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Arsenic fixation on iron-hydroxide-rich and plant litter-containing sediments in natural environments

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Abstract Iron-hydroxide-rich and plant litter-containing sediments from natural sites contaminated with uranium mine tailing leachates were examined for their ability to adsorb arsenic. The samples with high contents of iron hydroxides (Fe_{total} concentration, $> 300 \text{ g kg}^{-1}$) exhibited remarkable fixation of arsenic (up to 40 g As kg^{-1}). This value corresponded approximately to the supersaturation point for natural iron hydroxides under the present conditions, and it was significantly lower than the value found for synthetic iron hydroxides. There was a strong correlation ($R=0.8999$) between the concentration of iron and

that of arsenic at low arsenic contents, indicating adsorption on strong binding sites. Although all the samples had noticeable contents of organic carbon (plant litter), calcium, and manganese, no obvious effect of these elements on arsenic fixation could be detected. The amount of iron hydroxides was found the only fixation-controlling parameter immediately below a leaching water source.

Keywords Adsorption capacity · Alkaline neutral waters · Uranium tailings · Ore mountains

Introduction

Arsenic is a toxic element found ubiquitously in the environment. Arsenic accumulations in soil, groundwater, and surface water, resulting from natural processes (e.g., in Bangladesh and South India; Anawar et al. 2003) as well as from human activities (Pichler et al. 2001; Mkandawire and Dudel 2005), remain a major public health hazard.

Uranium mining activities in the Saxon Erzgebirge (Ore Mountains, southeastern Germany), which lasted several centuries, also created an arsenic problem. The last mining of uranium occurred in 1945–1990 (OECD 1999). The Bi–Co–Ni(–Ag–U) formation contains arsenic (Schuppan et al. 1994), suggesting that the element can accumulate in dumps and tailings as part of the residuals after digging and processing. The two commonly used methods of uranium extraction from ore are

alkaline treatment and extraction with strong acids. The fate of arsenic in tailings and dumps after acidic extraction ore processing is already the focus of research (acid mine drainage; e.g., Wang et al. 2003). But comparatively less research has been done to investigate the behaviour of arsenic in neutral and alkaline leachates resulting from application of alkaline ore processing (Mkandawire and Dudel 2005).

Remediation of arsenic-contaminated environments is based on different functional principles; however, long-term and cost-saving methods should be preferred (Banks et al. 1997; Dudel et al. 2004). Treatments exploiting (enhanced) natural attenuation offer the possibility of effective, low-cost remediation (Bissen and Frimmel 2003). Arsenic adsorption and coprecipitation on iron hydroxides were intensively studied (Pierce and Moore 1982; Fuller et al. 1993; Jain et al. 1999). Those experiments were generally restricted to synthetic, lab-

oratory-made iron hydroxides. In natural systems, however, the potentially adsorption-controlling parameters are more complex than they are under controlled laboratory conditions. Examples are:

1. More complex compositions of natural iron hydroxides, as compared with those of synthetic ones (Perret et al. 2000), and the influence of various iron/contaminant ratios on iron hydroxide formation (Robins 1988).
2. (Seasonal) Fluctuations of environmental parameters [pH, temperature, O₂ content (Laforce et al. 2000)] and alteration of iron hydroxides with time (Mc Geehan et al. 1998; Ford 2002).
3. Influence of primary production (organic carbon) on pristine water and allochthonous inputs (e.g., litter) in open systems (Hu et al. 2002).
4. Competition, complexation, and other interactions with the present organic and inorganic ions, e.g., with phosphate and (bi)carbonate (Holm 2002) and with dissolved organic matter (DOC) (Grafe et al. 2001).
5. Biotic interferences on arsenic removal (Heeraman et al. 2001).

In this work, we examine the fixation of arsenic on sediments at natural sites contaminated by circumneutral tailings leachates and we discuss the differences in arsenic adsorption between synthetic and natural iron hydroxides. Specifically, we seek answers to the following questions:

1. How does the elemental composition of the sediments rich in naturally formed iron hydroxides formed in seepage water differ from that of synthesized iron hydroxides?
2. Is there a significant relation between the content of iron hydroxides and the fixation of arsenic? What environmental factors influence the strength of the relationship?
3. What is the quantitative difference in arsenic fixation between samples rich in iron hydroxides [subsequently, iron-hydroxide-rich (IHR)] and samples predominated by plant litter [subsequently, litter-containing (LC)]?
4. What is the role of manganese oxides and calcium–arsenic phases, known for their ability to take up arsenic, in the total fixation of arsenic under the present neutral and alkaline conditions of the sampling sites?

Materials and methods

Sampling sites

Uranium tailing areas near Lengsfeld (southwestern Saxony, Germany) were chosen as the sampling sites

(Fig. 1). Each sampling site contained several sampling points.

The sampling sites showed different extents of contamination by the tailing leachates because of their different relative altitudes below the tailing. Although all the sites were located very close to the tailing, we distinguished between reference and contaminated sites on the basis of the most probable leachate flow path. In contrast to the reference site, the contaminated sites were situated around the points of the tailings leachate discharge. Because of the different water supply, one contaminated site was alternately wet and dry (contaminated site 1, CS1) whereas the other was permanently wet (contaminated site 2, CS2). We assumed that at all the sampling points, dissolved oxygen was available because we observed a constant precipitation of iron hydroxides. The earlier detection of nitrate in the sampling sites also indicated the existence of aerobic conditions. Sampling was conducted four times in February–June 2002.

