Helmholtz-Zentrum Dresden-Rossendorf (HZDR)

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ABSTRACT

In peatlands, arsenite was reported to be effectively sequestered by sulfhydryl groups of organic matter. To which extent porewater arsenite can react with reduced sulfur to form thioarsenates and how this affects arsenic sequestration in peatlands, is unknown. Here, we show that in the arsenic-rich peatland *Gola di Lago*, Switzerland, up to 93% of all arsenic species in surface and porewaters were thioarsenates. The dominant species, monothioarsenate, likely formed from arsenite and surface-associated zero-valent sulfur (S(0)). Laboratory incubations with sulfide-reacted peat showed for both, monothioarsenate and arsenite, increasing total arsenic sorption with decreasing pH from 8.5 to 4.5. However, X-ray absorption spectroscopy revealed no binding of monothioarsenate via sulfhydryl groups. The sorption observed at pH 4.5 was acid-catalyzed dissociation of monothioarsenate, forming arsenite. The lower the pH and the more sulfhydryl sites, the more arsenite sorbed which in turn shifted equilibrium towards further dissociation of monothioarsenate. At pH 8.5, monothioarsenate was stable over 41 days. In conclusion, arsenic is effectively sequestered in anoxic, acidic environments where arsenite is the only arsenic species. Where fluctuating redox conditions enable sulfide oxidation to S(0), monothioarsenate forms and at neutral to alkaline pH, slow transformation kinetics make this species highly mobile.

TOC
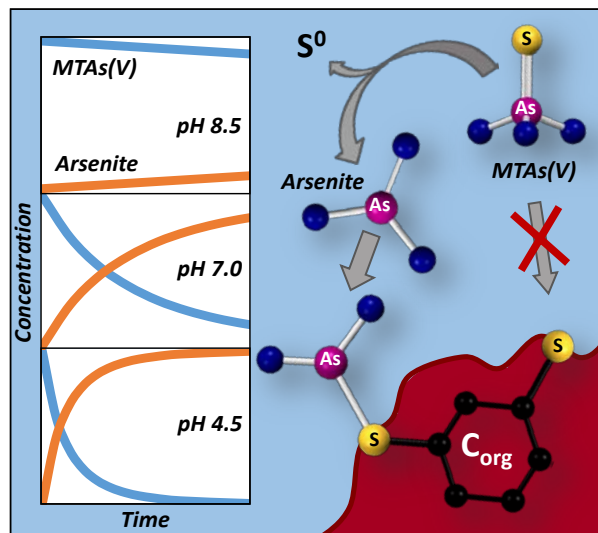
INTRODUCTION

Arsenic (As) is a toxic metalloid whose speciation and thus mobility is strongly affected by (microbially triggered) redox transformations.[1-3] In most terrestrial environments, inorganic arsenite ($H_xAs^{III}O_3^{3-x}$, x=1-3) and arsenate ($H_xAs^VO_4^{3-x}$, x=1-3) dominate aqueous As speciation[1], hence their sorption behavior to many environmentally relevant mineral phases has been extensively studied.[4] In particular, natural organic matter (NOM), for example in wetlands and peatlands has been recognized as an important sink for As in recent years.[5-8]

Several inner-sphere complexation mechanisms of As to NOM have been shown by X-ray absorption spectroscopy (XAS). Ternary complex formation between As oxyanions and Fe(III)-NOM complexes[9-11] has been revealed by XAS for both, arsenite[12] and arsenate.[13] Moreover, direct coordination with phenolate groups of NOM have at first been postulated for arsenite and arsenate by Buschmann, et al. [14] and have recently been verified for arsenite by Hoffmann et al..[12] Additionally, coordination of tri-valent As with sulfhydryl groups of NOM, presumably provided by organic sulfur from plant debris, was identified as prevailing sequestration mechanism in deep layers of the minerotrophic peatland *Gola di Lago*[15, 16] and in a laboratory study using XAS.[17]

Although arsenite generally dominates aqueous As speciation under reducing conditions, multiple studies showed that thioarsenates ($H_xAs^VS^{-II}_nO_{4-n}^{3-x}$; n=1-4; x=1-3) can form and dominate in sulfidic[18-20] environments and even in presence of high ferrous iron concentrations[21]. Thioarsenates are proposed to form in two steps from arsenite: First, at conditions of excess SH⁻ over OH⁻, ligand exchange leads to formation of thioarsenites ($H_xAs^{III}S^{-II}_nO_{3-n}^{3-x}$; n=1-3; x=1-3) as unstable intermediates.[22, 23] Second, addition of zero-valent sulfur (S(0)) transforms thioarsenites to thioarsenates.[24] Only formation of monothioarsenate ($H_xAs^VS^-$

$^{II}O_3^{3-x}$; x=1-3; MTAs(V)) does not require excess sulfide, because it forms directly from arsenite and S(0).[24]

Although sulfate-reducing conditions can prevail in peatlands, free sulfide concentrations are commonly low[25-27] since sulfide can be effectively incorporated into NOM as organic thiols and polysulfides[25, 28] or can form surface associated polysulfides during reduction of ferric (hydr)oxides.[29] A recent study observed thioarsenate formation after sulfidization of organic freshwater flocs from *Gola di Lago* peatland and related this to an excess of surface-bound S(0).[30] The authors postulated thioarsenates to be common porewater constituents in the As-enriched *Gola di Lago* peatland, however, direct evidence is still missing. Further, nothing is known about their mobility in sulfidic, organic rich systems, although sorption behavior of MTAs(V) and tetrathioarsenate ($H_xAs^VS^{-II}_4{}^{3-x}$; x=1-3; TetraTAs(V)) to iron oxy(hydr)oxides and –sulfides has been studied before[31, 32] and often showed higher mobility of thioarsenates compared to As oxyanions.

The purpose of this study therefore was (i) to investigate the natural occurrence of thioarsenates in surface and porewaters of several peat profiles in the As-enriched peatland *Gola di Lago* and (ii) to compare the sorption behavior of MTAs(V), which was found to be the dominant species in *Gola di Lago*, with that of arsenite to sulfide-reacted peat at different pH values and sulfide loadings, in order to elucidate the As retention processes in peatlands under different pH regimes.

