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"Antimonite Binding to Natural Organic Matter: Spectroscopic Evidence from a Mine Water Impacted Peatland"

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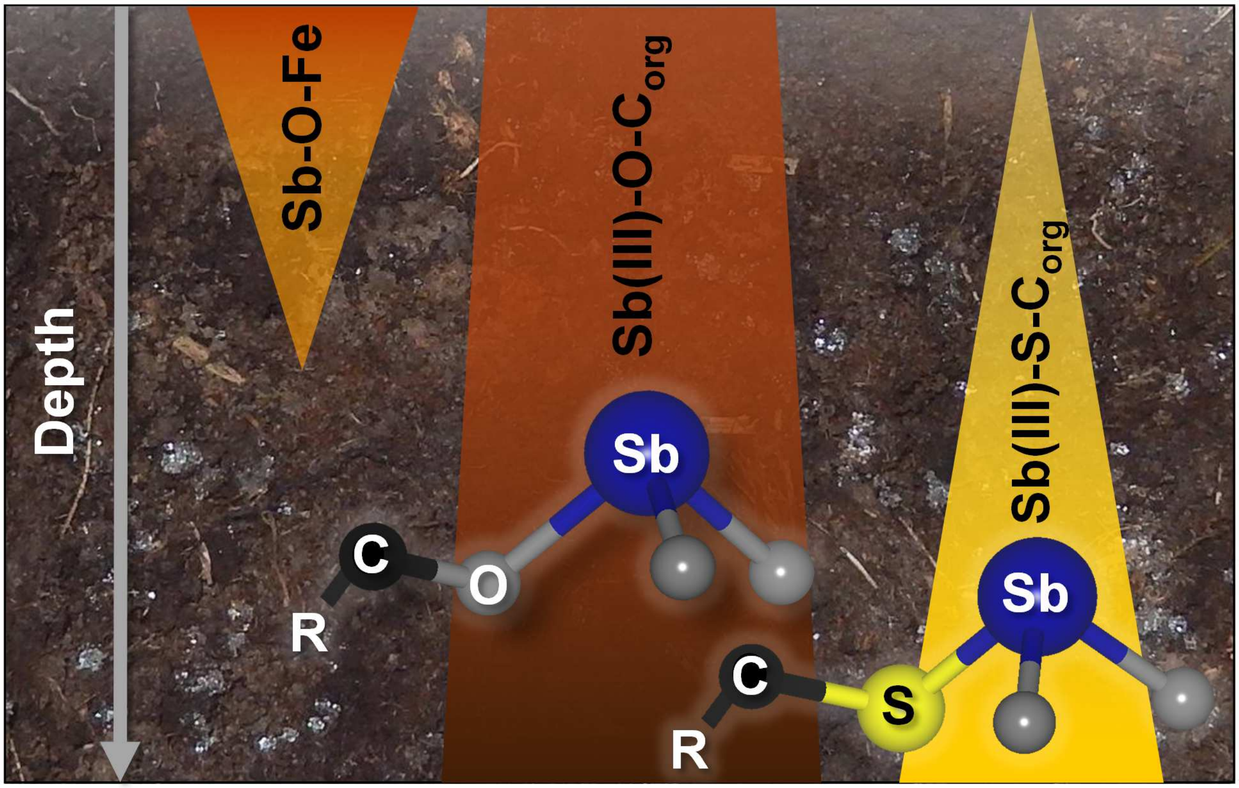
ABSTRACT

Peatlands and other wetlands are sinks for antimony (Sb). Solid natural organic matter (NOM) has thus been suggested to play an important role in controlling Sb binding in wetland sediments. However, direct spectroscopic evidence for this sequestration mechanism in natural peat samples is still lacking. In order to investigate Sb binding in peat, we sampled and characterized three profiles up to a depth of 80 cm in an Sb-impacted peatland in northern Finland. We used bulk *K*-edge X-ray absorption spectroscopy to study the speciation of Fe, S and Sb in the peat solid phase. Additionally, we determined the aqueous speciation of Sb in surface and pore waters. Based on linear combination fittings of extended X-ray absorption fine structure spectra, we found that Sb associated to the solid-phase is up to 100% coordinated to organic phenol and/or thiol groups. Even in the presence of iron, organically-bound Sb(III) was the dominant fraction in all peat profiles and across all depths. While aqueous antimonite concentrations were low, Sb(III) species were dominating solid-phase speciation, suggesting a high reactivity of Sb(III) towards peat surfaces. Our findings therefore confirm that Sb binding to solid NOM acts as an important sequestration mechanism under reducing conditions in NOM-rich wetlands.

TOC



INTRODUCTION

Wetlands span more than 6% of the global ice-free land area[1] and among those, peatlands, with ~3% land cover, are the dominant group of wetlands.[2] Next to important ecological functions regarding long-term carbon storage, niche for threatened animal and plant species or regulation of the water budget, peatlands are increasingly recognized as sinks for potentially toxic trace metal(loid)s[3-7] and therefore are an important factor controlling surface water and groundwater quality.

A potentially toxic trace element, which has only received increasing attention during the last decades due to increased mining activities[8,9] as well as increased industrial use[10-12] and proposed similar toxicity to arsenic[13,14], is antimony (Sb). Antimony is a redox-active trace metalloid that prevails, at environmentally relevant pH values, as pentavalent aqueous antimonate ($Sb(OH)_6^-$) under mostly oxic and as trivalent aqueous antimonite ($Sb(OH)_3$) under mostly anoxic conditions.[15]

The natural Sb background concentrations in soils and sediments (<10 mg kg^{-1})[12,16] as well as in surface and pore waters (<1 μg L^{-1})[12] are commonly low, however, anthropogenically impacted environments like shooting-range soils or mining impacted soils can reach Sb concentrations up to several thousand mg kg^{-1}, thereby jeopardizing water resources.[17,18]

Further, accumulation of Sb in peatlands or other wetlands rich in solid natural organic matter (NOM) has been reported in recent years.[16,19-26] Two main pathways of how antimony enters the peatlands or other wetlands have been described: either through atmospheric deposition related to smelter activities[19-22] or directly e.g. through Sb or gold mining, where (pre-purified) mining water gets in contact with wetland soils.[16,24,25]

Here, two mechanisms have mostly been discussed for Sb retention. In shallow layers, where water is still oxic and abundant (oxyhydr)oxides of iron (Fe) or manganese are thermodynamically stable, typically oxidized Sb(V) can be retained on the (oxyhydr)oxide surfaces by formation of innerspheric complexes.[17,27]

With increasing depth due to increasing water content and eventually saturation (anoxic conditions), iron and manganese (oxyhydr)oxides undergo reductive dissolution[28,29] typically accompanied by an initial release of associated Sb.[30] A (microbially catalyzed) reduction[31,32] of Sb(V) to Sb(III) can then facilitate reaction with (biogenic) dissolved sulfide to form authigenic amorphous Sb-S precipitates at low to neutral pH values, which has been considered as a main Sb retention mechanism in the anoxic zones of wetlands.[16,25,31,33]

As a third way of Sb retention, we recently demonstrated with purified model peat NOM and by use of X-ray absorption spectroscopy that Sb(III) can form innerspheric complexes with O-bearing groups of peat NOM.[34] Further, increased thiol content in the peat NOM lead to increased Sb(III) complexation via thiol bonds, demonstrating the higher affinity of Sb(III) to those organic moieties. These results suggest that retention of Sb in anoxic layers of peatlands may also be facilitated by direct complexation of Sb(III) with solid peat NOM and high dissolved sulfide concentrations for Sb(III) sulfide precipitation are not necessarily required.

