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1 “Antimonite Binding to Natural Organic Matter:
2 Spectroscopic Evidence from a Mine Water
3 Impacted Peatland”

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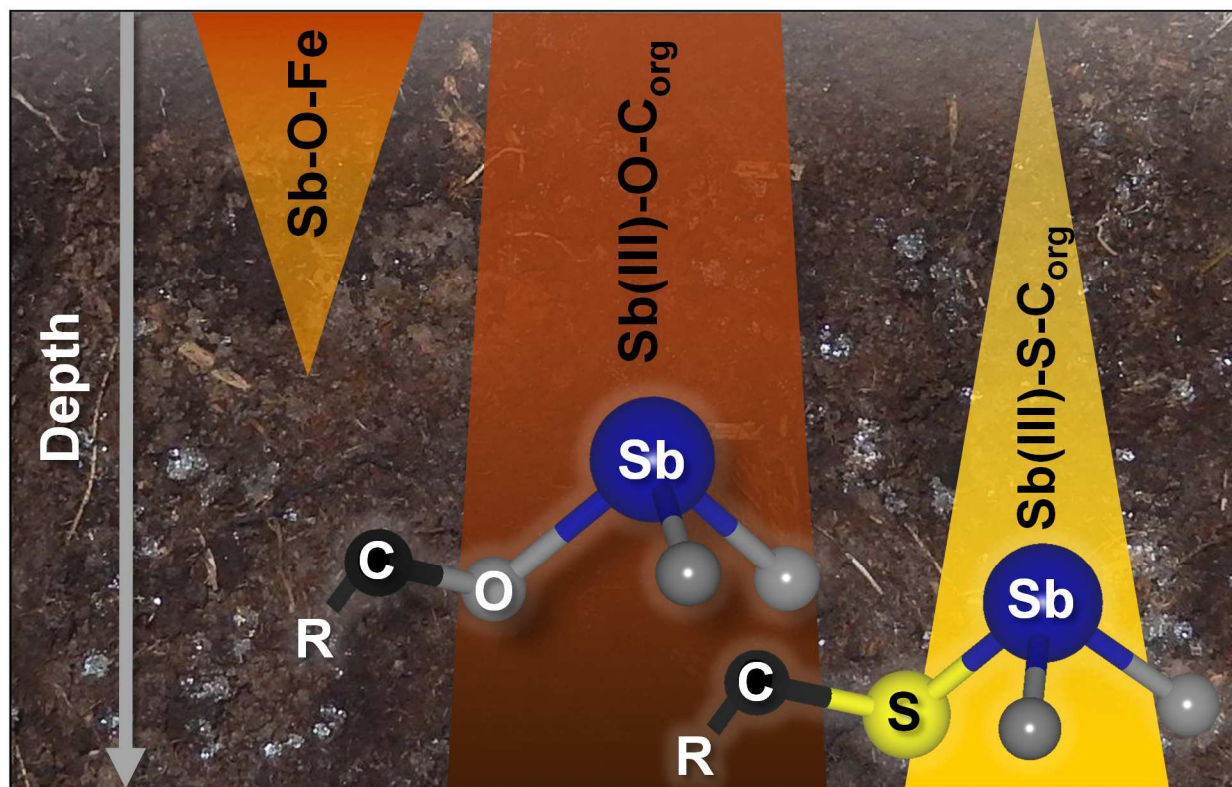
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19 ABSTRACT

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

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40 INTRODUCTION

41 Wetlands span more than 6% of the global ice-free land area¹ and among those, peatlands, with
42 ~3% land cover, are the dominant group of wetlands.² Next to important ecological functions
43 regarding long-term carbon storage, niche for threatened animal and plant species or regulation of
44 the water budget, peatlands are increasingly recognized as sinks for potentially toxic trace
45 metal(loid)s³⁻⁷ and therefore are an important factor controlling surface water and groundwater
46 quality.