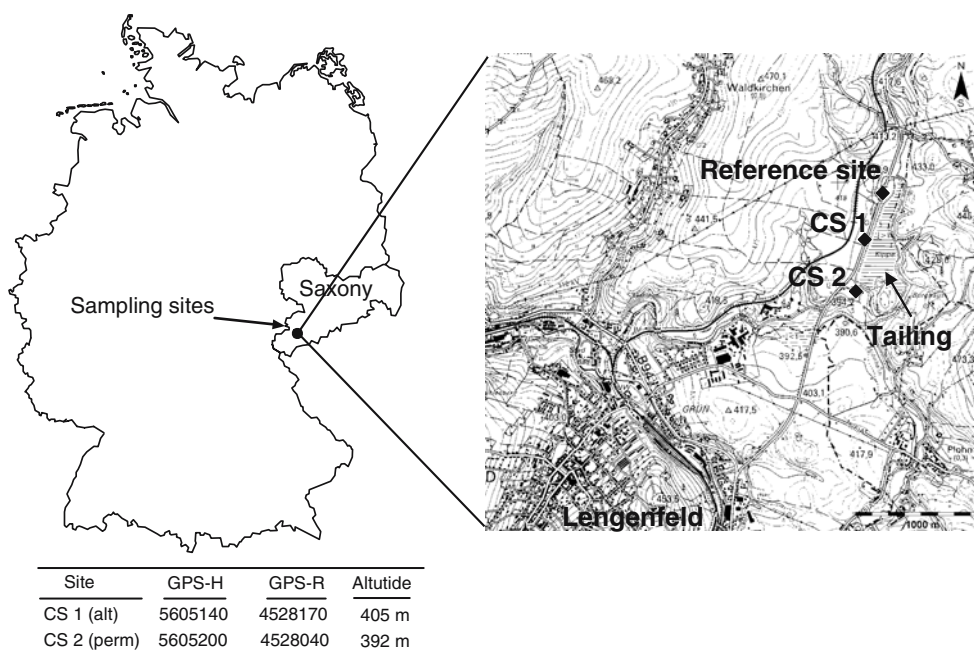
Analytical procedures

The water samples were filtered through 0.45- μm -pore-size cellulose nitrate filters (Sartorius AG, Germany) within 24 h after sampling. They were then acidified with 2 ml of 65% HNO₃ (Suprapur[®]; Merck, Germany) per 100 ml of sample. Before and after acidification, all water samples were stored in a (mobile) refrigerator at 4°C. All sediments showed similar muddy characteristics. A macroscopic litter fraction was found in the sediment samples, leading us to class the samples into those with a high content of iron hydroxides (IHR) and those predominated by vascular plant litter (LC). The litter fraction was dominated mainly by twigs, needles and leaf fragments but also contained roots, and grass. Both IHR and LC were air-dried for 2 weeks, then dried at 40°C until mass constancy, and finally ground in a planetary agate mill (Pulverisette 5; Fritsch, Germany). The ground samples were digested by microwave-assisted acid digestion (microwave MDS-2000; CEM, Germany) in Teflon containers.

For IHR sediments, 500 mg of sample was mixed with aqua regia [1:1 (v/v) 65% HNO₃ (Suprapur[®]) and 37% HCl (Rotipur[®]; Roth, Germany)]. For LC sediments, 200 mg of sample was treated with 3 ml of HNO₃ (Suprapur[®]) and 2 ml of 30% H₂O₂ (analytical grade; J. T. Baker, USA). The digested material was made up to 50 and 20 ml, respectively, with ultrapure deionised water (18.2 M Ω cm⁻¹; Barnstedt, USA).

The digested samples were used for the determination of arsenic, iron, manganese, calcium, and magnesium. Arsenic was measured by inductively coupled plasma mass spectrometry (ICP-MS; PQ 2 +; Thermo Elemental, USA), and the other elements were determined by flame atomic absorption spectrometry (FAAS, Solar

Fig. 1 Location of sampling sites. *Alt* alternately wet and dry, *CS* contaminated site, *GPS-H* global positioning system height value, *GPS-R* global positioning system right value, *Perm* permanently wet



M-Series; Thermo Elemental, USA). Some of the samples, chosen over a wide concentration range of arsenic, were analysed for arsenic simultaneously by ICP-MS and by graphite furnace AAS (Solaar M-Series; Thermo Elemental), to check the accuracy of the ICP-MS measurements (data not shown).

The micromilled sample material was used for C and N determination (Vario EL; Elementar Analysen GmbH, Germany). The samples were dried at 70°C before being weighed.

The temperature, electric conductivity (model Lf 95; WTW, Germany), and pH (model pH 96; WTW, Germany) of the leachates at the sampling points were determined on-site.