MATERIALS AND METHODS

Field Site and Sampling. Peat cores, surface and porewaters were collected in November 2012 in the minerotrophic peatland *Gola di Lago*, Switzerland.[5, 15] In total, five peat profiles were sampled close to the sampling sites already visited in 2009.[15, 16] Peat cores were sampled up to 210 cm using a HUMAX drilling system.[15] The sample cores were immediately removed from the plastic liners, packed into CO_2-filled sampling bags and were further processed in a field laboratory close to the peatland. Porewater was obtained by squeezing the water saturated peat samples in the CO_2-filled bags on-site and then quickly removing them from the bags for further analyses and preservation. A detailed description of the field site, sample handling and analyses can be found in the **Supporting Information.**

Materials. All reagents used were of analytical grade and purchased from Fluka, Alfa Aesar, or Sigma-Aldrich. Because of a lack of a commercially available standard, MTAs(V) was synthesized as $Na_3AsO_3S \cdot 7H_2O$ as described previously.[22] Considering exact molecular weight ($Na_3AsO_3S \cdot 4H_2O$, 296.01 g/mol) and purity (90%; 5% arsenite, 5% arsenate) of the synthesis product, the exact concentrations of nominal 50 μM experiments were 53 μM MTAs(V). All solutions were prepared with doubly deionized (DDI) water (Milli-Q, Millipore, $\geq$18.2 MΩ cm) and all glassware was treated with acid before use.

Peat, which was used as a model sorbent for natural organic matter (NOM), was collected from the ombotrophic *Federseemoor* peatland near Bad Buchau, Germany.[17] The peat was wet-sieved to a size fraction of 63-250 μm and, after an initial washing step with 0.1 M HCl to solve potentially interfering metal(oid)s, washed several times with anoxic DDI water until a starting pH of ~4.5 was reached. Afterwards, the peat was freeze-dried, homogenized and stored in a

glovebag (pO$_2$ <1 ppm) in the dark until use. In this paper, the term peat is used when referring to the above described 63-250 μm[17] size fraction. After microwave digestion (MARS Xpress, CEM) using a 5:3 ratio of 30% H$_2$O$_2$ and 65% HNO$_3$, the elemental composition was analyzed by inductively coupled plasma mass-spectrometry (ICP-MS, XSeries2, Thermo-Fisher[19]). Carbon, S, and N contents of the peat were determined with a Thermo Quest, Flash EA 1112 analyzer. For functional group characterization, Fourier transform infrared (FT-IR) spectroscopy and ^{13}C cross-polarization/magic-angle spinning−nuclear magnetic resonance (CP/MAS−NMR) spectroscopy were used. All described methods confirm similar chemical composition and functional groups as in a previous study of Hoffmann et al. [17], enabling direct comparison of results. A detailed description of the methods and their results can be found in the **Supporting Information.** Furthermore, the Ambersep GT74 resin (Rohm & Haas) was used as a sulfhydryl-rich synthetic organic model adsorbent. After purchase, the resin was washed several times with anoxic DDI water and stored under anoxic conditions in a glovebag until use. A detailed chemical characterization of the resin can be found elsewhere.[33]

Arsenic Sorption to Sulfide-Reacted Peat. An MTAs(V) and arsenite time-resolved sorption experiment (0-984 h) on sulfide-reacted peat was conducted at pH 4.5, 7.0 and 8.5, respectively. The peat suspensions (0.2 M C) were reacted with 3.0 mM sulfide (S(-II)) solution (15 mmol S(-II)/mol C) in a 30 mM NaCl electrolyte under anoxic conditions (pO$_2$ <1 ppm) and shaken in the dark for 24 h. The respective pH (±0.2) was adjusted using anoxic HCl and NaOH. Sodium azide (NaN$_3$, 0.75 mmol/mol C) was added to prevent microbial growth. After reaction for 24 h to reach equilibrium[17], the suspensions were filtered off (12 μm, cellulose acetate) and subsequently washed with electrolyte to remove dissolved sulfide. A wet weight equivalent of

100 mg dry sulfide-reacted peat (0.2 M C) was equilibrated with 50 μM MTAs(V) or arsenite at pH 4.5, 7.0 and 8.5 in anoxic electrolyte, respectively. The samples were incubated for a maximum time of 984 h (41 days) at room temperature and in the dark. Sampling of sacrifying butyl-rubber capped serum bottles (triplicates) was done at 13 (MTAs(V) incubations) and 7 (arsenite incubations) sampling times during the experiment. At every sampling time, the peat suspensions were filtered (0.2 μm, Nylon) and an aliquot of the filtrate was immediately shock-frozen on dry ice. Another aliquot was stabilized in 0.5% H_2O_2 and 0.8% HNO_3 prior to analysis of total aqueous As and S with ICP-MS. After freeze-drying, one part of the solid-phase was used for XAS analysis and another sample aliquot was microwave-digested as described above. The pH dependency of S content in peat was similar compared to Hoffmann et al. [17] assuming equal incorporation as sulfhydryl-S (Figure SI-11). The total amount of As sorbed was determined by analyzing the digests with ICP-MS. The pH and the redox potential (E_h) were monitored during the experiment.

Additionally, an experiment where peat suspensions (0.2 M C) were equilibrated with sulfide loadings of 0.3, 3 and 30 mM (1.5, 15 and 150 mmol S(-II)/mol C) was performed at pH 4.5, 7.0 and 8.5 with 50 μM MTAs(V) addition for 96 h to examine the influence of sulfide loadings on MTAs(V) affinity to sulfide-reacted peat. Otherwise the experimental protocol was identical to the one described above. Monothioarsenate stability in the NaCl and NaN_3 electrolyte solution was tested prior to experiments at pH 4.5, 7.0 and 8.5 (SI-9d).

Arsenic Sorption to Ambersep GT74 Resin. In order to examine the potential of MTAs(V) binding to sulfhydryl groups, 100 mg of washed resin was equilibrated with 200-250 μM MTAs(V) and arsenite for 96 h, respectively. The pH was adjusted to ~ pH 7 (arsenite) and pH

7.5 or 8.5 (MTAs(V)). Otherwise, the experimental setup was the same as the one described above.

Aqueous Arsenic and Sulfur Speciation. After thawing the shock-frozen samples in a glovebag, arsenite, arsenate, and thioarsenate species as well as sulfate and thiosulfate were determined by anion-exchange chromatography (AEC, ICS-3000, Dionex) coupled to an ICP-MS (XSeries2, Thermo-Fisher).[19] Calibration standards were prepared from sodium arsenate dibasic-heptahydrate ($Na_2HAsO_4 \cdot 7H_2O$), sodium (meta)arsenite ($NaAsO_2$), ammonium sulfate ((NH_4)$_2SO_4$) and sodium thiosulfate. Due to a lack of commercially available standards, thioarsenates were quantified via the arsenate calibration curve.[19]

Arsenic Solid-Phase Speciation. Arsenic *K*-edge (11867 eV) X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine-structure (EXAFS) spectra were collected at The Rossendorf Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France and at beamline 4-1 of the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA. Anoxic peat and resin samples were freeze-dried, homogenized, filled into sample holders and sealed with Kapton tape. All sample measurements were performed in fluorescence mode using Ge array fluorescence detectors and a liquid He cryostat at 15 K to avoid beam damage and thermal disorder. Spectra of As reference compounds were analyzed in transmission mode or were taken from Suess et al. [22]. Details on the measurements, data reduction, and analyses are provided in the **Supporting Information**.

