sci. Soc. Am. J.* 68, 326–335.
- Gambrell, R.P., 1994. Trace and toxic metals in wetlands – a review. *J. Environ. Qual.* 23, 883–891.
- Graf, M., Lair, G.J., Zehetner, F., Gerzabek, M.H., 2007. Geochemical fractions of copper in soil chronosequences of selected European floodplains. *Environ. Pollut.* 148, 788–796.
- Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? *J. Colloid. Interf. Sci.* 314, 490–501.
- Grybos, M., Davranche, M., Gruau, G., Petitjean, P., Pedrot, M., 2009. Increasing pH drives organic matter solubilization from wetland soils under reducing conditions. *Geoderma* 154, 13–19.
- Herbel, M.J., Suarez, D.L., Goldberg, S., Gao, S., 2007. Evaluation of chemical amendments for pH and redox stabilization in aqueous suspensions of three California soils. *Soil Sci. Soc. Am. J.* 71, 927–939.
- World reference base for soil resources. In: IUSS-ISRIC-FAO (Ed.), A Framework for International Classification, Correlation and Communication, 103. World Soil Resources Reports, S., Rome (FAO), p. 128.
- Kalbitz, K., Wennrich, R., 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Sci. Total Environ.* 209, 27–39.
- Kaplan, D.I., Knox, A.S., 2007. Wet/Dry cycling effects on soil contaminant stabilization with apatite and Fe(O). *J. Mater. Civ. Eng.* 19, 49–57.
- Knox, A.S., Paller, M.H., Nelson, E.A., Specht, W.L., Halverson, N.V., Gladden, J.B., 2006. Metal distribution and stability in constructed wetland sediments. *J. Environ. Qual.* 35, 1948–1959.
- Kojima, C., Ramirez, D.C., Tokar, E.J., Himeno, S., Drobna, Z., Stylo, M., Mason, R.P., Waalkes, M.P., 2009. Requirement of arsenic biomethylation for oxidative DNA damage. *J. Natl. Cancer J.* 101, 1670–1681.
- Koretsky, C.M., Haveman, M., Beuving, L., Cuellar, A., Shattuck, T., Wagner, M., 2007. Spatial variation of redox and trace metal geochemistry in a minerotrophic fen. *Biogeochemistry* 86, 33–62.
- Kumpiene, J., Ragnvaldsson, D., Lövgren, L., Tefalidit, S., Gustavsson, B., Lättström, A., Leffler, P., Maurice, C., 2009. Impact of water saturation level on arsenic and metal mobility in the Fe-amended soil. *Chemosphere* 74, 206–215.
- Lair, G.J., Graf, M., Zehetner, F., Gerzabek, M.H., 2008. Distribution of cadmium among geochemical fractions in floodplain soils of progressing development. *Environ. Pollut.* 156, 207–214.
- Langer, U., Rinklebe, J., 2009. Lipid biomarkers for assessment of microbial communities in floodplain soils of the Elbe River (Germany). *Wetlands* 29, 353–362.
- Laveuf, C., Cornu, S., 2009. A review on potentiality of Rare Earth Elements to trace pedogenetic processes. *Geoderma* 154, 1–12.
- Liu, F., Colombo, C., Adamo, P., He, J.Z., Violante, A., 2002. Trace elements in manganese-iron nodules from a Chinese alfisol. *Soil Sci. Soc. Am. J.* 66, 661–670.
- Liu, J., Valsaraj, K.T., DeLaune, R.D., 2009. Inhibition of mercury methylation by iron sulfides in an anoxic sediment. *Environ. Eng. Sci.* 26, 833–840.
- Masscheleyn, P.H., DeLaune, R., William, H.P., 1991. Effect of redox potential and pH on arsenic speciation and solubility in a contaminated soil. *Environ. Sci. Technol.* 25, 1414–1419.
- Massmann, G., Pekdeger, A., Merz, C., 2004. Redox processes in the Oderbruch polder groundwater flow system in Germany. *Appl. Geochem.* 19, 863–886.
- Mehra, O.P., Jackson, M.L., 1960. Iron removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. *Clays Clay Miner.* 7, 317–327.
- Miller, F.S., Kilminster, K.L., Degens, B., Firms, G.W., 2010. Relationship between metals leached and soil type from potential acid sulphate soils under acidic and neutral conditions in Western Australia. *Water Air Soil Poll.* 205, 133–147.
- Mitsunobu, S., Harada, T., Takahashi, Y., 2006. Comparison of antimony behaviour with that of arsenic under various soil redox conditions. *Environ. Sci. Technol.* 40, 7270–7276.
- Mustafa, G., Kookana, R.S., Singh, B., 2006. Desorption of cadmium from goethite: effects of pH, temperature and aging. *Chemosphere* 64, 856–865.
- Palumbo, B., Bellanca, A., Neri, R., Roe, M.J., 2001. Trace metal partitioning in Fe–Mn nodules from Sicilian soils Italy. *Chem. Geol.* 173, 257–269.
- Patrick, W.H., Verloo, M., 1998. Distribution of soluble heavy metals between ionic and complexed forms in a saturated sediment as affected by pH and redox conditions. *Wat. Sci. Technol.* 37, 165–172.
- Ponnamperuma, F.N., 1972. Chemistry of submerged soils. *Adv. Agron.* 24, 29–96.
- Reddy, K.R., DeLaune, R.D., 2008. *Biogeochemistry of Wetlands: Science and Applications*. Taylor & Francis Group, LLC, Boca Raton/London, New York.
- Rennert, T., Mansfeldt, T., 2006. Release of trace metals, sulfate and complexed cyanide from soils contaminated with gas-purifier wastes: a microcosm study. *Environ. Pollut.* 139, 86–94.