Results and discussion

Iron-hydroxide-rich sediments with various contents of carbon

The differences in the on-site determined parameters between the sampling sites were minor, excepting those in electric conductivity (Table 1). The pH conditions were generally neutral, in consequence of accumulation of the residuals after alkaline ore processing (Wismut GmbH 1999).

According to the water classification of Furtak and Langguth (1967), CS1 belongs to the category of alkaline earth waters with elevated contents of alkaline metals while CS2 is of the alkaline water type (Fig. 2).

The sediments showed a typical rust-red colouration, especially in the alkaline waters of CS2. This type of

colouration, indicative of a high content of iron hydroxides (Table 2), was also described by Langner et al. (2001).

Both types of sediments had high contents of iron, but the mean values differed significantly due to dilution of the LC samples by organic carbon originating from plant litter. The LC samples had a lower iron concentration than did the comparatively pure IHR sediments (by 63% (reference area), 43% (CS1), and 70% (CS2), relative to the iron content in the IHR sediments). Because all the samples had appreciable iron concentrations, one could infer that they also were high in iron hydroxides. A coating consisting mainly of iron hydroxides was often found on the plant litter surface.

The amount of approximately 300 g iron (kg IHR sample)⁻¹ is absolutely in the range of the iron contents present in synthetic iron hydroxides. Dodge et al. (2002) used synthetic ferrihydrite (Fe₂O₃ × H₂O), which exhibited a concentration of 420 g Fe kg⁻¹ after adsorption experiments with uranium. This value was

Table 1 Main parameters of the sampling sites

Site	pH		Conductivity (μS cm ⁻¹)		Temperature (°C)	
	Mean	N	Mean	N	Mean	N
Reference	6.7 (±0.5)	6	721 (±26)	9	8.0 (±1.8)	9
CS 1 (alt)	6.7 (±1.3)	5	1,063 (V64)	8	8.7 (±1.7)	8
CS 2 (perm)	7.3	2	1,238 (±108)	3	7.6 (±3.1)	3

The values in parentheses represent the 95% confidence interval *Alt* Alternately wet and dry, *CS* contaminated site, *N* number of measurements, *Perm* permanently wet

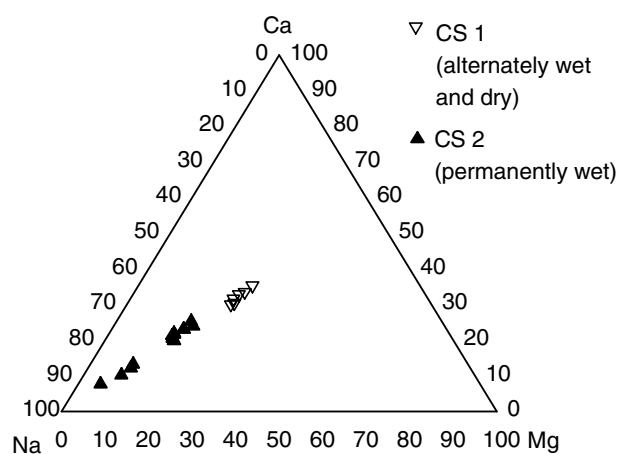


Fig. 2 Percentage contents of Ca, Na, and Mg in the leachates. CS Contaminated site

also obtained by us with some single samples. In their work with naturally formed iron hydroxides, Nikolaidis et al. (2004) obtained an iron concentration of $27.8 \text{ g Fe kg}^{-1}$, which is approximately ten times lower than the values recorded in this study.

As expected, the carbon and nitrogen concentrations in the IHR sediments, though present in noticeable amounts, were lower than those in the LC samples. Perret et al. (2000) also found carbon in their naturally formed iron hydroxides. They ascribed a fundamental role in the formation of iron hydroxides to macromolecular natural organic matter, suggesting that it forces the microbial mediated (autotrophic) oxidation of Fe^{2+} to Fe^{3+} to produce sediments rich in iron and carbon. Additionally, the close associations between inorganic and organic components (biofilms) in natural environments are an important part of naturally formed sediments (Hamilton et al. 1993).

Influence of the surface heterogeneity of iron hydroxides on arsenic adsorption

The analysed samples were of two types: IHR sediments, with carbon contents ranging between 70 and 110 g C

$(\text{kg sediment})^{-1}$, and LC sediments, with iron-hydroxide coatings mainly on the plant litter surface. This fact demonstrates that synthetic and naturally formed iron hydroxides differ in their composition. Consequently, one could assume that they also would adsorb arsenic differently.

There was a statistically significant correlation between iron and arsenic concentrations at the reference and contaminated sites, indicating that natural iron hydroxides possessed a distinct affinity for arsenic (Fig. 3). Principally saturation kinetics should be assumed. However in the investigated range a direct linear relation exists between iron and arsenic. Figure 3 also shows that the slopes for the linear regression equation are similar for both sediment types (IHR sediments: $\text{As} [\text{mmol kg}^{-1}] = -6.0 + 2.9 \text{ Fe} [\text{mol kg}^{-1}]$; LC sediments: $\text{As} [\text{mmol kg}^{-1}] = -0.3 + 2.2 \text{ Fe} [\text{mol kg}^{-1}]$).