RESULTS AND DISCUSSION

Thioarsenates in Surface and Porewater of *Gola di Lago* Peatland. Total aqueous As in the slightly acidic (pH 5.2 to 6.1) surface and porewaters of *Gola di Lago* peatland ranged from 1.8 to 180 μg/L. Arsenic initially entering the peatland via the intermittent inflow (IF) was mainly arsenate (Figure 1a). With increasing lateral distance to the IF, the percentage of arsenate decreased while thioarsenates increased (profiles B1L < B2L and B1R<B2R<B3R in Figure 1a; Figure SI-2 to 6). The percentage of arsenite remained comparatively low (2-30%) in surface water samples. At greater depth (~90 cm), arsenite increased to 25-80% of total As (Figure 1b). Overall, the maximum percentage of thioarsenates reached 93% of total As (profile B3R, 60 cm depth, Figure SI-3). Concentration and fraction of thioarsenates did not show significant correlation with any of the obvious aqueous parameters such as pH, redox potential or concentration of total As and S in the solid-phase (Figure SI-2-6, Table SI-1). Mostly the dominant species in all profiles was MTAs(V) with up to 91% of total As followed by significantly lower fractions of tri- and dithioarsenate (median 3 and 2%, respectively). Tetrathioarsenate is instable at these low pH values.[34] To our knowledge,[5, 7, 8, 15, 16] this is the first report of thioarsenates in porewaters of peatlands. Unsuitable preservation and analytical methods probably prevented their detection before. The significant fractions of MTAs(V) observed in *Gola di Lago* versus a complete lack of information on the effect of MTAs(V) formation on the overall As mobility in sulfur and organic carbon-rich environments, were the basis for the following laboratory sorption studies.

Total As Sorption upon Monothioarsenate versus Arsenite Addition to Sulfide-Reacted Peat. In the time series experiments with 3 mM sulfide-reacted peat, total As sorption upon MTAs(V) addition increased in the order pH 8.5 < 7.0 < 4.5, whereby sorption at pH 4.5 (32 μmol As/mol C) was ~5 times higher than at pH 8.5 (7 μmol As/mol C, Figure 2). The same trend occurred for arsenite but the difference between As sorption at pH 4.5 (29 μmol As/mol C) and 8.5 (14 μmol As/mol C) was only factor 2. Compared to arsenite, the initial sorption of total As was slower in experiments where we added MTAs(V), but after 984 hours (41 days), extent of sorption was almost comparable, at least for pH 4.5 and 7.0. For pH 8.5, the amount of total As sorbed remained at only ~ 50 % of that observed in the arsenite experiments (Figure 2). Comparing the influence of 0.3, 3, and 30 mM sulfide loadings after 96 hours, a strong increase of total As sorbed with increasing sulfide loadings was observed at pH 4.5 (6 up to 85 μmol As/mol C), while at pH 7.0 and 8.5 almost no influence of sulfide loadings was detected. However, sorption of As at pH 7.0 was always higher than at pH 8.5 (Figure SI-14).

Processes during Arsenite Sorption to Sulfide-Reacted Peat. Aqueous As speciation analysis showed that over 41 days of incubation no As species other than arsenite occurred in solution (except for transformations to arsenate ($< 18\%$) and dithioarsenate ($< 11\%$) at pH 8.5, Figure 3). Compared to a previous study by Hoffmann et al., [17] the extent of arsenite sorption at pH 7.0 after 96 h (7.3 μmol As/mmol S) was lower, but generally comparable. A remarkable difference was, however, observed for arsenite sorption at lower pH.

In their study, Hoffmann et al. [17] used besides sulfide-reacted peat at pH 7.0 also sulfide-reacted humic acid at pH 5.0 and found that at a given S content, arsenite sorption was lower at lower pH. They explained the difference with sulfhydryl groups having a wide range of proton

dissociation constants (pK$_a$) from 5-11[35], obtaining increasing nucleophilicity and hence reactivity with increasing pH.

In our experiments, the arsenite sorption strongly increased with lower pH (4.5 > 7.0 > 8.5) as shown above (Figure 2). These findings indicate that a high abundance of sulfhydryl groups with lower pK$_a$ values seem to be present in the peat, acting as strong nucleophiles. This observation is in general accordance with the proposed acid-catalyzed reaction of sulfide to unsaturated carbon bonds in Hoffmann et al. [17] (Figure SI-7 and 8). Additionally, the peak at ~1715 cm^{-1} in the FT-IR spectrum (Figure SI-7) indicates that significant amounts of aryl ketones were present in the peat, which can form sulfhydryl groups with lower pK$_a$ values (e.g. thiobenzoic acid, pK$_a$ 3.6), compared to other organic groups with thiol moieties, after acid catalyzed reaction with sulfide.[36]

However, also if sulfhydryl groups with lower pK$_a$ values were present, their nucleophilicity usually increases with increasing pH, which should lead to higher sorption at higher pH. But As sorption was higher at lower pH, even at similar S contents for pH 4.5 and 7.0 (Figure SI-11b). Also differences in released total S over time (Figure SI-11a) between pH 4.5 and 7.0 cannot fully explain higher As sorption at low pH, since As sorption was already significantly higher at pH 4.5 at the early time steps, when total S release was similar for pH 4.5 and 7.0.

Maybe the increase of global negative charge of (sulfide-reacted) NOM with pH[37] lead to mutual attenuation of sorption sites, thus favoring a nucleophilic attack of sulfhydryl groups towards the uncharged arsenite (pK$_a$ = 9.17[38]) at lower pH. At pH 8.5, arsenite is partially negatively charged which may lead to stronger electrostatic repulsion due to increased deprotonation of organic functional groups at high pH and thus explains low sorption to sulfide-reacted peat.