47 A potentially toxic trace element, which has only received increasing attention during the last
48 decades due to increased mining activities^{8,9} as well as increased industrial use¹⁰⁻¹² and proposed
49 similar toxicity to arsenic^{13,14}, is antimony (Sb). Antimony is a redox-active trace metalloid that
50 prevails, at environmentally relevant pH values, as pentavalent aqueous antimonate (Sb(OH)_6^-)
51 under mostly oxic and as trivalent aqueous antimonite (Sb(OH)_3) under mostly anoxic
52 conditions.¹⁵

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

57 Further, accumulation of Sb in peatlands or other wetlands rich in solid natural organic matter
58 (NOM) has been reported in recent years.^{16,19-26} Two main pathways of how antimony enters the
59 peatlands or other wetlands have been described: either through atmospheric deposition related to
60 smelter activities¹⁹⁻²² or directly e.g. through Sb or gold mining, where (pre-purified) mining water
61 gets in contact with wetland soils.^{16,24,25}

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

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

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

79 Indeed, dissolved sulfide concentrations in peatlands are commonly low³⁵⁻³⁸ since the
80 (biogenically) produced sulfide can be effectively incorporated into NOM as organic thiols^{35,39},
81 often the dominant sulfur species in such systems.⁴⁰ Further, several studies have already observed
82 a strong association of Sb with solid NOM,^{19-23,25} however, direct spectroscopic evidence for Sb
83 binding to NOM from field samples was lacking.

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

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

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

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101 MATERIALS AND METHODS

102 **Field Work.** Peat profiles were sampled at three different locations along the water flow from near
103 to the inflow to close to the outflow of the peatland (B1-B3, Figure SI-1). Location and field-site
104 characteristics have been published before¹⁶ and are summarized in the **Supporting Information**.

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

112 Within a radius of ~30 cm to each peeper location, peat cores were sampled up to a maximum
113 sampling depth of 80 cm using a Russian Peat Borer. Then, the peat cores were separated into 10
114 cm sections to match the pore water information obtained from peepers. Each depth section was
115 immediately transferred to a separate argon filled glass bottle (50 mL), purged again with argon
116 before closing and screwed with PTFE-sealed screw caps. Afterwards, the bottles were transported
117 under refrigerated conditions on ice packs to the laboratory in Bayreuth, where they were
118 immediately processed within an anaerobic glove bag (Coy, N₂/H₂ 95/5 % (v/v), pO₂ <1 ppm).
119 Details about the pore water and peat core sampling procedure can be found in the **Supporting**
120 **Information**.

121 **Aqueous-Phase Analyses.** Redox potential, pH and electrical conductivity were determined
122 directly after sampling the chambers using a special set-up to minimize redox changes and to
123 handle small sample volumes (Figure SI-2). Dissolved sulfide was quantified using the methylene

124 blue method⁴³ and ferrous iron (Fe(II)) as well as total dissolved iron (Fe(tot)) were measured
125 using the phenanthroline method⁴⁴ with a portable photometer (LASA 100, Dr. Lange) at
126 wavelengths of 605 nm and 480 nm, respectively. Total aqueous Sb and S concentrations were
127 determined by inductively coupled plasma mass-spectrometry (ICP-MS, XSeries2, Thermo-
128 Fisher) in stabilized pore water samples (0.44% (v/v) H₂O₂ (Fisher Scientific), 0.78 % (v/v) HNO₃
129 (Kraft)). Aqueous Sb speciation of samples stabilized in 0.2% (v/v) HCl (Kraft) was carried out
130 with an anion-exchange chromatography (AEC, ICS-3000, Dionex; PRPX-100, 250 x 4.1 mm,
131 10 µm, Hamilton) coupled to an ICP-MS using an isocratic elution with 10 mM NH₄NO₃, 10 mM
132 NH₄H₂PO₄, and 500 mg/L Na₂-EDTA at a flow rate of 1.0 mL/min. Calibration standards were
133 prepared from potassium antimonyl tartrate sesquihydrate (Acros) and potassium
134 hexahydroxoantimonate (Fluka) stock solutions.

135 **Solid-Phase Analyses.** Back in the laboratory in Bayreuth, the peat of each depth section was
136 homogenized in its bottle inside a glovebag and transferred into a 50 mL polyethylene tube
137 (Sarstedt) for freeze-drying.⁴⁵ One part of freeze-dried peat was stored anoxically, dry and dark
138 until solid-phase analyses and another part was milled to <45 µm in a ball mill (MM2000, Retsch)
139 for total element determination. Total Sb content was determined by ICP-MS and total Fe and S
140 contents by inductively coupled plasma optical emission spectrometry (ICAP 6300 Duo View,
141 Thermo-Fisher) after microwave digestion (MARS Xpress, CEM) using a 5:3 ratio of 30% H₂O₂
142 and 65% HNO₃. To get an overview of the down-core distributions of many other major and trace
143 elements, ground peat samples were analyzed by an energy dispersive X-ray fluorescence
144 spectrometer (XEPOSTM, Spectro X Lab) together with a NIST 2711 certified reference material.
145 Total C content was analyzed with a TOC analyzer (multi N/C 2100, Analytik Jena).