This result indicates that iron hydroxides have a major role in the uptake of arsenic in natural systems at relatively low arsenic concentrations. The difference in the amount of organic carbon between LC and IHR samples did not influence arsenic uptake clearly. Presumably in iron rich water, arsenic fixation by organic matter [e.g., by dead or living ([microbial]) biomass; Bender et al. 1995] was, if at all, only a minor process in relation to the total arsenic uptake by iron hydroxides.

At CS1, a relationship was found between iron concentration and arsenic uptake that differed from the correlation present in the reference area. Separate consideration of IHR and LC samples did not show a significant correlation between iron and arsenic contents. However, when considering both sample categories, we again found a statistically significant correlation (Fig. 4), implying that in CS1, the role of iron hydroxides in arsenic uptake could be demonstrated only by consideration of a wide range of iron concentrations.

Arsenic concentrations in CS1 were noticeably (up to 1.5 orders of magnitude) higher than the amounts of arsenic adsorbed on iron hydroxides in the reference area. The correlation between iron hydroxides and arsenic uptake was less strong at high arsenic loadings. The arsenic content in the IHR samples was higher than it was in the LC samples, because of the larger amount

Table 2 Concentrations of Fe, C, and N in the IHR and LC sediments

	Fe (g kg^{-1})		C (g kg^{-1})		N (g kg^{-1})	
	Mean	<i>N</i>	Mean	<i>N</i>	Mean	<i>N</i>
IHR sediments						
Reference	316.7 (± 56.2)	8	110.2 (± 17.9)	8	5.6 (± 1.0)	8
CS 1 (alt)	324.4 (± 42.2)	8	89.0 (± 29.8)	8	7.4 (± 2.9)	8
CS 2 (perm)	351.0 (± 13.0)	3	70.0 (± 31.1)	3	3.8 (± 3.0)	3
LC sediments						
Reference	118.6 (± 28.5)	26	326.8 (± 37.0)	25	9.3 (± 0.9)	25
CS 1 (alt)	184.7 (± 21.3)	12	238.8 (± 43.2)	12	14.4 (± 0.4)	12
CS 2 (perm)	106.1	1	380.7	1	10.1	1

The values in parentheses represent the 95% confidence interval

Alt Alternately wet and dry, *CS* contaminated site, *N* number of measurements, *Perm* permanently wet

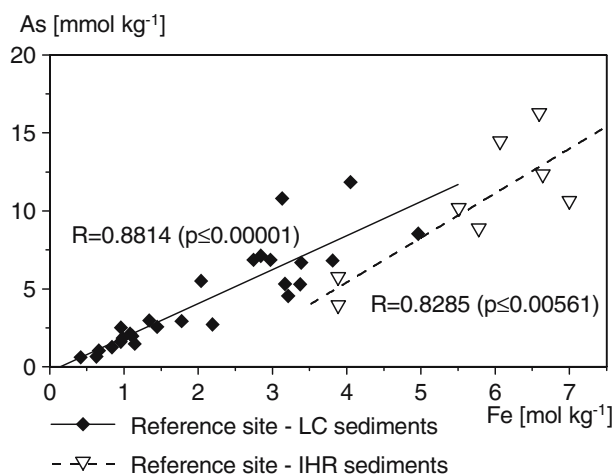


Fig. 3 Arsenic versus iron concentrations in the reference-site samples. Correlation significant at $p=0.01$ (Pearson's correlation coefficient). *IHR* Iron-hydroxide-rich, *LC* litter-containing

of iron hydroxides present in the IHR sediments. For CS1, the linear regression model described the relationship between iron and arsenic less exactly than it did for the reference area [correlation coefficients, $0.8999_{(\text{reference area})}$ vs. $0.6748_{(\text{CS1})}$]. Apparently, parameters other than the content of iron hydroxides became more important for uptake at high arsenic loadings. A possible explanation may come from the adsorption model for iron hydroxides proposed by Dzombak and Morel (1990). They found that the adsorption of arsenic on iron hydroxides can be modelled more precisely by including

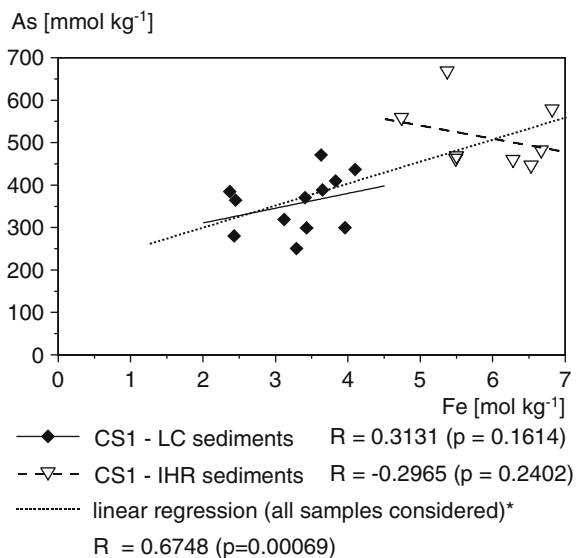


Fig. 4 Arsenic versus iron concentrations in the samples from contaminated site 1 (alternately wet and dry). Correlation significant at $p=0.01$ (Pearson's correlation coefficient). *CS* Contaminated site, *IHR* iron-hydroxide-rich, *LC* litter-containing

two types of binding sites for arsenic: strong and weak binding sites. This approach originates from modelling the simultaneous adsorption of cations and anions on iron hydroxides. Wilkie and Hering (1996) used 0.005 mol "strong" sites per mole Fe and 0.2 mol "weak" sites per mol Fe in their studies. In our case, it is obvious that the amount of the "strong" sites exceeded the amount of adsorbed arsenic in the reference area (Fig. 5).