Aqueous As Speciation upon Monothioarsenate Addition to Sulfide-Reacted Peat. Aqueous As speciation analysis for the MTAs(V) experiments with 3 mM sulfide loadings, showed, in contrast to the arsenite experiments described above, significant transformations of MTAs(V) to mainly arsenite (Figure 3; corresponding pH and E_h values can be found in the **Supporting Information** (Figure SI-10). Transformation rates decreased with increasing pH from half-lives of ~35 h to ~470 h at pH 4.5 and 7.0, respectively, to almost no transformation at pH 8.5 over the duration of the experiment (984 h, Figure 3a, c and e). In DDI water, MTAs(V) was stable (Figure SI-9a) and addition of background electrolyte or NaN$_3$, (Figure SI-9b, c) respectively, accelerated transformation of MTAs(V) only little at pH 4.5. A blank experiment with background electrolyte and NaN$_3$ combined, showed only minor transformation of MTAs(V) to arsenite at pH 4.5 (8%) and no species change at pH 7.0 and 8.5 after 120 h (Figure SI-9d) which is in line with previous observations on the stability of MTAs(V) in solution after acidification[34], aeration[39] or in the absence of S(0).[24] Furthermore, no significant increase in sulfur oxidation products (sulfate and thiosulfate) occurred during these experiments (Figure SI-12) confirming anaerobic conditions and indicating no microbial influence. The transformation of MTAs(V) was therefore not driven by pH or ionic strength, but clearly triggered by the presence of sulfide-reacted peat.

One possible explanation is that sulfide was released from sulfide-reacted peat to solution and this drove MTAs(V) transformation to arsenite. From their experiments on arsenate reduction by sulfide where MTAs(V) was observed as by-product, Rochette et al. [40] postulated such an acid-catalyzed (no reaction at pH 7.0), sulfide-driven MTAs(V) reduction via formation of dithioarsenate (DTAs(V)), reduction to MTAs(V), and, finally hydrolyzation to arsenite. In our

experiments, we could not determine whether there were significant amounts of free sulfide in solution. Although we washed our sulfide-reacted peat in order to remove any dissolved sulfide before the As sorption experiments, we observed some further release of total S to the aqueous phase during the experiment (Figure SI-11). The fraction of sulfide of this total S was impossible to determine due to strong interferences with DOC using the methylene blue method.[41] However, if a reaction of this kind with potentially dissolved or even surface-bound sulfide would have occurred, then a DTAs(V) peak would have appeared during aqueous As analysis, which was not the case. The facts that DTAs(V) occurred only in trace amounts (max. ~2.5% of As species, Figure 3) and that Rochette et al. [40] found no transformation at pH 7.0, make this reaction pathway unlikely.

Another explanation is that the presence of the solid-phase (sulfhydryl-S on peat) itself drives MTAs(V) transformation. As described above, MTAs(V) is in equilibrium with arsenite and S(0). Low pH will drive the equilibrium towards arsenite and S(0)[42] (equation 1), but kinetics in solution are so slow that any MTAs(V) transformation is not likely to be observed over several days (Figure SI-9a).

$$[H_2As^VS^{-II}O_3]^- + H^+ \leftrightarrow H_3As^{III}O_3 + S^0 \qquad (1)$$
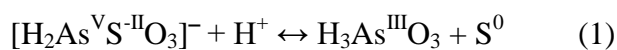
However, both previous reports[15, 17] and our own experiments (Figure 2) show that arsenite sorbs strongly to sulfhydryl-rich NOM, particularly at low pH. This is consistent with the observed order of MTAs(V) transformation kinetics. We therefore conclude that arsenite sorption drives the chemical equilibrium towards arsenite and S(0), therefore accelerating MTAs(V) transformation. Sorption of S(0)[29, 30, 43] has the same effect.

Figure SI-14 shows aqueous As speciation and total As sorption of peat reacted with different amounts of sulfide (3 mM in comparison to 0.3 and 30 mM; 96 h) at pH 4.5, 7.0, and 8.5 and

total S content is depicted in Figure SI-15. At pH 8.5, MTAs(V) remained stable regardless of the sulfide loading, probably stabilized by the low proton concentration and lower sorption affinity of arsenite at high pH. Total As sorption increased strongly with S content at low pH and only tendentially at pH 7.0, which shows a clear influence of sulfide loadings on MTAs(V) transformation and As sorption, particularly at pH 4.5. But pH seems to be the rate-controlling variable, since MTAs(V) transformation was significantly higher at low pH, possessing similar S contents at pH 4.5 and 7.0 (0.3 and 3 mM sulfide loadings experiments, Figure S-14 and 15). No increased shift of MTAs(V) towards arsenite was observed between 3 and 30 mM sulfide loadings at pH 4.5 and 7.0, despite significantly higher S contents on the peat when higher amounts of sulfide were used (Figure SI-15b). The lack of correlation might be due to small increases of pH (max. 0.7 pH units) during incubation (Table SI-4) since no special buffers were used in order not to change organic functional groups of the peat. In general, all results show that extent and kinetics of MTAs(V) transformation strongly depended on pH because of the pH-dependent removal of arsenite through sorption.

While aqueous As speciation already implied that arsenite sorption is an important mechanism in the MTAs(V) experiments, it could not answer the question whether sorption observed in the MTAs(V) experiments occurred exclusively as arsenite or also included direct sorption of MTAs(V) to sulfide-reacted peat, which is addressed in the next section.

Solid-Phase As Speciation upon Monothioarsenate Addition to Sulfide-Reacted Peat. In order to follow As solid-phase speciation over a wide range of concentrations (8-280 ppm), we used principal component analysis (PCA) and iterative transformation factor analysis (ITFA)[44] of normalized As K-edge XANES spectra. The 20 spectra from selected sampling points of the time

series and sulfide loading experiments could be reproduced by only three principle components, as indicated by a minimum of the Malinowski indicator value and 99.9% of the variance in the dataset explained. This observation was confirmed by the almost perfect reproduction of the experimental spectra by these three PCs (Figure 4). Further, target transform testing revealed that with the following three standards excellent to good empirical Malinowski SPOIL values (0.8-2.5) were achieved. These standards were the already described arsenite sorbed via sulfhydryl-S to peat (As(III)-S-NOM[17]) and arsenite directly sorbed to untreated peat (As(III)-NOM[12] besides arsenate directly sorbed to untreated peat (As(V)-NOM as inner-sphere complexes. The latter binding mechanism has already been postulated to play an important role in a previous sorption study[14]. Inclusion of these spectra in the experimental series and re-analysis with PCA and subsequent ITFA did not increase the number of statistically significant components and confirmed the standards indeed as end-member components. Aqueous and solid thioarsenate standards did not give acceptable SPOIL values and showed an increased number of PCs. The structure As(III)-S-NOM was resolved and confirmed by EXAFS shell fitting (Figure SI-16, Table SI-5) and by using wavelet transform analysis[45] we excluded any influence of amorphous As-S precipitates[46] (Figure SI-17). Finally, species distribution of the experimental spectra was calculated with iterative target transformation (ITT) giving an average sum of species of $100 \pm 1\%$ without using any constraints (Figure 4).