Indeed, dissolved sulfide concentrations in peatlands are commonly low[35-38] since the (biogenically) produced sulfide can be effectively incorporated into NOM as organic thiols[35,39], often the dominant sulfur species in such systems.[40] Further, several studies have already observed a strong association of Sb with solid NOM,[19-23,25] however, direct spectroscopic evidence for Sb binding to NOM from field samples was lacking.

In order to study the fate of anthropogenic Sb in peatlands impacted by mine water, we exemplarily determined the speciation of Sb as well as Fe and S, elements which often govern Sb biogeochemistry, in three profiles in a mine water impacted treatment peatland located in Finnish Lapland (Figure SI-1). The peatland (~17 ha) has been used for purification of pre-treated drainage water from open pits and underground gold mining and is in operation since 2006. Inflow to the peatland contains high loads of SO_4^{2-}, N, P and various metals and metalloids including Ni, As and Sb. Previous water analyses showed that Sb inflow concentrations were higher than the outflow concentrations, indicating that the peatland sequesters Sb.[16]

The objective of our study was hence to identify the dominant Sb solid-phase binding mechanisms in natural peat impacted by Sb containing mine water. Therefore, we geochemically characterized three peat profiles distributed over the peatland and analyzed selected peat samples by means of bulk Sb, Fe and S X-ray absorption spectroscopy.

Additionally, we used aqueous Sb speciation supplemented by thermodynamic calculations to further investigate Sb sequestration potential.

MATERIALS AND METHODS

Field Work. Peat profiles were sampled at three different locations along the water flow from near to the inflow to close to the outflow of the peatland (B1-B3, Figure SI-1). Location and field-site characteristics have been published before[16] and are summarized in the **Supporting Information**.

Peat pore water was sampled using equilibrium dialysis samplers (peepers) of type Hesslein[41,42] with a length of 80 cm and 5 cm resolution for the first 20 cm and 10 cm resolution from 20 to 80 cm. Peepers were installed in mid-May 2017 for four weeks to guarantee equilibrium conditions.[42] After collection, peepers were transported in Argon-filled bags to avoid redox-induced sample change to the close-by provisional field laboratory. There, pore water was sampled from the chambers of the peepers using syringe and needle. Samples were filtered (0.2 µm, cellulose acetate), stabilized and cooled or analyzed directly on-site.

Within a radius of ~30 cm to each peeper location, peat cores were sampled up to a maximum sampling depth of 80 cm using a Russian Peat Borer. Then, the peat cores were separated into 10 cm sections to match the pore water information obtained from peepers. Each depth section was immediately transferred to a separate argon filled glass bottle (50 mL), purged again with argon before closing and screwed with PTFE-sealed screw caps. Afterwards, the bottles were transported under refrigerated conditions on ice packs to the laboratory in Bayreuth, where they were immediately processed within an anaerobic glove bag (Coy, N_2/H_2 95/5 % (v/v), pO_2 <1 ppm). Details about the pore water and peat core sampling procedure can be found in the **Supporting Information.**

Aqueous-Phase Analyses. Redox potential, pH and electrical conductivity were determined directly after sampling the chambers using a special set-up to minimize redox changes and to handle small sample volumes (Figure SI-2). Dissolved sulfide was quantified using the methylene blue method[43] and ferrous iron (Fe(II)) as well as total dissolved iron (Fe(tot)) were measured using the phenanthroline method[44] with a portable photometer (LASA 100, Dr. Lange) at wavelengths of 605 nm and 480 nm, respectively. Total aqueous Sb and S concentrations were determined by inductively coupled plasma mass-spectrometry (ICP-MS, XSeries2, Thermo-Fisher) in stabilized pore water samples (0.44% (v/v) H_2O_2 (Fisher Scientific), 0.78 % (v/v) HNO_3 (Kraft)). Aqueous Sb speciation of samples stabilized in 0.2% (v/v) HCl (Kraft) was carried out with an anion-exchange chromatography (AEC, ICS-3000, Dionex; PRPX-100, 250 x 4.1 mm, 10 µm, Hamilton) coupled to an ICP-MS using an isocratic elution with 10 m NH_4NO_3, 10 mM $NH_4H_2PO_4$, and 500 mg/L Na_2-EDTA at a flow rate of 1.0 mL/min. Calibration standards were prepared from potassium antimonyl tartrate sesquihydrate (Acros) and potassium hexahydroxoantimonate (Fluka) stock solutions.

Solid-Phase Analyses. Back in the laboratory in Bayreuth, the peat of each depth section was homogenized in its bottle inside a glovebag and transferred into a 50 mL polyethylene tube (Sarstedt) for freeze-drying.[45] One part of freeze-dried peat was stored anoxically, dry and dark until solid-phase analyses and another part was milled to <45 µm in a ball mill (MM2000, Retsch) for total element determination. Total Sb content was determined by ICP-MS and total Fe and S contents by inductively coupled plasma optical emission spectrometry (ICAP 6300 Duo View, Thermo-Fisher) after microwave digestion (MARS Xpress, CEM) using a 5:3 ratio of 30% H_2O_2 and 65% HNO_3. To get an overview of the down-core distributions of many other major and trace elements, ground peat samples were analyzed by an energy dispersive X-ray fluorescence spectrometer (XEPOSTM, Spectro X Lab) together with a NIST 2711 certified reference material. Total C content was analyzed with a TOC analyzer (multi N/C 2100, Analytik Jena).

Selected peat samples were examined by scanning electron microscopy (SEM) using a Leo Gemini 1530 (Carl Zeiss, Germany) with a Schottky emitter and elemental composition analysis was conducted by energy-dispersive X-ray spectrometry (EDS, Oxford X-Max 20, Oxford Instruments). Therefore, selected freeze-dried and homogenized peat samples were ground in a mortar, mounted on aluminum specimen stubs and coated with carbon.