In view of the preferential adsorption of arsenic on the "strong" sites (Pierce and Moore 1982), we expected that the entire amount of arsenic would be associated with them. Consequently, the arsenic found on the CS1 iron hydroxides was expected to be bound mainly to the "weak" sites (Fig. 5).

This finding could explain the weaker iron–arsenic correlation observed in CS1. If other anions are present, a competition for the "weak" sites arises (Wilkie and Hering 1996). Anawar et al. (2004) reported a higher arsenic release with increasing loadings of arsenic under the influence of 0.1 M NaHCO_3 . We suppose that the same processes also take place in CS1. C&E (1997) determined a bicarbonate (HCO_3^-) concentration of 235–238 mg l^{-1} for this site, an amount clearly below that used by Anawar et al. (2004; 6,100 $\text{mg HCO}_3^- \text{ l}^{-1}$). Nevertheless, bicarbonate influence on the adsorption of arsenic and its release from the CS1 iron hydroxides is possible because the bicarbonate concentration clearly exceeds the arsenic amount in the CS1 leachates. However, the dissolved arsenic concentration in the CS1 leachates (60–140 $\mu\text{g l}^{-1}$) was significantly higher than that found in CS2 (0–20 $\mu\text{g l}^{-1}$; Fig. 6) despite the nearly identical bicarbonate concentrations (CS2: 247–268 $\mu\text{g l}^{-1}$; C&E 1997). A possible explanation for this fact is that the CS1 and CS2 sediments differ remarkably

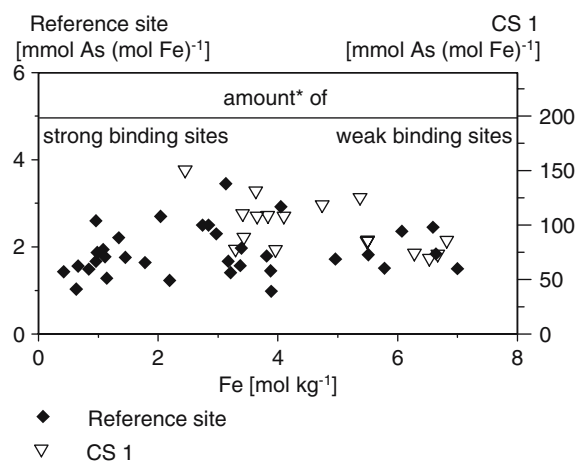


Fig. 5 Calculated amount of adsorbed arsenic per mole Fe on "strong" and "weak" sites in the reference area and in CS1 (alternately wet and dry). *Taken from Wilkie et al. (1996). *CS* Contaminated site

in their arsenic loadings (Fig. 6). Whereas CS1 and CS2 had similar contents of iron, the arsenic concentration in the CS2 sediments was only half of that found in CS1. With adsorption sites still available and the “strong” sites already occupied, there seemed to be little release of adsorbed arsenic and little competition for adsorption from the surrounding anions.

Arsenic adsorption capacity of iron hydroxides

The most probable reason for the weaker correlation and the comparably high concentration of dissolved arsenic in CS1 is the supersaturation of the iron hydroxides with arsenic. The content of iron did not differ significantly between CS1 and CS2 (Fig. 6). In contrast, the average amount of arsenic in the CS1 sediments ($38,000 \text{ mg As kg}^{-1}$) was more than twice that found in CS2 ($14,000 \text{ mg As kg}^{-1}$). The continuing precipitation of iron hydroxides and the presence of nitrate led us to assume the presence of oxic conditions. Except in the anaerobic microsites, a reductive redissolution of arsenic or iron hydroxides (Harrington et al. 1998) could be excluded. That the iron hydroxides had different arsenic loadings may be explained by exposure to different tailing leachates. The leachates had different loadings of arsenic because of the different paths of their flow through the tailing.

According to Dixit and Hering (2003), the CS1 amount of $38,000 \text{ mg As kg}^{-1}$ does not cause supersaturation on iron hydroxides. Using hydrous ferric oxide (HFO), Fuller and others (1993) determined maximum amounts of $0.25 \text{ mol As (mol Fe)}^{-1}$ and $0.7 \text{ mol As (mol Fe)}^{-1}$ by adsorption and coprecipitation, respectively. An adsorption of 112 g As kg^{-1} seems possible when these data are applied to the average iron concentration