The ITFA calculations revealed that the solid-phase contained one arsenate and two arsenite end-members without any contribution of MTAs(V) binding to sulfide-reacted peat. The general error of this kind of calculations is $\pm 5\%$ of relative concentration[22], however MTAs(V) was not detected on the solid-phase even if present in high aqueous concentrations at pH 4.5-8.5 (Figure 3, Figure SI-14). This finding was further confirmed by EXAFS shell-fitting of resin spectra

from MTAs(V) solutions reacted with the sulfhydryl-rich Ambersep GT74 resin at pH 7.5 and 8.0 (Figure SI-19-20). Though MTAs(V) was stable in the aqueous solution at both pHs (Figure SI-19), no contribution of a double-bound S (typically 2.13-2.18 Å[22]) was observed (Table SI-6, Figure SI-20) on the solid-phase. Instead, As was 3-fold coordinated at each pH to S with distances of 2.26 Å, indicating typical bond lengths of arsenite bound via sulfhydryl-S.[33] This finding was confirmed by a control experiment with arsenite showing similar coordination numbers (CN) and atomic distances (Figure SI-20, Table SI- 6).

Thus, in the experiments where MTAs(V) was added, sorption extent and kinetics (Figure 2, Figure SI-14) were all determined by the behavior of the arsenite newly formed from MTAs(V). The ITT calculations revealed an increase of As(III) fractions with decreasing pH in the same manner as MTAs(V) transformation to arsenite (Figure 4, Figure 3). Hereby, a systematically higher portion of As was complexed via sulfhydryl-S to peat at pH 4.5 compared to pH 7.0. No sulfhydryl complexation higher than the detection limit (5%) was observed at pH 8.5 (Figure 4). These findings are in close agreement with the behavior of arsenite sorption discussed in the previous section and re-calculation of ITFA including the XANES spectra from arsenite sorption experiments (96 h) confirmed the same trend of ITT fractions (Figure SI-18). Increasing sulfide loadings at pH 4.5 increased MTAs(V) transformation through increased arsenite complexation via sulfhydryl-S and therefore As sorption to peat. The lower reactivity of arsenite towards sulfide-reacted peat at higher pH, as discussed above, is further confirmed by the sulfide loading experiments at pH 7.0 and 8.5 (Figure 4, Figure SI-14).

In summary, the solid-phase speciation data clearly show that there was no significant MTAs(V) sorption to sulfide-reacted peat via sulfhydryl groups. The reason for MTAs(V) showing no detectable sorption to S-NOM is probably twofold. First, MTAs(V) has pK_a values of 3.30

(pK$_{a1}$), 7.20 (pK$_{a2}$) and 11.0 (pK$_{a3}$)[42] and was therefore single or double-negatively charged under our experimental conditions (pH 4.5-8.5). The negative charge causes a strong electrostatic repulsion with the negatively charged sulfide-reacted peat, thus excluding MTAs(V) sorption regardless the pH value and S content (Figure 4). Second, however, arsenate with very similar pK$_a$ values[38] showed, though to very low extent (Figure 2), sorption to sulfide-reacted peat (Figure 4). Buschmann et al. [14] hypothesized that arsenate sorption to NOM occurred via deprotonated phenolic groups reacting with the formal positively charged electrophilic metal center of arsenate (+V) under release of water and stabilized by additional chelation by other functional groups, and/or H-bridges. While MTAs(V) has the same formal positive charge, substitution of double bound O by less electronegative S in MTAs(V) leads to longer As-S (2.14-2.15 Å[22]) distances compared to As-O (1.69-1.71 Å[47, 48]) in arsenate. This decreased electrophilicity at the central As atom possibly causes lower affinities of MTAs(V) forming bonds with phenolic groups of the sulfide-reacted peat (Figure SI-7) which typically start deprotonating at high pH.[35]

Environmental Implications. Combining all information from the field site, our laboratory study and the current literature, we propose the following conceptual model for MTAs(V) in the *Gola di Lago* peatland (Figure 5) which may be exemplary for other As enriched wetlands. As long as there is no reduced sulfur, As prevails as arsenate or arsenite (Scenario 1, Figure 5). Under more reducing conditions, MTAs(V) forms from arsenite and S(0) as reported elsewhere[24] (Scenario 2, Figure 5). Zero-valent sulfur occurs either as dissolved polysulfides or associated with solid-phases. For *Gola di Lago*, S(0) has been reported to be primarily associated with the surfaces of organic iron flocs after sulfidization.[30] Furthermore, ferric (hydr)oxides have been shown to dominate the iron solid-phase at the shallow layers of this peatland[15, 16], which may be

even more effective than the organic iron flocs in sorbing S(0) at their surfaces.[29] Further reduction of S(0) to sulfide could lead to the formation of higher thiolated arsenates[24] (Scenario 3, Figure 2), formation of thioarsenites[22, 23] and eventually precipitation of As-S mineral phases (Scenario 4, Figure 2). Even though realgar (As_4S_4) has been described for *Gola di Lago* before[15, 16], its coexistence with ferric (hydr)oxides indicates its intermittent formation in sulfide-rich micro-environments or during sulfide-rich times e.g. of high flooding and persistence because of slow oxidation kinetics rather than equilibrium conditions with excess sulfide.[16, 49] But the fact that no free dissolved sulfide was detected in any of the porewater samples (detection limit $0.3 \mu M$) explains the overall low proportion of higher thiolated arsenates (Scenario 3, Figure 5) and renders the occurrence of thioarsenites unlikely (Scenario 4, Figure 5; thioarsenites can currently not be detected at environmentally relevant concentrations).[23]

At greater depths, arsenite forms at the expense of MTAs(V). This transformation is likely to be the kinetically constrained acid-catalyzed MTAs(V) transformation reaction to arsenite and its subsequent sorption to sulfhydryl groups as shown in our laboratory experiments. Occurrence of sulfhydryl groups which sequester arsenite, has previously been described in deeper peat layers of *Gola di Lago* (pH ~5.8)[15, 16] and agrees with the proposed conceptual model (Scenario 5, Figure 5). The dominance of MTAs(V) (besides arsenite) in peatlands versus higher thiolated arsenates in sulfur-rich environments with less organic carbon[19, 34, 39, 50] can therefore be explained by the high sorption affinity of reduced sulfur species to organic matter, causing aqueous As-S speciation presumably to be controlled mostly by reactions at solid-phase surfaces.