146 Selected peat samples were examined by scanning electron microscopy (SEM) using a Leo Gemini
147 1530 (Carl Zeiss, Germany) with a Schottky emitter and elemental composition analysis was
148 conducted by energy-dispersive X-ray spectrometry (EDS, Oxford X-Max 20, Oxford
149 Instruments). Therefore, selected freeze-dried and homogenized peat samples were ground in a
150 mortar, mounted on aluminum specimen stubs and coated with carbon.

151 For synchrotron measurements at the Stanford Synchrotron Radiation Lightsource (SSRL),
152 Stanford, USA, selected freeze-dried, homogenized and ground peat samples from all three sample
153 locations were filled into aluminum sample holders and sealed with Kapton tape. Thereby, samples
154 were always kept under anoxic conditions until the end of XAS experiments. Bulk Sb *K*-edge
155 (30,491 eV), Fe *K*-edge (7,112 eV), and S *K*-edge (2,472 eV) XAS spectra were collected in
156 fluorescence mode at beamlines 11-2 (Sb), 4-1 (Fe), and 4-3 (S) under cryogenic (10 K, 11-2 and
157 4-1) or ambient (inert He (<0.1% (v/v) O₂) atmosphere, 4-3) temperatures. The collected Fe *K*-
158 edge X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure
159 (EXAFS) spectra and Sb *K*-edge EXAFS spectra were analyzed by linear combination fitting
160 (LCF) using Athena⁴⁶ after principal component analysis and target-transform testing (PCA-TT)
161 using SIXpack.⁴⁷ The Sb *K*-edge EXAFS shell-by-shell fitting analysis was performed in
162 Artemis.⁴⁶ Spectral deconvolutions of normalized S *K*-edge XANES spectra were done in
163 Athena.⁵⁹ Details on all XAS measurements, data reduction, and analyses are provided in the
164 **Supporting Information.**

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168 RESULTS AND DISCUSSION

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

177 Down-core distributions of total solid Sb, S, Fe and C_{org} are illustrated in Figure 1 and
178 distributions of additional major and trace elements are displayed in Table SI-3. Antimony
179 contents ranged from <0.1 to 2.2 mmol kg^{-1} ($\bar{x}=0.6 \text{ mmol kg}^{-1}$). They were highest close to the
180 peat surface in all profiles and decreased with increasing depth. Iron exhibited a similar distribution
181 pattern to Sb, whereas the contents of S only slightly decreased and the contents of C_{org} slightly
182 increased with depth by maintaining minimum Fe:Sb, S:Sb and C_{org} :Sb molar ratios of 64, 136 and
183 17,000, respectively.

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

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

201 Solid-phase Fe speciation revealed up to 43% of Fe occurring as phyllosilicates in the upper peat
202 layers which was additionally supported by SEM-EDS results (Figure SI-3, Table SI-4).
203 Phyllosilicates most probably originated from the underlying bedrock of greenschist⁴⁸ and
204 presumably entered the peatland via the inflow of treated mine drainage water. Organic Fe(III)
205 complexes (up to 47%) generally decreased with increasing peat depth, whereas Fe(II)-NOM
206 complexes (up to 48%) increased. Organic Fe(III) complexes can form in substantial amounts,
207 even at neutral pH values, in oxic layers of environments with abundant NOM such as peatlands
208 and can even dominate over Fe (oxyhydr)oxides.⁴⁹ Although, PCA-TT analyses of EXAFS spectra
209 suggested that ferrihydrite, lepidocrocite, and/or schwertmannite, all representatives of Fe
210 (oxyhydr)oxides, were suitable reference compounds (Table SI-7 and 9), no Fe (oxyhydr)oxides
211 could be fitted to the sample spectra in significant percentages (>10%). Nonetheless, the existence
212 of at least small amounts of Fe (oxyhydr)oxides could be demonstrated by SEM-EDS, where a

213 particle of most likely lepidocrocite, an Fe (oxyhydr)oxide forming through oxidation of aqueous
214 Fe(II) e.g. induced through an oscillating water table, was observed. (citation)

215 Further, the formation of substantial amounts of Fe(II)-NOM complexes in deeper peat layers
216 suggests that solid NOM plays an active role in (re)-sequestering aqueous Fe(II)⁵⁰ (Table SI-2)
217 after (microbially catalyzed) reductive dissolution of Fe (oxyhydr)oxides²⁸, Fe containing
218 phyllosilicates^{51,52} or Fe(III)-NOM complexes.