For synchrotron measurements at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, USA, selected freeze-dried, homogenized and ground peat samples from all three sample locations were filled into aluminum sample holders and sealed with Kapton tape. Thereby, samples were always kept under anoxic conditions until the end of XAS experiments. Bulk Sb *K*-edge (30,491 eV), Fe *K*-edge (7,112 eV), and S *K*-edge (2,472 eV) XAS spectra were collected in fluorescence mode at beamlines 11-2 (Sb), 4-1 (Fe), and 4-3 (S) under cryogenic (10 K, 11-2 and 4-1) or ambient (inert He ($<0.1\%$ (v/v) O_2) atmosphere, 4-3) temperatures. The collected Fe *K*-edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectra and Sb *K*-edge EXAFS spectra were analyzed by linear combination fitting (LCF) using Athena[46] after principal component analysis and target-transform testing (PCA-TT) using SIXpack.[47] The Sb *K*-edge EXAFS shell-by-shell fitting analysis was performed in Artemis.[46] Spectral deconvolutions of normalized S *K*-edge XANES spectra were done in Athena.[59] Details on all XAS measurements, data reduction, and analyses are provided in the **Supporting Information.**

RESULTS AND DISCUSSION

General Geochemical Parameters and Vertical Element Distributions. Geochemical on-site parameters revealed a slightly acidic to circumneutral pH (5.8-7.4) and oxic to sub-oxic redox conditions (148-454 mV). Both pH and redox potential decreased with increasing depth in the peat profiles (Table SI-2). Electrical conductivity remained almost constant across the profile closest to the inflow (B1; 2.0 ±0.2 mS cm^{-1}) but decreased with increasing depth in the other profiles. High total aqueous S concentrations (10.4±2.3 mmol L^{-1}, Table SI-2) thereby mainly contributed to the electrical conductivity (Figure SI-3) of the peatland and originated from oxidation of sulfide ores to aqueous sulfate (Table SI-1) during the mining process.[16]

Down-core distributions of total solid Sb, S, Fe and C_{org} are illustrated in Figure 1 and distributions of additional major and trace elements are displayed in Table SI-3. Antimony contents ranged from <0.1 to 2.2 mmol kg^{-1} ($\bar{x}$=0.6 mmol kg^{-1}). They were highest close to the peat surface in all profiles and decreased with increasing depth. Iron exhibited a similar distribution pattern to Sb, whereas the contents of S only slightly decreased and the contents of C_{org} slightly increased with depth by maintaining minimum Fe:Sb, S:Sb and C_{org}:Sb molar ratios of 64, 136 and 17,000, respectively.

Total aqueous Sb in surface waters was highest close to the inflow (B1, 1,566 nmol L^{-1}) and only slightly decreased towards the outflow (B3) to 1,439 nmol L^{-1}. Within peat profiles, total aqueous Sb concentrations ranged from 63 to 2,275 nmol L^{-1} ($\bar{x}$=480 nmol L^{-1}) and showed a similar pattern as for solid-phase Sb (Figure 1a). However, aqueous Sb concentrations in B2 were low (max. 380 nmol L^{-1}) throughout the profile and solid-phase Sb contents were elevated in the first 40 cm, suggesting high Sb retention within the peat (Figure 1).

Iron and Sulfur Solid-Phase Speciation. Solid-phase Fe speciation results from Fe *K*-edge XANES and EXAFS spectra of peat samples as well as Fe reference compounds identified as peat compounds during spectra evaluation are illustrated in Figure 2 and summarized in Table SI-10 and 11. Identification of major Fe species and quantification of their respective fractions within peat samples was done by means of PCA-TT followed by LCF analysis of XANES and EXFAS spectra. Firstly, the number of potential Fe species within the peat samples was elucidated by PCA and suitable reference compounds were identified with TT out of a comprehensive library (Table SI-7 and 9). Afterwards, LCF analysis was performed and the significant number of fitted components for the respective sample spectra was confined with the Hamilton test. Best LCF fit models for XANES and EXAFS spectra thereby were almost identical, suggesting overall realistic fit results (Table SI-10 and 11).

Solid-phase Fe speciation revealed up to 43% of Fe occurring as phyllosilicates in the upper peat layers which was additionally supported by SEM-EDS results (Figure SI-3, Table SI-4). Phyllosilicates most probably originated from the underlying bedrock of greenschist[48] and presumably entered the peatland via the inflow of treated mine drainage water. Organic Fe(III) complexes (up to 47%) generally decreased with increasing peat depth, whereas Fe(II)-NOM complexes (up to 48%) increased. Organic Fe(III) complexes can form in substantial amounts, even at neutral pH values, in oxic layers of environments with abundant NOM such as peatlands and can even dominate over Fe (oxyhydr)oxides.[49] Although, PCA-TT analyses of EXAFS spectra suggested that ferrihydrite, lepidocrocite, and/or schwertmannite, all representatives of Fe (oxyhydr)oxides, were suitable reference compounds (Table SI-7 and 9), no Fe (oxyhydr)oxides could be fitted to the sample spectra in significant percentages (>10%). Nonetheless, the existence of at least small amounts of Fe (oxyhydr)oxides could be demonstrated by SEM-EDS, where a particle of most likely lepidocrocite, an Fe (oxyhydr)oxide forming through oxidation of aqueous Fe(II) e.g. induced through an oscillating water table, was observed. (citation)

Further, the formation of substantial amounts of Fe(II)-NOM complexes in deeper peat layers suggests that solid NOM plays an active role in (re)-sequestering aqueous Fe(II)[50] (Table SI-2) after (microbially catalyzed) reductive dissolution of Fe (oxyhydr)oxides[28], Fe containing phyllosilicates[51,52] or Fe(III)-NOM complexes.

Additionally, with increasing depth and subsequently increasing reducing conditions (Table SI-2), the presence of (authigenic) iron mono sulfides (FeS) increased and dominated the Fe speciation in deeper peat layers (up to 71%). Here, our SEM-EDS analyses also added supporting information about presence of FeS precipitates (Figure SI-3, Table SI-4).

Sulfur *K*-edge XANES spectra of selected peat samples are shown in Figure 3 and the results from Gaussian deconvolutions, which represent s → p transitions of major S fractions, are illustrated in Figures SI-5-6 and Tables SI-12-13. The S XANES spectra could generally be divided into two main spectral regions. The first region ("reduced S") with white line energies <2774.5 eV corresponded to inorganic (mono) sulfide, exocyclic/elemental S and heterocyclic S. The second region with white line energies >2780.6 eV ("oxidized S") was characterized as sulfonate S and sulfate S. The region with energies in between ($2774.5< x <2780.6$ eV) and with only minor importance in our samples (max. 14% of fitted fractions) was summarized as "intermediate oxidized S" which was deconvoluted as sulfoxide S and sulfone S fractions and was likely to be overestimated due to post-edge absorption features of reduced S species.[53]

Validity of the Fe and S solid-phase speciation results was verified by comparing fitted FeS fractions (from Fe XANES and EXAFS analyses) and inorganic (mono) sulfide fractions (from S XANES analyses) and deviations were found to be reasonable ($\bar{x}$=43±32%, Table SI-14).

Two main down-core trends were observed for S in each peat profile. The fractions of oxidized S, which dominated all spectra at the peat surfaces (27-41%), decreased with increasing peat depth to 20-27%, whereas the reduced S fractions increased and dominated deep peat layers (66-71%) (Figure 3, Table SI-13). The oxidized S fraction hereby was mainly represented through sulfate S (Figure SI-5), which most likely originated from the high sulfate inflow concentrations (Table SI-1) and at least partly precipitated as artificial calcium sulfate ($CaSO_4$) during the freeze-drying process of peat samples (Figures SI-4 and SI-6, Table SI-4) due to the low solubility of $CaSO_4$ (K_{SP} = 4.36).