ASSOCIATED CONTENT

Supporting Information

Field site description, sampling methods and geochemical characterization of *Gola di Lago* peatland, characterization of *Federseemoor* peat, monothioarsenate stability experiments, chemical background information for monothioarsenate and arsenite sorption to sulfide-reacted peat, a detailed methods description of As *K*-edge XAS analyses, shell fits of As *K*-edge EXAFS spectra of reference standards including respective wavelet transformation analysis and monothioarsenate and arsenite sorption to Ambersep GT74 resin. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

Stanford, USA. The SSRL is a national user facility operated by Stanford University on behalf of the U.S. Department of Energy.

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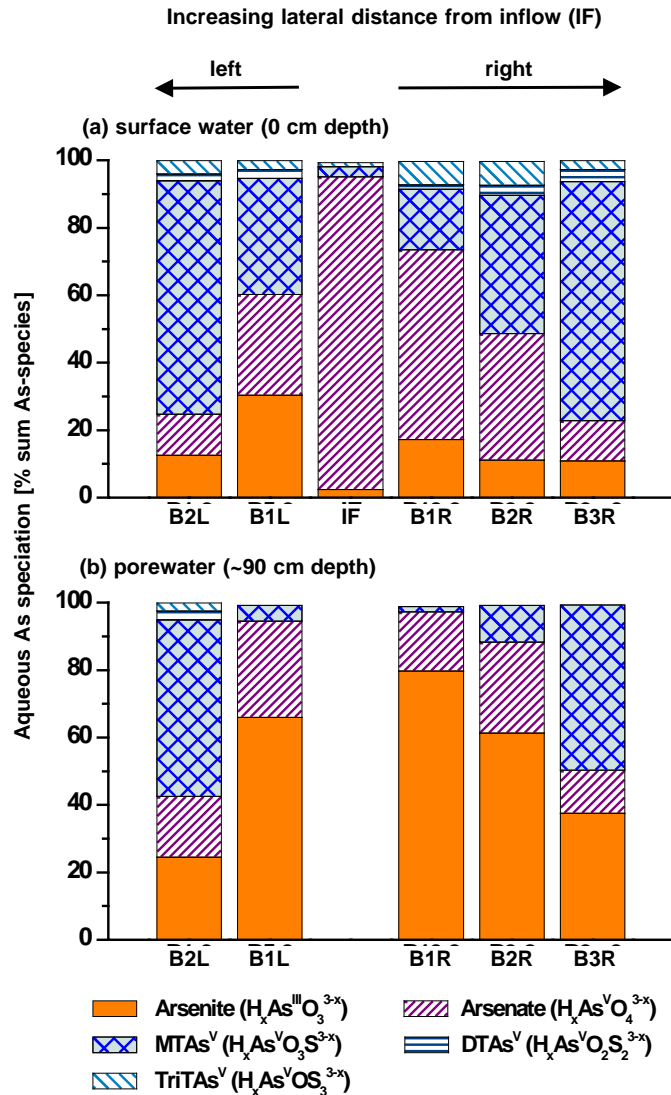
Increasing lateral distance from inflow (IF)

←— left   right —→

(a) surface water (0 cm depth)

(b) porewater (~90 cm depth)

Aqueous As speciation [% sum As-species]

Legend:
- Arsenite ($H_xAs^{III}O_3^{3-x}$)
- Arsenate ($H_xAs^VO_4^{3-x}$)
- MTAs^V ($H_xAs^VO_3S^{3-x}$)
- DTAs^V ($H_xAs^VO_2S_2^{3-x}$)
- TriTAs^V ($H_xAs^VOS_3^{3-x}$)