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

223 Sulfur *K*-edge XANES spectra of selected peat samples are shown in Figure 3 and the results
224 from Gaussian deconvolutions, which represent $s \rightarrow p$ transitions of major S fractions, are
225 illustrated in Figures SI-5-6 and Tables SI-12-13. The S XANES spectra could generally be
226 divided into two main spectral regions. The first region (“reduced S”) with white line energies
227 <2774.5 eV corresponded to inorganic (mono) sulfide, exocyclic/elemental S and heterocyclic S.
228 The second region with white line energies >2780.6 eV (“oxidized S”) was characterized as
229 sulfonate S and sulfate S. The region with energies in between ($2774.5 < x < 2780.6$ eV) and with
230 only minor importance in our samples (max. 14% of fitted fractions) was summarized as
231 “intermediate oxidized S” which was deconvoluted as sulfoxide S and sulfone S fractions and was
232 likely to be overestimated due to post-edge absorption features of reduced S species.⁵³

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

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

244 Within reduced S fractions, the exocyclic/elemental S fraction, often represented as thiol-S in
245 organic-rich sediments,⁴⁰ prevailed in deep peat layers (32-35%) followed by inorganic (mono)
246 sulfides (20-27%) (Figure SI-6). Both are suitable entities for antimonite sequestration.^{34,54}
247 Formation of organic thiol groups and/or inorganic (mono) sulfides in deeper peat layers often is
248 linked to (microbial) sulfate reduction⁴⁰, although in all measured samples, dissolved sulfide
249 concentrations were low (max. $3.6 \mu\text{mol L}^{-1}$, Table SI-2).

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

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

258 4a). Edge positions fell between Sb(III) and Sb(V) reference compounds indicating mixtures of Sb
259 species (Figure 4e).

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

266 Several similar Sb down-core trends were observed in all peat profiles. With fractions of 22-
267 24%, Sb(V) associated with Fe solely existed in the uppermost peat layers and only in profile B1
268 at 40 cm, a significant fraction of Sb(III) associated with Fe (18%) could be fitted; despite the
269 general correlation between down-core total Sb and Fe contents and a minimum molar Fe:Sb ratio
270 of 64 in all profiles described before (Figure 1). A similar observation was made by Mikutta and
271 Rothwell⁵⁵ in British peat bogs, where a correlation between As and Fe contents was observed, but
272 contribution of As-Fe associations was only moderate.

273 The exact Sb-O-Fe binding mechanisms hereby remain elusive, since our best-fit references
274 “Sb(III)/(V)-ferrihydrite” have to be considered as proxies for Fe coordination environments such
275 as the before described Fe (oxyhydr)oxides, Fe containing phyllosilicates and/or Fe(II)/Fe(III)-
276 NOM complexes. The Fe(II)/Fe(III)-NOM complexes can provide Fe as bridging cation for ternary
277 complex formation (as e.g. described for As⁵⁶⁻⁵⁸). Despite up to 100% of Fe-NOM complexes
278 found, no ternary As-Fe-OM complex formation was observed in an EXAFS study on As binding
279 in peatlands before.⁵⁵ These results suggest that ternary Sb-Fe-NOM complexes tend to be of minor
280 importance, which is underlined by the fact that up to 62% (Figure 2) of Fe-NOM complexes were

281 found in the studied peatland while a maximal of only 25% of Sb was associated with Fe (Figure
282 4).