Within reduced S fractions, the exocyclic/elemental S fraction, often represented as thiol-S in organic-rich sediments,[40] prevailed in deep peat layers (32-35%) followed by inorganic (mono) sulfides (20-27%) (Figure SI-6). Both are suitable entities for antimonite sequestration.[34,54] Formation of organic thiol groups and/or inorganic (mono) sulfides in deeper peat layers often is linked to (microbial) sulfate reduction[40], although in all measured samples, dissolved sulfide concentrations were low (max. 3.6 μmol L^{-1}, Table SI-2).

Overall, our solid-phase speciation results demonstrate that independent of the electronic state of Fe and S, which followed the oxic-anoxic down-core redox gradient, NOM plays an important role as reaction partner or binding site in the peatland and thus may also be an important factor for Sb retention.

Antimony Solid-Phase Speciation. Figure 4 shows Sb *K*-edge XANES and EXAFS spectra from selected peat samples as well as Sb reference compounds identified as peat compounds during spectra evaluation. The edge positions of XANES spectra varied between 30,492.5 and 30,493.8 eV and showed a clear decreasing trend with increasing peat depth within each peat profile (Figure

4a). Edge positions fell between Sb(III) and Sb(V) reference compounds indicating mixtures of Sb species (Figure 4e).

Similar to Fe solid-phase analyses, we used PCA-TT followed by LCF of EXAFS spectra to elucidate the coordination environment of Sb in peat samples. Best LCF models revealed the presence of five major Sb species, specifically Sb(III) and Sb(V) inorganically associated with Fe, Sb(III) associated with O-bearing groups of NOM (Sb(III)-O-C_{org}), Sb(III) associated with thiol groups of NOM (Sb(III)-S-C_{org}) and an amorphous Sb(III) sulfide phase. All LCF results are illustrated in Figure 4d and summarized in Table SI-18.

Several similar Sb down-core trends were observed in all peat profiles. With fractions of 22-24%, Sb(V) associated with Fe solely existed in the uppermost peat layers and only in profile B1 at 40 cm, a significant fraction of Sb(III) associated with Fe (18%) could be fitted; despite the general correlation between down-core total Sb and Fe contents and a minimum molar Fe:Sb ratio of 64 in all profiles described before (Figure 1). A similar observation was made by Mikutta and Rothwell[55] in British peat bogs, where a correlation between As and Fe contents was observed, but contribution of As-Fe associations was only moderate.

The exact Sb-O-Fe binding mechanisms hereby remain elusive, since our best-fit references "Sb(III)/(V)-ferrihydrite" have to be considered as proxies for Fe coordination environments such as the before described Fe (oxyhydr)oxides, Fe containing phyllosilicates and/or Fe(II)/Fe(III)-NOM complexes. The Fe(II)/Fe(III)-NOM complexes can provide Fe as bridging cation for ternary complex formation (as e.g. described for As[56-58]). Despite up to 100% of Fe-NOM complexes found, no ternary As-Fe-OM complex formation was observed in an EXAFS study on As binding in peatlands before.[55] These results suggest that ternary Sb-Fe-NOM complexes tend to be of minor importance, which is underlined by the fact that up to 62% (Figure 2) of Fe-NOM complexes were found in the studied peatland while a maximal of only 25% of Sb was associated with Fe (Figure 4).

With 63-100% ($\bar{x}$=82%), organically coordinated Sb(III) was found to be the dominant fraction in every peat profile and across all depths (Figure 4, Table SI-18). Hereby, Sb(III) associated with O-bearing groups, abundant in peat NOM, revealed the highest percentages (52-64%, $\bar{x}$=60%). High affinity of antimonite to O-bearing groups of microbial extracellular polymeric substances and solid model peat NOM has just recently been shown.[34,59] However, Sb-C distances in Besold et al.[34] were considerably longer (2.90 Å) than the fitted Sb-C distance of our best-fit reference compound “Sb(III) complexed with Aldrich humic acid” (2.83 Å, Figure SI-8, Table SI-19), but both lay in the range of published Sb-C distances of ~2.85 - ~2.92 Å[60,61], indicative for phenol groups.

Regardless of the fact that we could observe an Sb-C(O) backscatter feature in the Fourier transforms of our sample spectra, we were not able to model a significant Sb-C(O) contribution within our shell-by-shell fit approach, probably due to partly overlaying Sb-S resonances (Figure SI-9). Nevertheless, systematic exclusion of this Sb(III)-O-C reference in test fits lead to clearly worse fit qualities (Table SI-20) and therefore suggest the Sb(III)-O-C reference to be a true component in the studied peat samples.

The LCF results further revealed that with increasing depth, Sb(III) was increasingly bound to thiol groups of NOM (14-37%, $\bar{x}$=22%) and therefore showed a similar down-core pattern as the exocyclic/elemental S fraction fitted to the S XANES spectra as described before (Figure SI-6). In one case an Sb(III) sulfide phase was fitted with 37% to the spectrum of sample B2 60 cm (Figure 4, Table SI-18). Shell-by-shell fitting of Sb-S distances of 2.46±0.01 Å for thiol-bonds and a fitted Sb-S distance of 2.48 Å for the Sb(III) sulfide containing sample confirmed our LCF results

(Figure SI-10 and Table SI-21). Formation of Sb(III)-S surface associations on FeS phases in peat samples (Figure 2) with similar Sb-S distances of 2.46 Å[54] cannot be fully excluded, however, in a previous study[34] we demonstrated that spectral differences between organic thiols and inorganic Sb(III) on FeS phases exist and during our LCF analysis we found no best fit model where the latter significantly contributed to or improved fit quality (Table SI-18). Interestingly, sample B2 60 cm, where the Sb(III) sulfide phase was found and redox potential was lowest (148 mV), also exhibited the highest contribution of inorganic (mono) sulfides within all S XANES spectra (Figure SI-6), indicating required natural conditions for inorganic Sb-S sequestration in our system.

In summary, our Sb speciation results suggest that organically complexed Sb dominates solid-phase Sb in all peat samples even in the presence of Fe phases and formation of thiol-bound Sb with increasing depth correlates with the thiol group content in peat.

Geochemical Factors Leading to Low Sb Purification Efficiency in the Studied Peatland. Our Sb solid-phase speciation results showed high affinities of Sb to organic functional groups of peat and recent results from Besold et al.[34] moreover demonstrated high sorption capacities of model peat NOM for Sb under reducing conditions, both indicating a high Sb removal potential of peatlands. However, the long-term purification efficiency in the investigated peatland is low (~30%).[16]

The peatland received high Sb inflow concentrations (1884±876 nmol L^{-1}) over the past ten years. High hydrological loads (41±20 mm d^{-1}) (Table SI-1), which lead to mostly water overflow conditions (~20 cm), may be considered as a suitable explanation for low Sb retention.[62] However, geochemical factors also have to be regarded in order to obtain a comprehensive understanding of this system.