in the sediments in our studies. Probably, coprecipitation also took place in CS1 and CS2, since some sampling points were located very close to leachate sources. Assuming that coprecipitation is the only determining process and according to Fuller et al. (1993), arsenic loadings on HFO could even reach approximately $314 \text{ g As (kg HFO)}^{-1}$. Richmond et al. (2004) used a constant Fe/As ratio of 12 to obtain stable ferrihydrite–arsenic precipitates. This ratio is in approximate agreement with the concentrations measured in the CS1 sediments. Ford (2002) worked with about $30,000 \text{ mg As (kg ferrihydrite)}^{-1}$; however, Fuller et al. (1993), Richmond et al. (2004), and Ford (2002) used synthetic iron hydroxides for their experiments. In contrast, Nikolaidis et al. (2004), in examining naturally formed iron hydroxides, observed a concentration of $137.67 \text{ mg As kg}^{-1}$ at an iron level of $27.8 \text{ g Fe kg}^{-1}$. Kneebone et al. (2002) found $200 \text{ mg As kg}^{-1}$ at an iron content of 40 g kg^{-1} . Thus, the maximum adsorbable amount of arsenic by naturally formed iron hydroxides seems to be much lower. However, the amount of arsenic on natural iron hydroxides examined in this work was remarkably high. Only Bowell (1994), in his studies on the fixation of arsenic in soils, found a similar As amount ($35,600 \text{ mg As kg}^{-1}$) at an iron content of approximately 60 g kg^{-1} . He also determined a pH value of 4. Low pH favours the adsorption of As on iron hydroxides (Jain et al. 1999). The sampling areas in our study had neutral pH values, remarkably lowering the capacity for arsenic adsorption (Jain et al. 1999).

Thus, it can be presumed that the CS1 iron hydroxides reached the upper limit of possible arsenic loadings under the present environmental conditions. Whereas synthetic HFO and ferrihydrite obviously can adsorb more arsenic, naturally formed iron hydroxides have a lower uptake capacity, possibly because of their more complex composition, the manifold environmental conditions, and the interaction between abiotic and biotic processes. However, at low arsenic concentrations, which are below the adsorbable amount by the “strong” binding sites, these factors seemed unimportant for uptake. In general, the fixation of arsenic is mainly dependent on the amount of iron hydroxides present; this also holds true for natural environments.

Assessment of total arsenic fixation by calcium–arsenic phases and by manganese oxides

Apart from iron hydroxides, manganese oxides (Deschamps et al. 2003) and calcium phases (Pichler et al. 2001) also can play a role in arsenic fixation. As a rule, calcium–arsenic phases consist of amorphous structures and still possess an unpredictable solubility. Crystalline structures are formed only at very high pH >11.5 (Pichler et al. 2001). The requirement for the formation

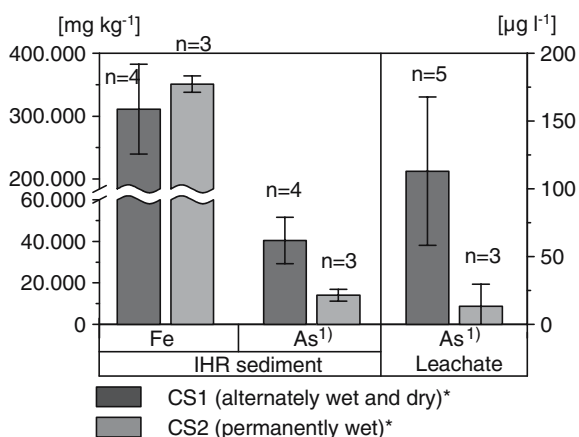


Fig. 6 Comparison of iron and arsenic concentrations in the CS1 and CS2 sediments and leachates. *Only sampling points at which water and sediments were sampled concurrently were considered. ¹⁾Differences significant (Wilcoxon test). Means + 95% confidence interval. CS Contaminated site, IHR iron-hydroxide-rich

Table 3 Concentrations of Ca, Mg, and Mn in the IHR and LC sediments

	Ca (mg kg ⁻¹)		Mg (mg kg ⁻¹)		Mn (mg kg ⁻¹)	
	Mean	<i>N</i>	Mean	<i>N</i>	Mean	<i>N</i>
IHR sediments						
Reference	22883.9 (± 3183.9)	8	2141.3 (± 165.1)	8	10220.9 (± 4935.7)	6
CS 1 (alt)	22377.1 (± 7152.3)	8	2616.8 (± 537.0)	8	1207.8 (± 577.9)	8
CS 2 (perm)	31759.3 (± 4881.7)	3	2882.5 (± 1203.4)	3	21772.1 (± 25315.6)	3
LC sediments						
Reference	14580.0 (± 1751.6)	26	1572.7 (± 218.1)	26	5708.7 (± 1781.1)	24
CS 1 (alt)	22767.7 (± 6399.7)	12	2822.6 (± 603.1)	12	1281.1 (± 869.7)	12
CS 2 (perm)	18885.3	1	1388.7	1	7016.6	1

The values in parentheses represent the 95% confidence interval

Alt Alternately wet and dry, *CS* contaminated site, *N* number of measurements, *Perm* permanently wet, *IHR* iron-hydroxide-rich, *LC* litter-containing

of calcium–arsenic phases is high contents of gypsum and calcite. Because of the use of Na₂CO₃ as a detergent during the soda leaching of uranium-containing ores (Wismut GmbH 1999), a release of calcium from the soil and tailing material near the sampling areas would be possible. The reason could be elevated concentrations of dissolved sodium in the tailings leachates, whose presence could lead to an ion-exchange reaction with soil-associated and ore processing debris calcium, resulting in an increase in dissolved calcium. This increase would favour the formation of calcium–arsenic phases. Indeed, such elevated concentrations of dissolved sodium were present in the leachates (Fig. 2). The calcium content reported by Pichler et al. (2001; CaO: 13–62.6 g kg⁻¹) is similar to those determined in this work (Table 3).