Figure 1: Aqueous As speciation [% of sum As species] of sampling profiles B2L, B1L, intermittent inflow (IF), B1R, B2R and B3R at the surface (a) and in ~90 cm depth (b) from *Gola di Lago* peatland. Note: for B2R, results are depicted for 60 cm depth because this was the greatest depth achieved for that core. Details regarding sampling depths can be found in Table SI-1. Lateral distances of profiles from IF do not increase on linear scale. Aqueous As speciation in ~ 90 cm comprises porewater plus easily mobilizable soil-bound fraction.
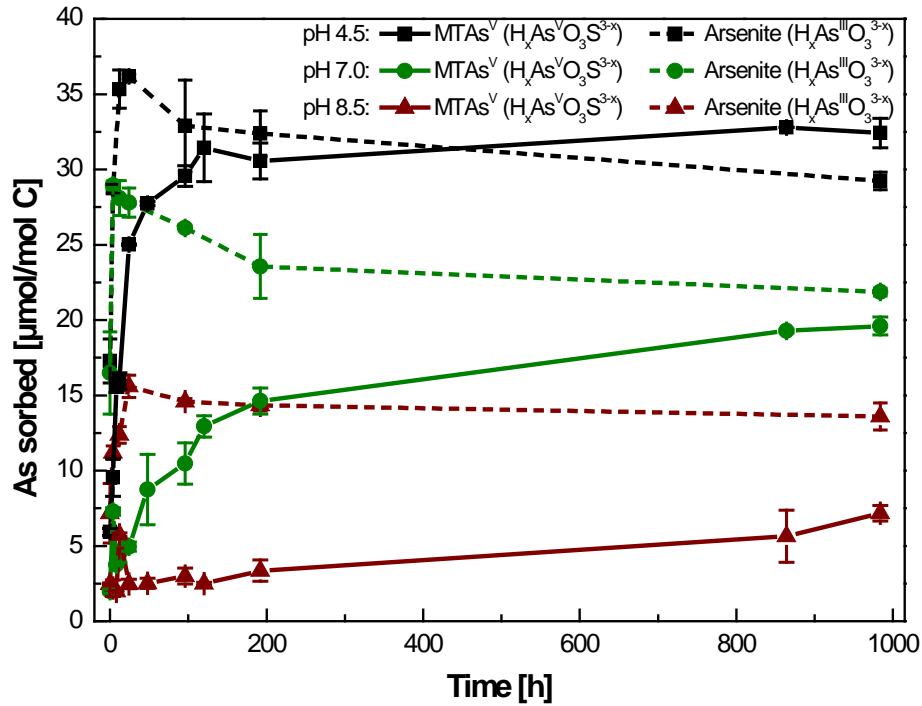
Figure 2: Time series of total As sorbed in experiments where MTAs(V) (straight lines) or arsenite (dashed lines) was added to sulfide-reacted (3 mM sulfide) peat suspensions (0.2 M C) at pH 4.5, 7.0 and 8.5. Error bars represent standard deviations of triplicates. Straight or dashed lines serve to guide the eye.
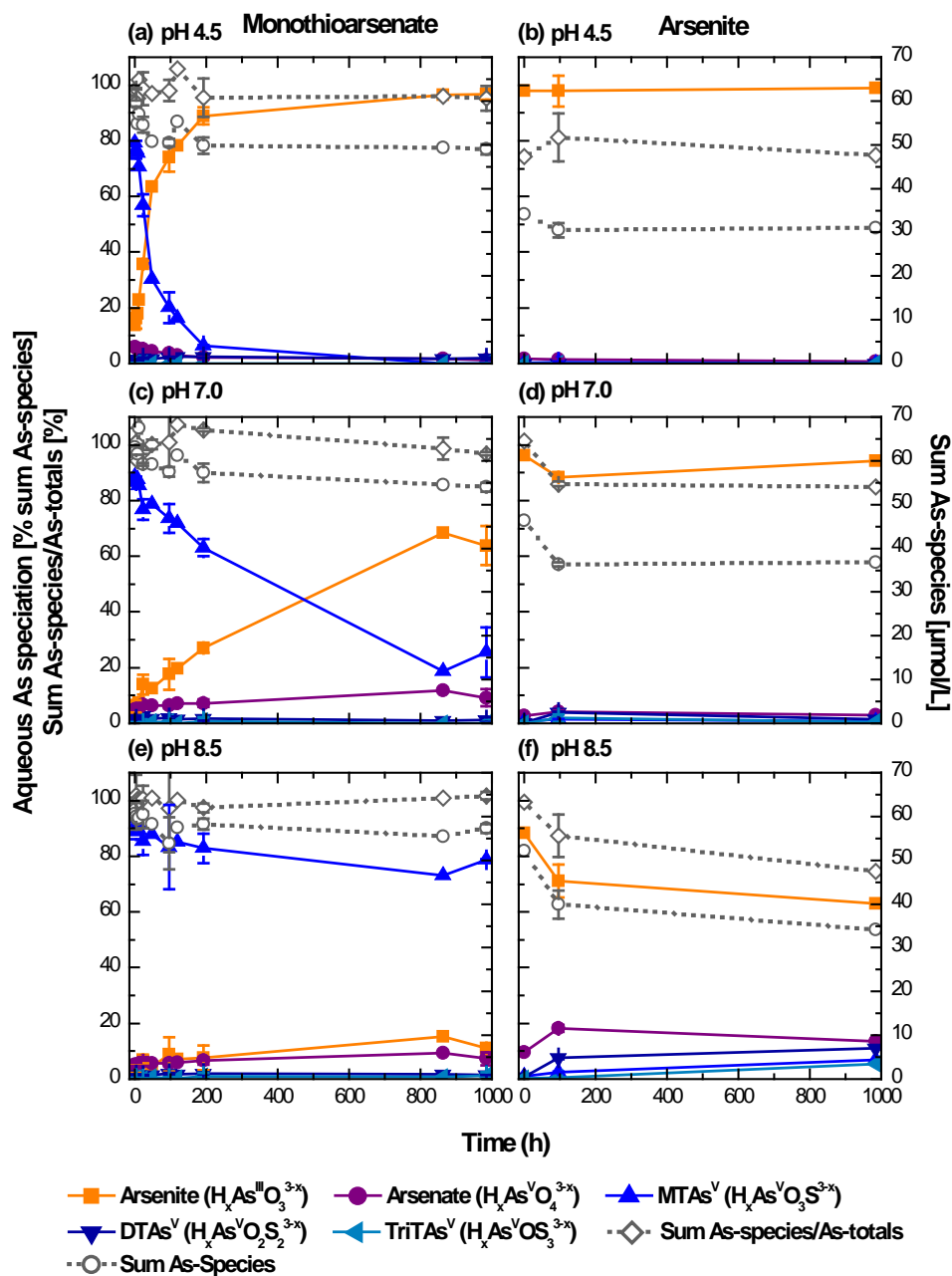
Figure 3: Aqueous As speciation [% of sum As species] of the time series experiments where MTAs(V) (left panel) or arsenite (right panel) was added to sulfide-reacted (3 mM sulfide) peat suspensions (0.2 M C) of pH 4.5 (a, b), pH 7.0 (c, d) and pH 8.5 (e, f). Error bars represent standard deviations of triplicates for 4, 24, 96, 192 and 984 h. Otherwise, single data points. Straight or dotted lines serve to guide the eye.
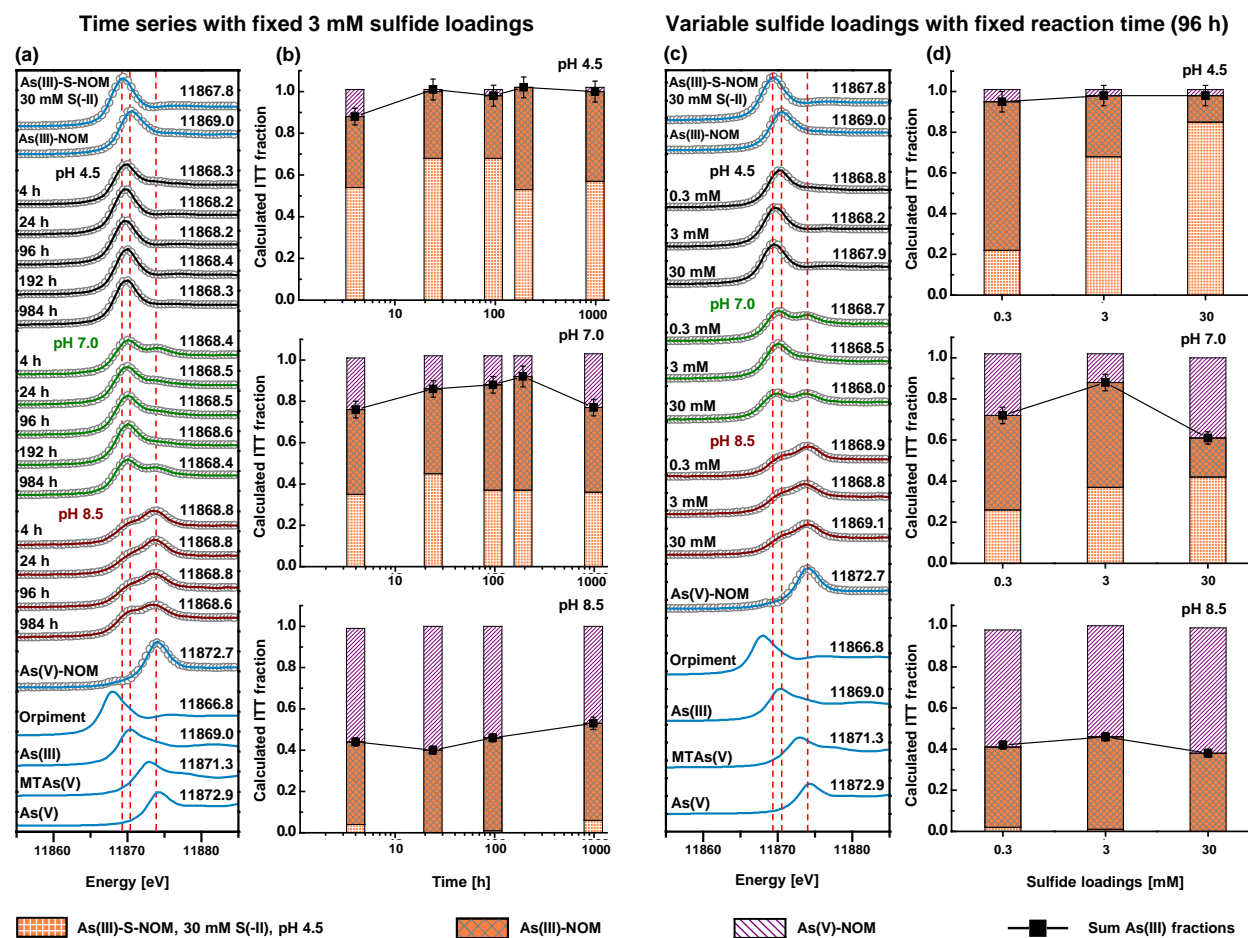
Figure 4: Normalized As *K*-edge XANES spectra and their respective edge-energies (eV) from the MTAs(V) time series experiment (4, 24, 96, 192 and 984 h) with fixed sulfide loadings (3 mM) (a) and variable sulfide loadings (0.3, 3, and 30 mM) but fixed time (c) and their respective ITT calculations (b), (d). Straight lines represent experimental data, the reconstruction of the whole series (experimental spectra form (a) and (c) is shown as circles. The vertical lines indicate the white line positions of the three identified components As(III)-S-NOM, As(III)-NOM and As(V)-NOM. Abbreviations: As(III): tri-valent As, As(V): penta-valent As, The S in As(III)-S-NOM is sulfhydryl-S. Sum As(III) fractions = As(III)-S-NOM + As(III)-NOM. For the ITT calculation of relative species concentrations, the concentrations of the three identified references were fixed at 100%, while the concentrations of the mixtures were calculated without