Aqueous antimony speciation of surface waters revealed solely the presence of antimonate and only little increase of antimonite with increasing depth was found in profile B2 (Figure SI-11). Aqueous thio-antimony species using another chromatographic method (not shown) were not detected in any of the profiles. Pourbaix diagrams for the Sb-O-H-S system were calculated with PhreePlot using peatland Sb and S concentrations (Figure SI-12). Plotting respective pH-E_h-values from B1-B3 (Table SI-2) in the Pourbaix diagram confirmed that all surface water samples were located in the predominance field of antimonate. Further, all samples from profile B1 and upper layers of B3 were located in the predominance field of antimonate and only samples from B2 and low B3 layers ranged around the boundary between antimonate and antimonite, generally supporting results from aqueous Sb speciation.

Thus, both thermodynamic calculations and aqueous Sb speciation show that the majority of aqueous Sb was present in form of the negatively charged antimonate oxyanion ($Sb(OH)_6^-$).

Natural organic matter has a net negative surface charge which further increases with increasing thiol group content and increasing pH[63], thus, probably leading to electrostatic repulsions with the negatively charged antimonate at pH>4.[64,65] This repulsion is considered as main factor for overall low Sb retention.[66]

Additionally, dissolved organic matter in the peatland, though not analyzed, may have a negative effect on antimonate sorption capacity to metal (oxyhydr)oxides (e.g. ferrihydrite and/or lepidocrocite) by competitive sorption and through organic-mineral interactions. These interactions in turn can lead to a loss of sorption sites as well as steric and electrostatic repulsions towards other species like arsenate or antimonate[67-69] and may partly explain the low affinity of antimonate to Fe surfaces in our system. This effect is probably supported by the relatively high pH of ~7 in the peatland and points of zero charge of naturally existing (oxyhydr)oxides being usually lower than the ones in synthetic precipitates (e.g. 5.3-7.5 vs. 8.0-8.3 for ferrihydrite[61,62]). Therefore, lowered outer-sphere complexation of Sb with metal (oxyhydr)oxides through less protonated surface sites is also suspected.[70]

While geochemical reasons for low antimonate retention were elucidated before, an efficient (microbially catalyzed) transformation of antimonate to antimonite in the peatland would certainly increase total Sb retention on phyllosilicates or (oxyhydr)oxides as well as on peat NOM surfaces.[34,70] Slightly acidic inflow conditions (pH 5-6) then could probably further increase Sb(III) thiol-binding or even lead to Sb(III) sulfide precipitation as described in the literature for arsenic.[38]

The low concentrations of aqueous antimonite (Figure SI-11) on the one hand, but almost only Sb(III) species found during Sb solid-phase speciation (Figure 4) on the other hand, hereby suggest a high reactivity of Sb(III) towards peat surfaces.[25] Therefore, antimonate reduction kinetics probably are a key limiting factor in this system. Low reduction rates may explain, together with the high Sb inflow concentrations, why antimonate dominates aqueous Sb speciation in most peat layers despite sulfate-reducing conditions, as verified by FeS formation (Figure 2 and Figure 3). Almost identical sulfate inflow-outflow concentrations (Table SI-1) and low dissolved sulfide concentration in peat profiles (Table SI-2) further show that the peatland chemistry was substantially governed by the inflow water chemistry.

In sum, the high hydrological load, which leads to short water residence times and preferential flow in the peatland[62] in combination with the high antimonate inflow concentrations as well as the cold climate in Finnish Lapland (-0.5°C mean annual temperature)[16], which probably results in lowered microbial activity and therefore reduced antimonate and sulfate reduction rates, are considered as main factors hindering efficient Sb retention.

Environmental Implications. Peatlands and other wetlands have been reported to act as geochemical sinks for Sb before,[16,19-25] but direct spectroscopic evidence elucidating the Sb coordination environments of natural peat was missing. Our results therefore add important information about the biogeochemistry of Sb in (mine water impacted) peatlands, supported by solid-phase spectroscopic data of Fe and S, elements which often govern the geochemistry of Sb.

Our molecular findings reveal that Sb was not primarily coordinated to Fe phases, even close to peat surfaces, as implied by the macroscopic correlation between Sb and Fe, but rather that organic functional groups of abundant peat NOM are the main controlling factor for Sb, Fe, and S biogeochemistry in peatlands. Our results therefore highlight the complex interplay of metal(loid)s such as Sb in peatlands, where NOM not only serves as carbon source for Sb redox dynamics[71] or competing molecule (DOM) for Sb sorption on mineral surfaces[17], but also as effective sorption site for Sb sequestration.

The innerspheric binding of antimonite to phenol and/or thiol groups may therefore also explain why Sb showed similar distribution pattern as organically-bound lead in ombotrophic peat profiles after atmospheric deposition.[19-21] The post-depositional immobility of Sb over long time periods[20,21] thus let us speculate about the long-term stability of these Sb-NOM associations.

Solid-phase Sb speciation results further imply that abundant peat organic phenol and thiol groups are key binding sites in natural wetland samples for reduced antimonite and demonstrate their high importance in comparison to Sb sulfide precipitation. Although important for Sb sequestration, Sb(III) sulfide phases seem not to form primarily under sub-oxic conditions and low dissolved sulfide concentrations, as they prevailed in the studied peatland.

ASSOCIATED CONTENT

Supporting Information

Field site characteristics and sampling, Additional general geochemical characterization, Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy analyses and results, Iron solid-phase speciation analyses and results, Sulfur solid-phase speciation analyses and results, Antimony solid-phase speciation analyses and results, Aqueous Sb speciation results

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Notes

The authors declare no competing financial interest.