When assuming a fixation of arsenic by amorphous Ca–As phases, there must be an obvious relation between the concentrations of calcium and arsenic in the samples. A statistically significant correlation between Ca and As was only recognised in the reference area. In CS 1 such a correlation could not be detected (Fig. 7).

This did not agree with the assumption hypothesised above. The reference site was only less affected by the tailing leachates, which were supposed to force a formation of Ca–As phases. The Ca–As relation should rather have been found in CS 1. Consequently, other processes than the formation of Ca–As-phases were responsible for the significant correlation found for the reference site. An obvious relation of Ca to the iron content at the reference site is demonstrated (Fig. 8a) while a correlation between Fe and Ca at CS 1 is missing (Fig. 8b).

This is an explanation for the Ca–As correlation in the reference site. With increasing Fe content, the concentration of Ca also increased. Consequently, higher contents in iron are also related to higher concentrations of As. A dependence of Ca on Fe could not be found for CS 1; therefore, a relation between Ca and As was not present.

Thus, the formation of Ca–As phases, which may also exhibit fixation of dissolved arsenic in the tailing

leachates, could be excluded in this work. Additionally, the Ca uptake by iron hydroxides did not raise the adsorption of arsenic on iron hydroxides. The correlation coefficient is obviously weaker for the Ca–As

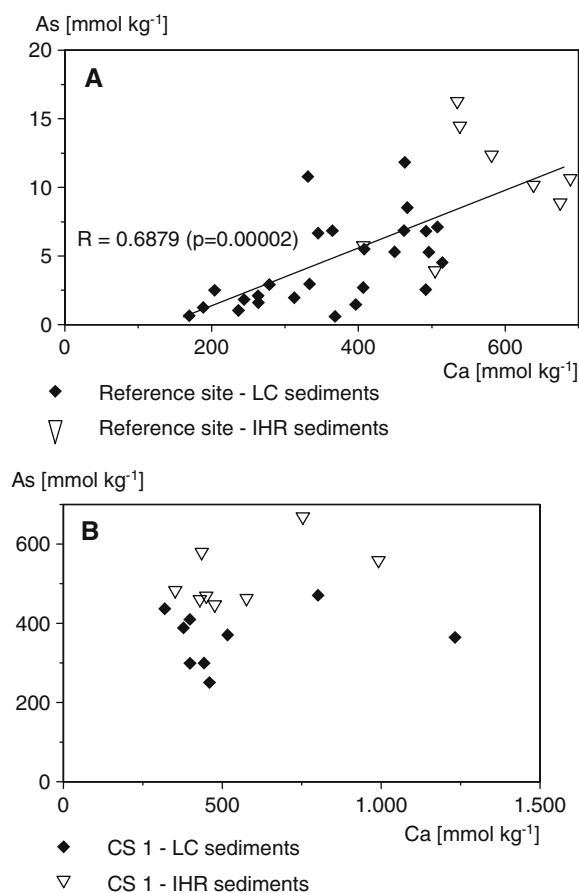


Fig. 7 Arsenic versus calcium concentrations. **a** Reference site. Correlation significant at $p=0.01$ (Pearson's correlation coefficient). **b** CS 1 (alternately wet and dry). *CS* Contaminated site, *IHR* iron-hydroxide-rich, *LC* litter-containing

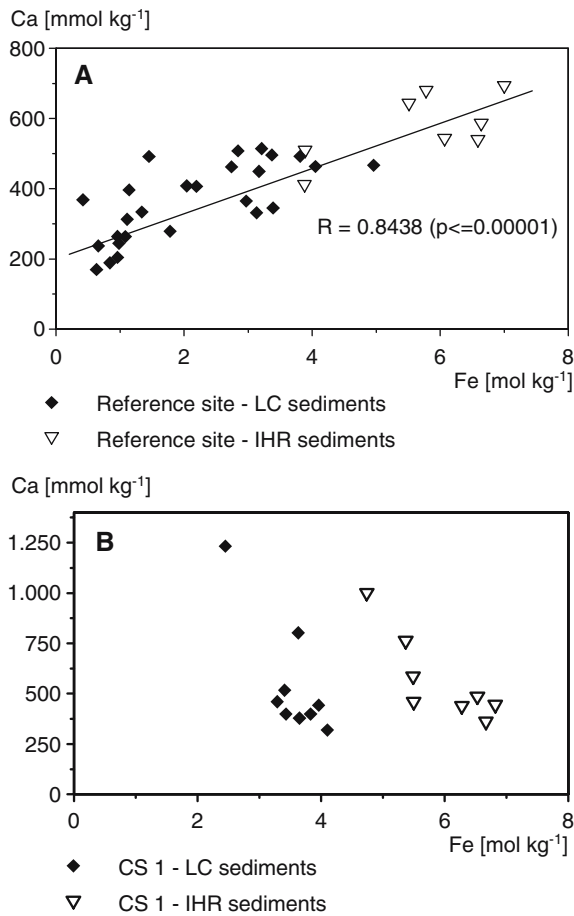


Fig. 8 Calcium versus iron concentrations. **a** Reference site. Correlation significant at $p=0.01$ (Pearson's correlation coefficient). **b** CS 1 (alternately wet and dry). *CS* Contaminated site, *IHR* iron-hydroxide-rich, *LC* litter-containing