constraints; i.e., they were not normalized to 100%. Error bars represent general error of ITFA procedure of about 5% of relative concentrations. Straight lines in (b) and (d) serve to guide the eye.
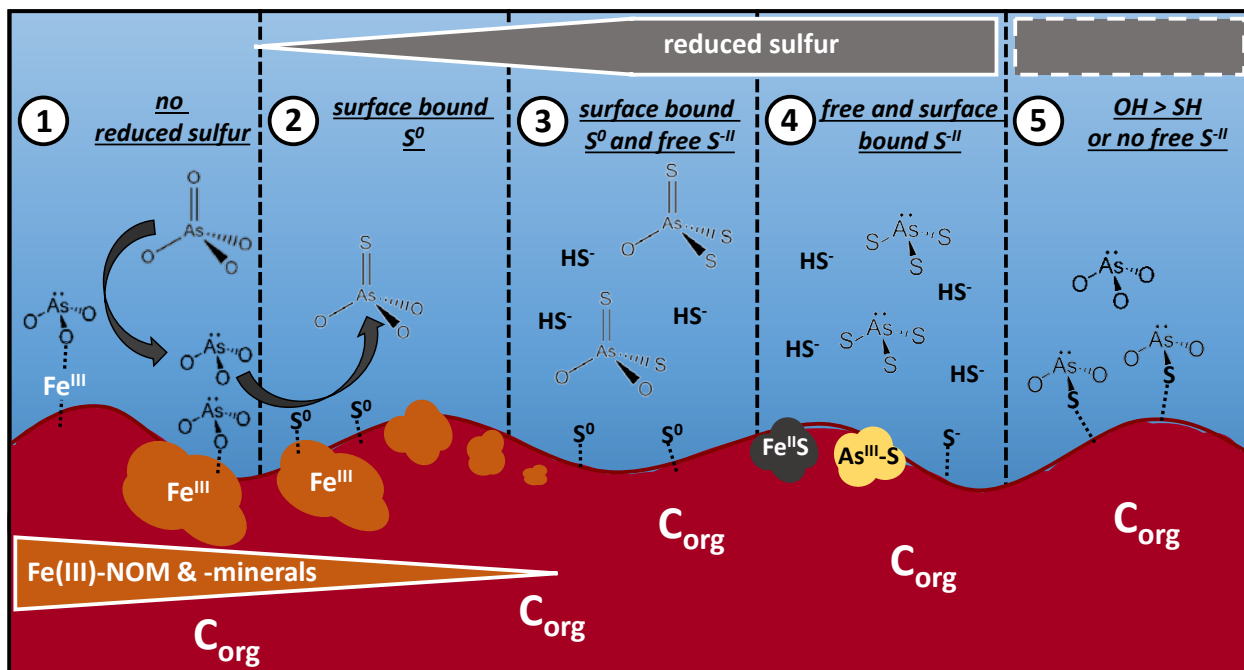
Figure 5: Conceptual model for As-S chemistry in *Gola di Lago* peatland. Scenario 1: arsenate and arsenite prevail as long as no reduced sulfur is present. Scenario 2: monothioarsenate formation from arsenite and surface bound zero-valent sulfur. Scenario 3: formation of higher thiolated arsenates from monothioarsenate under conditions of available free sulfide. Scenario 4: thioarsenite formation and eventually Fe-S and As-S precipitation in sulfide-rich micro-environments or during sulfide-rich times. Scenario 5: arsenite sorption to sulfhydryl groups of peat. Scenario 3 and 4 seem to be unlikely in *Gola di Lago* peatland since no free sulfide was detected. Dotted lines illustrate general inner-spheric coordination of the respective species but no specific coordination environments.