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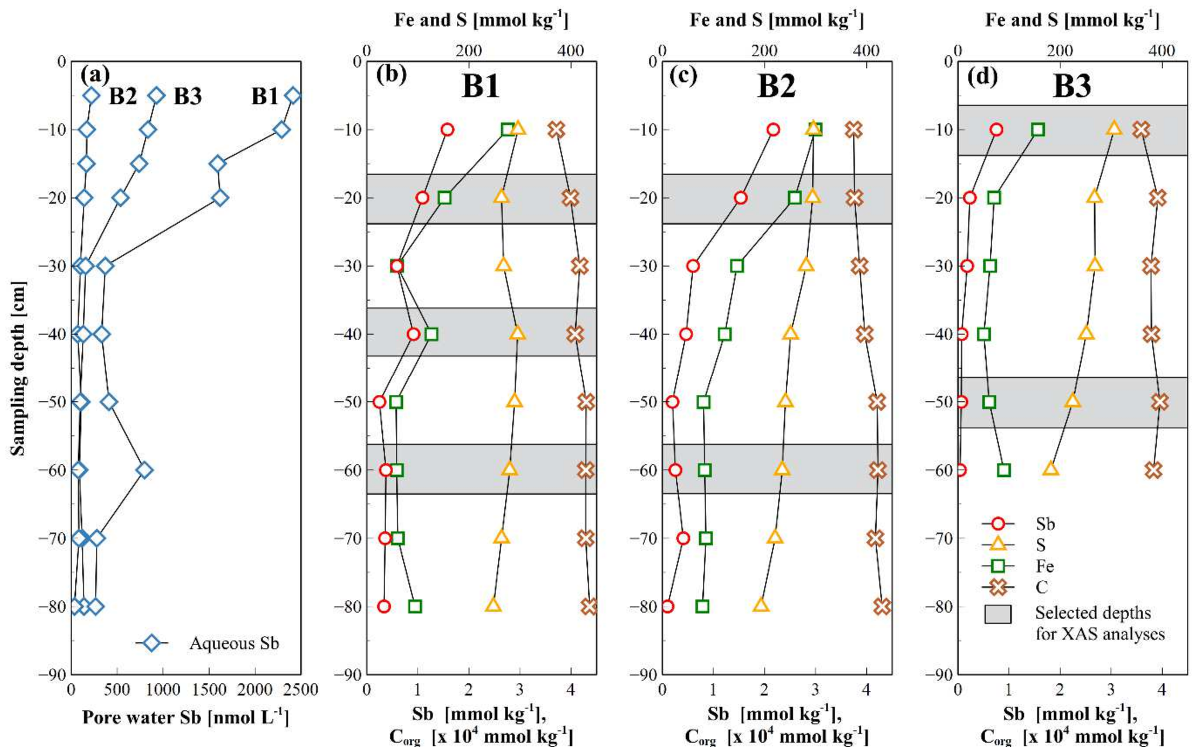
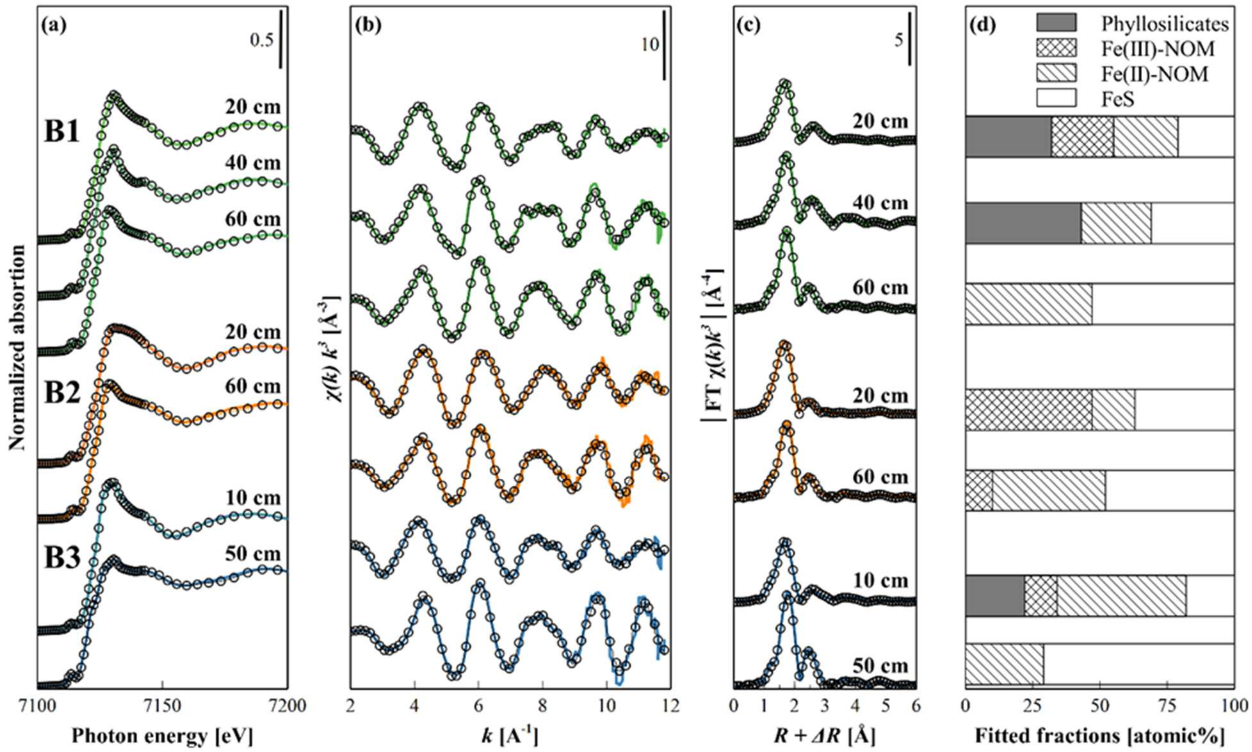


Figure 1: Vertical element distributions in peat samples for sampling points B1-B3. Total aqueous Sb concentrations (a) and down core contents of Sb, S, Fe, and C_{org} for sampling points B1-B3, respectively (b-d). Element contents are given on dry-weight basis. Total C represents organic C (C_{org}) only as absence of carbonates was tested with 10% HCl. Depth resolution for aqueous Sb: 0-20 cm: 5 cm; 20-80 cm: 10 cm. Solid-phase element distribution resolution: 10 cm, whereby e.g. 10 cm depth means an integrated sample from 0-10 cm. At sampling location B3, solid-phase sampling was only possible down to 60 cm. Please note that the scales differ between upper and lower x-axes.