relationship than it is for the Fe–Ca dependence in the reference site ($R_{Ca-As}:0.6879 < R_{Fe-Ca}:0.8438$). Wilkie and Hering (1996) demonstrated a less negative surface charge of ferric oxides when Ca is attached, also when the point of zero charge was exceeded. This favoured an adsorption of anionic arsenate. But their studies referred to the adsorption of As on HFO under conditions of $pH=9$, which is about two pH units above the value determined in the sampling areas. Therefore, the surface charge of HFO in the experiments of Wilkie and Hering (1996) is predicted to be more negative than that of the iron hydroxides analysed in our work. Hence, an effect of attached Ca on iron hydroxides would be more distinctive in experiments at elevated pH, as Wilkie and Hering (1996) showed.

The effect of changes in surface charge by sorption of cations also concerns manganese oxides. They gain importance for total arsenic fixation when high concentrations of bivalent cations are present (Driehaus 1994). The point of zero charge of manganese oxides is

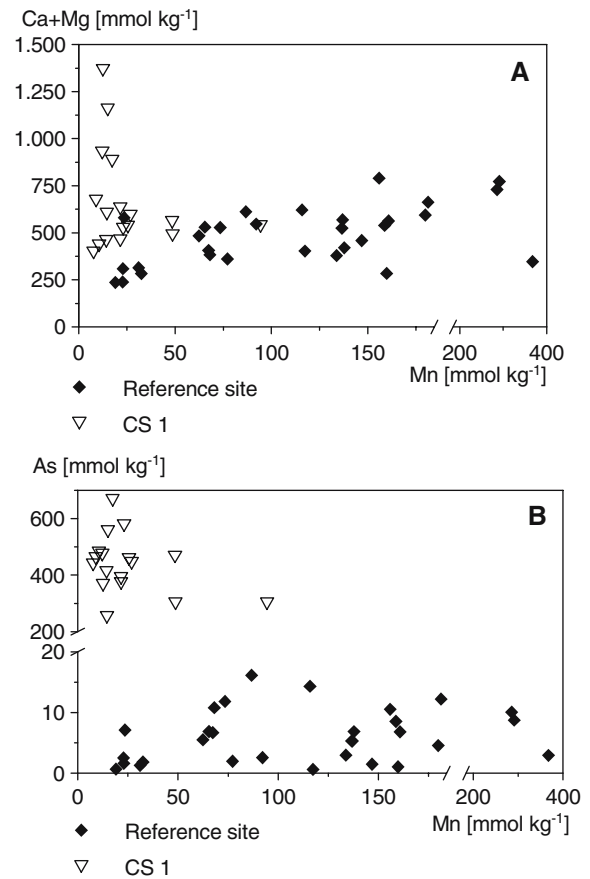


Fig. 9 **a** $\sum Ca + Mg$ versus manganese concentrations in IHR and LC sediments. **b** Arsenic versus manganese concentrations in IHR and LC sediments; *CS* contaminated site

achieved at pH as low as 3. The sorption of cations could lower the negative charge, which is distinct at $pH > 3$. Consequently, this favours a sorption of anions (Martin and Pedersen 2002) like arsenate. However, manganese oxides with remarkable loadings of calcium and magnesium were not detected in any of the sampling areas. The missing correlation between Mn and Ca + Mg is an indicator for this argumentation (Fig. 9a). Because of probably nonexistent Mn-oxides, a Mn–As relationship was not supposed to be present in the reference site as well as in CS 1 (Fig. 9b).

De Vitre et al. (1991) and Driehaus (1994) characterised Mn^{IV} as an efficient oxidant for As^{III} . This was also confirmed by Deschamps et al. (2003). Therefore, a role of manganese in arsenic uptake cannot be excluded entirely for this work. But its influence does not include direct sorption to Mn oxides.

Conclusions

This study showed the great importance of freshly precipitated iron hydroxides for arsenic uptake also in

natural environments. To a special extent, it is possible to use the knowledge about arsenic sorption on synthetic ferric hydroxides to understand sorption on naturally formed iron hydroxides. Other compounds like manganese oxides or amorphous Ca-phases did not have much effect on total arsenic sorption under the proved neutral and alkaline conditions. The role of included or attached organic matter associated with iron hydroxides has to be defined more precisely since it is found in large amounts. Effects of organic matter like changes in surface char-

acteristics of iron hydroxides, appearance of autotrophic microbial activity leading to production of organic carbon and concurrent Fe^{II} oxidation or formation of anaerobic micro-sites by microbial metabolic activity are possible. However, the direct influence of organic C on As fixation could not be proved in this work.

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