- Rennert, T., Rinklebe, J., 2010. Release of Ni and Zn from contaminated floodplain soils under saturated flow conditions. *Water Air Soil Pollut.* 205, 93–105.
- Rennert, T., Meißner, S., Rinklebe, J., Totsche, K.U., 2010. Dissolved inorganic contaminants in a floodplain soil: comparison of in-situ soil solutions and laboratory methods. *Water Air Soil Pollut.* 209, 489–500.
- Rinklebe, J., Langer, U., 2006. Microbial diversity in three floodplain soils at the Elbe River (Germany). *Soil Biol. Biochem.* 38, 2144–2151.
- Rinklebe, J., Langer, U., 2008. Floodplain soils at the Elbe River, Germany, and their diverse microbial biomass. *Arch. Agron. Soil Sci.* 54, 259–273.
- Rinklebe, J., Franke, C., Neue, H.-U., 2007. Aggregation of floodplain soils as an instrument for predicting concentrations of nutrients and pollutants. *Geoderma* 141, 210–223.
- Rinklebe, J., Düring, A., Overesch, M., Du Laing, G., Wennrich, R., Stärk, H.-J., Mothes, S., 2010. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. *Environ. Pollut.* 158, 308–318.
- Rupp, H., Rinklebe, J., Bolze, S., Meissner, R., 2010. A scale depended approach to study pollution control processes in wetland soils using three different techniques. *Ecol. Eng.* 36, 1439–1447.
- Schenk, R., 1994. Verteilung und Dynamik von Schwermetallen in Sedimenten der Wupper. Heinrich-Heine Universität Düsseldorf, Dissertation.
- Schlichting, E., Blume, H.-P., Stahr, K., 1995. *Bodenkundliches Praktikum*. Blackwell, Berlin.
- Schröder, T.J., Van Riemsdijk, W.H., Van der Zee, S.E.A.T.M., Vink, J.P.M., 2008. Monitoring and modelling of the solid-solution partitioning of metals and As in a river floodplain redox sequence. *Appl. Geochem.* 23, 2350–2363.
- Schulz-Zunkel, C., Krüger, F., 2009. Trace metal dynamics in floodplain soils of the river Elbe: a review. *J. Environ. Qual.* 38, 1349–1362.
- Schwertmann, U., 1964. Differenzierung der Eisenoxide des Bodens durch Extraktion mit Ammoniumoxalat-Lösung. *Z. Pflanzenernähr. Bodenk.* 105, 194–202 (former: *Zeitschrift für Pflanzenernährung, Düngung und Bodenkunde*).
- Spark, K.M., Johnson, B.B., Wells, J.D., 1995. Characterizing heavy-metal adsorption on oxides and oxyhydroxides. *Eur. J. Soil Sci.* 46, 621–631.
- Tack, F.M.G., Singh, S.P., Verloo, M.G., 1998. Heavy metal concentrations in consecutive saturation extracts of dredged sediment derived surface soils. *Environ. Pollut.* 103, 109–115.
- Takeno, N., Atlas of Eh–pH diagrams, Intercomparison of thermodynamic databases, Geological Survey of Japan Open File Report No. 419, 2005. <http://www.gsj.jp/GDB/openfile/files/no0419/openfile419e.pdf>. Cited 11 February 2010.
- Thayer, J.S., 2002. Review: biological methylation of less-studied elements. *Appl. Organomet. Chem.* 16, 677–691.
- Van den Berg, G.A., Gustav Loch, J.P., Van der Heijden, L.M., Zwolsman, J.J.G., 2000. Geochemical behaviour of trace metals in freshwater sediments. In: Markert, B., Friese, K. (Eds.), *Trace Elements: Their Distribution and Effects in the Environment*. Elsevier, Amsterdam.
- Van der Geest, H.G., Paumen, M.L., 2008. Dynamics of metal availability and toxicity in historically polluted floodplain sediments. *Sci. Total Environ.* 108, 419–425.
- Van Griethuysen, C., Luitwieler, M., Joziassie, J., Koelmans, A.A., 2005. Temporal variation of trace metal geochemistry in floodplain lake sediment subject to dynamic hydrological conditions. *Environ. Pollut.* 137, 281–294.
- Vink, J.P.M., 2002. Measurement of heavy metal speciation over redox gradients in natural water – sediment interfaces and implications for uptake by benthic organisms. *Environ. Sci. Technol.* 36, 5130–5138.
- Deutscher Wetterdienst, 2009. Wetter und Klima - Deutscher Wetterdienst - Klimadaten. http://www.dwd.de/bvbw/appmanager/bvbw/dwdwww/Desktop?_nfpb=true&_pageLabel=_dwdwww_klima_umwelt_klimadaten_deutschland%282002gsbDocumentPath=Navigation%2FOeffentlichkeit%2FKlima_Umwelt%2FKlimadaten%2FKldaten_kostenfrei%2Fausgabe_mittelwerte_node.html_nnn%3Dtrue. Cited 2 Dec 2009.
- Wiegand, J., Aschan, G., Kraus, U., Pointek, J., Mederer, J., 2009. Chemical fractionation and soil-to-plant transfer characteristics of heavy metals in a sludge deposit field of the river Ruhr, Germany. *Soil Sediment Contam.* 18, 14–29.
- Wuppertal, 2009. FluGGs: FlussgebietsGeoinformationsSystem des Wuppertalverbandes. <http://fluggs.wuppertal.de/internet/initParams.do>. Cited 15 Dec 2009.
- Yu, K., Böhme, F., Rinklebe, J., Neue, H.-U., DeLaune, R.D., 2007. Major biogeochemical processes in soils – a microcosm incubation from reducing to oxidizing conditions. *Soil Sci. Soc. Am. J.* 71, 1406–1417.