Fe Samples



Fe References

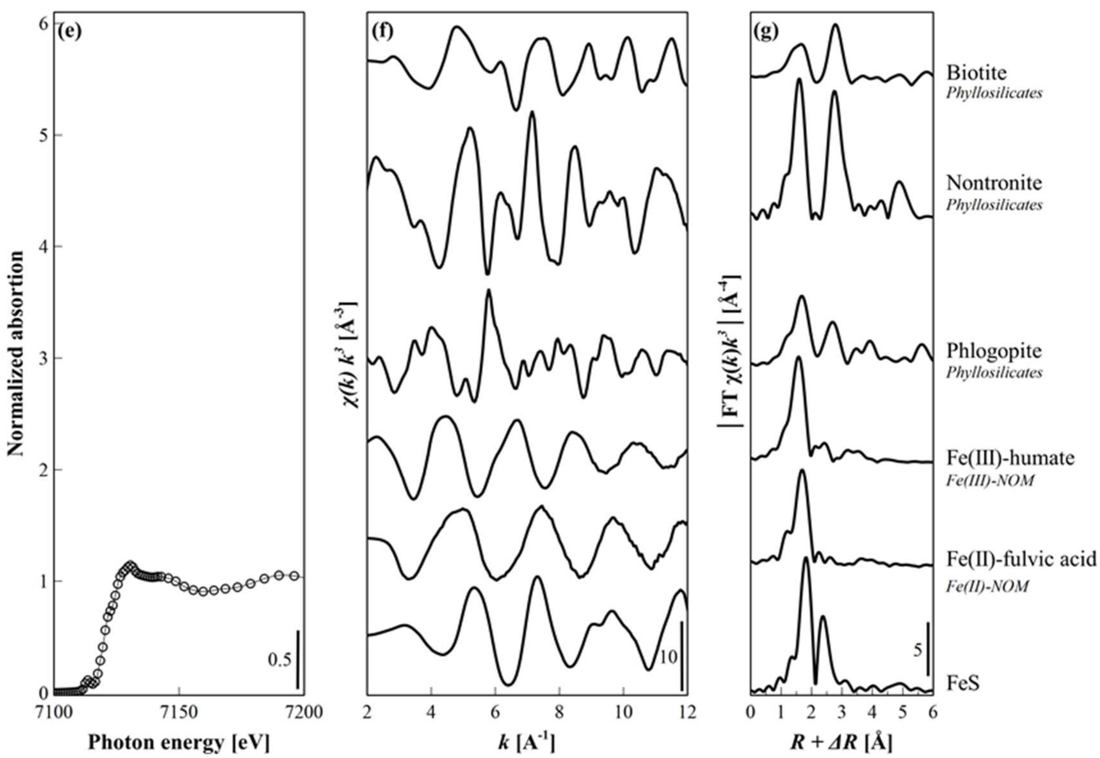


Figure 2: Normalized Fe *K*-edge XANES spectra (a, e), k^3-weighted Fe *K*-edge EXAFS spectra (b, f) and their corresponding Fourier-transform (FT) magnitudes (c, g) of selected peat samples and Fe references. Best linear combination fits of Fe *K*-edge EXAFS peat spectra (d). The Fe EXAFS spectra are illustrated here as LCF results since similarities of XANES spectra for different iron sulfides and oxides do not appear for EXAFS spectra and make EXAFS LCF a more powerful method for Fe solid-phase speciation. Detailed results about Fe *K*-edge XANES and EXAFS best fit models can be found in Table SI-10 and 11. Individual fractions were constrained to values between 0 and 100%, the sum of fractions was not constrained. Linear combination fits of the samples are shown as black circles. Fit references: Phyllosilicates=∑(Biotite, Nontronite, Phlogopite). Fe(III)-NOM = Fe(III)-humate. Fe(II)-NOM = Fe(II)-DOM (Suwannee River Fulvic Acid (SRFA)). FeS = FeS from microbial sulfate reduction.

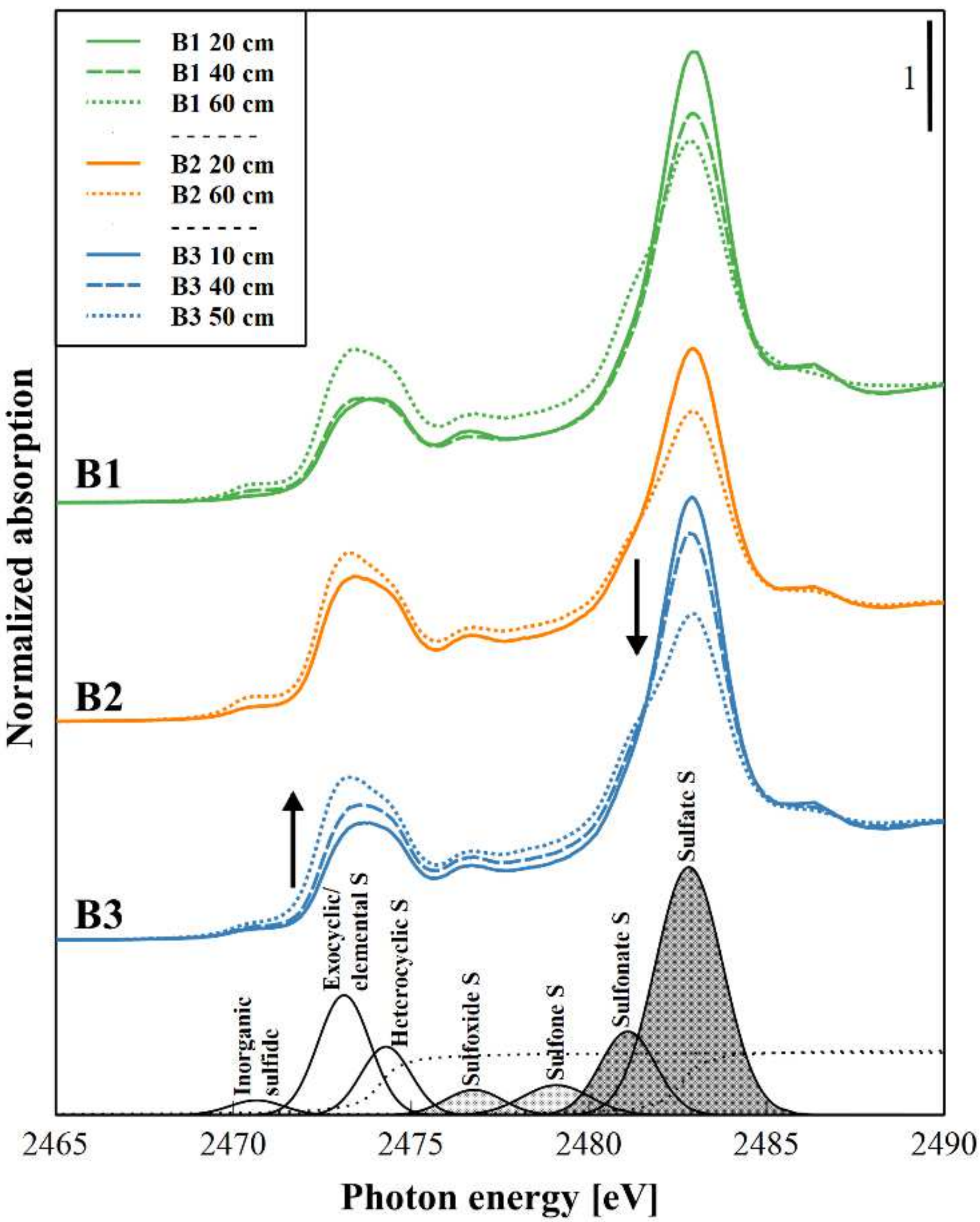
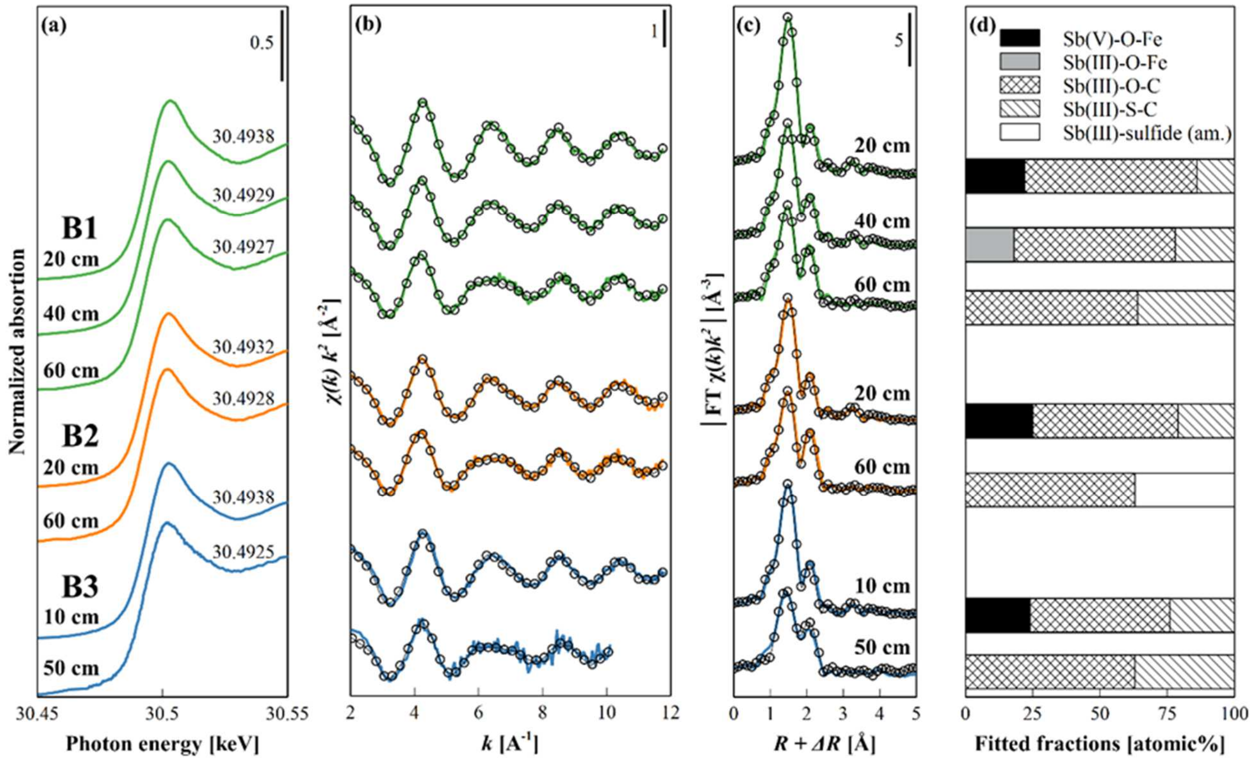


Figure 3: Sulfur solid-phase speciation of selected peat samples from sampling points B1-B3. The normalized S *K*-edge XANES spectra of peat are plotted as a function of sampling depth. Spectral decomposition is illustrated as an example for sample B3 50 cm (with offset from the other spectra). The two arctan functions are shown as dotted lines and the Gaussian functions as straight lines correspond to <u>reduced S (oxidation states –II to + I; no shading):</u> inorganic (mono) sulfide,

exocyclic/elemental S, heterocyclic S; intermediate oxidized S (oxidation states >+I to + III; light grey shading): sulfoxide S, sulfone S and oxidized S (oxidation states >+III to +VI; dark grey shading): sulfonate S, sulfate S. The experimental data and fit envelopes as well as all fit parameters for every sample can be found in Figure SI-5 and SI-6 as well as Table SI-12 and 13. Please note that the intermediate oxidized fractions (sulfoxide and sulfone S) are likely to be overestimated due to post-edge absorption features of reduced S species.[53]

Sb Samples



Sb References

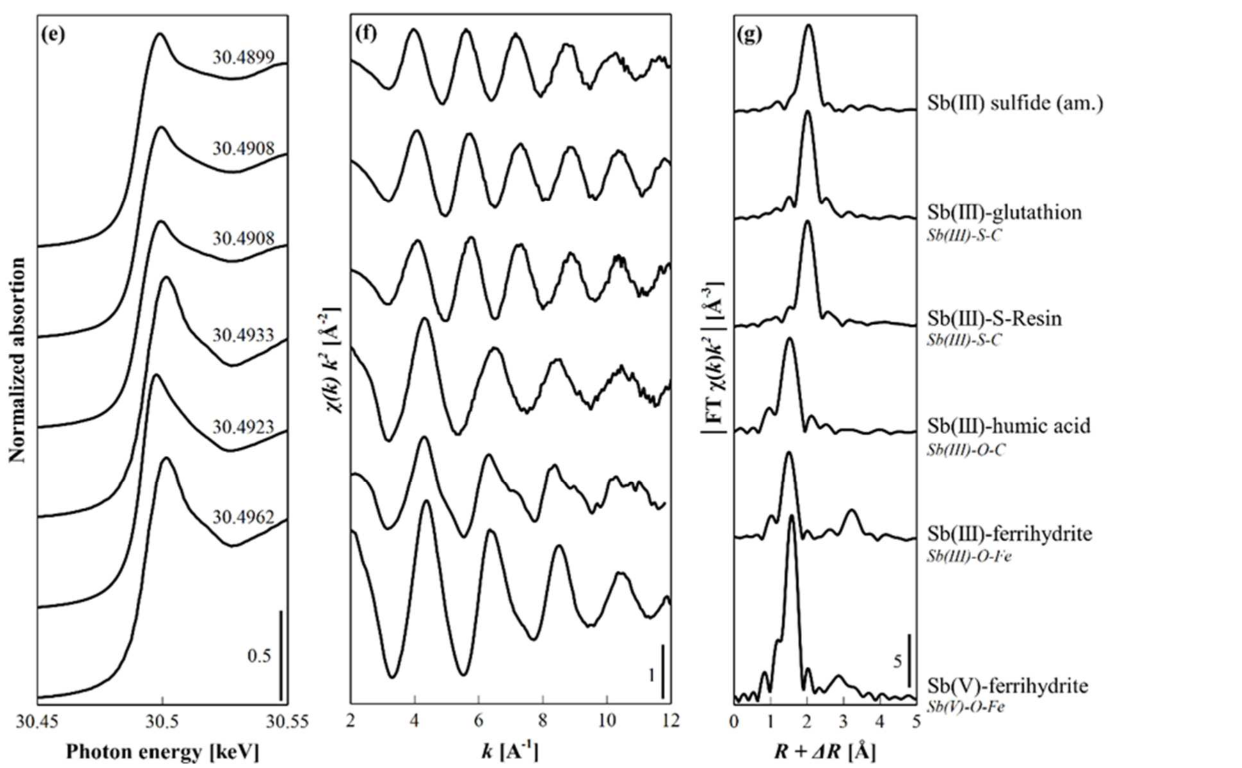


Figure 4: Normalized Sb *K*-edge XANES spectra and their respective edge-energies (keV) (a, e), k^2-weighted Sb *K*-edge EXAFS spectra (b, f) and their corresponding Fourier-transform (FT) magnitudes (c, g) of selected peat samples and Sb references. Best linear combination fits of Sb *K*-edge EXAFS peat spectra (d). Detailed results can be found in Table SI-18. Individual fractions were constrained to values between 0 and 100%, the sum of fractions was not constrained. Linear combination fits of the samples are shown as black circles. Fit references: Sb(V)-O-Fe = Sb(V) adsorbed to ferrihydrite, Sb(III)-O-Fe = Sb(III) adsorbed to ferrihydrite, Sb(III)-O-C= Sb(III) complexed with phenol groups of OM (Sb(III)-Aldrich humic acid), Sb(III)-S-C = Sb(III) complexed with thiol groups of OM: sum of Sb(III)-thiol resin (Ambersep GT74) and Sb(III)-glutathione), Sb(III) sulfide (am.) = amorphous Sb(III) sulfide.