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

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

298 The LCF results further revealed that with increasing depth, Sb(III) was increasingly bound to
299 thiol groups of NOM (14-37%, \bar{x} =22%) and therefore showed a similar down-core pattern as the
300 exocyclic/elemental S fraction fitted to the S XANES spectra as described before (Figure SI-6). In
301 one case an Sb(III) sulfide phase was fitted with 37% to the spectrum of sample B2 60 cm (Figure
302 4, Table SI-18). Shell-by-shell fitting of Sb-S distances of 2.46 ± 0.01 Å for thiol-bonds and a fitted
303 Sb-S distance of 2.48 Å for the Sb(III) sulfide containing sample confirmed our LCF results

304 (Figure SI-10 and Table SI-21). Formation of Sb(III)-S surface associations on FeS phases in peat
305 samples (Figure 2) with similar Sb-S distances of 2.46 \AA ⁵⁴ cannot be fully excluded, however, in
306 a previous study³⁴ we demonstrated that spectral differences between organic thiols and inorganic
307 Sb(III) on FeS phases exist and during our LCF analysis we found no best fit model where the
308 latter significantly contributed to or improved fit quality (Table SI-18). Interestingly, sample B2
309 60 cm, where the Sb(III) sulfide phase was found and redox potential was lowest (148 mV), also
310 exhibited the highest contribution of inorganic (mono) sulfides within all S XANES spectra
311 (Figure SI-6), indicating required natural conditions for inorganic Sb-S sequestration in our
312 system.

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

316 **Geochemical Factors Leading to Low Sb Purification Efficiency in the Studied Peatland.** Our
317 Sb solid-phase speciation results showed high affinities of Sb to organic functional groups of peat
318 and recent results from Besold et al.³⁴ moreover demonstrated high sorption capacities of model
319 peat NOM for Sb under reducing conditions, both indicating a high Sb removal potential of
320 peatlands. However, the long-term purification efficiency in the investigated peatland is low
321 (~30%).¹⁶

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

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

337 Thus, both thermodynamic calculations and aqueous Sb speciation show that the majority of
338 aqueous Sb was present in form of the negatively charged antimonate oxyanion (Sb(OH)₆⁻).

339 Natural organic matter has a net negative surface charge which further increases with increasing
340 thiol group content and increasing pH⁶³, thus, probably leading to electrostatic repulsions with the
341 negatively charged antimonate at pH>4.^{64,65} This repulsion is considered as main factor for overall
342 low Sb retention.⁶⁶

343 Additionally, dissolved organic matter in the peatland, though not analyzed, may have a negative
344 effect on antimonate sorption capacity to metal (oxyhydr)oxides (e.g. ferrihydrite and/or
345 lepidocrocite) by competitive sorption and through organic-mineral interactions. These
346 interactions in turn can lead to a loss of sorption sites as well as steric and electrostatic repulsions
347 towards other species like arsenate or antimonate⁶⁷⁻⁶⁹ and may partly explain the low affinity of
348 antimonate to Fe surfaces in our system. This effect is probably supported by the relatively high
349 pH of ~7 in the peatland and points of zero charge of naturally existing (oxyhydr)oxides being

350 usually lower than the ones in synthetic precipitates (e.g. 5.3-7.5 vs. 8.0-8.3 for ferrihydrite^{61,62}).
351 Therefore, lowered outer-sphere complexation of Sb with metal (oxyhydr)oxides through less
352 protonated surface sites is also suspected.⁷⁰

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

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

368 In sum, the high hydrological load, which leads to short water residence times and preferential
369 flow in the peatland⁶² in combination with the high antimonate inflow concentrations as well as
370 the cold climate in Finnish Lapland (-0.5°C mean annual temperature)¹⁶, which probably results
371 in lowered microbial activity and therefore reduced antimonate and sulfate reduction rates, are
372 considered as main factors hindering efficient Sb retention.

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

378 Our molecular findings reveal that Sb was not primarily coordinated to Fe phases, even close to
379 peat surfaces, as implied by the macroscopic correlation between Sb and Fe, but rather that organic
380 functional groups of abundant peat NOM are the main controlling factor for Sb, Fe, and S
381 biogeochemistry in peatlands. Our results therefore highlight the complex interplay of metal(loid)s
382 such as Sb in peatlands, where NOM not only serves as carbon source for Sb redox dynamics⁷¹ or
383 competing molecule (DOM) for Sb sorption on mineral surfaces¹⁷, but also as effective sorption
384 site for Sb sequestration.

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

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

394 ASSOCIATED CONTENT

395 **Supporting Information**

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

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403 **Notes**

404 The authors declare no competing financial interest.

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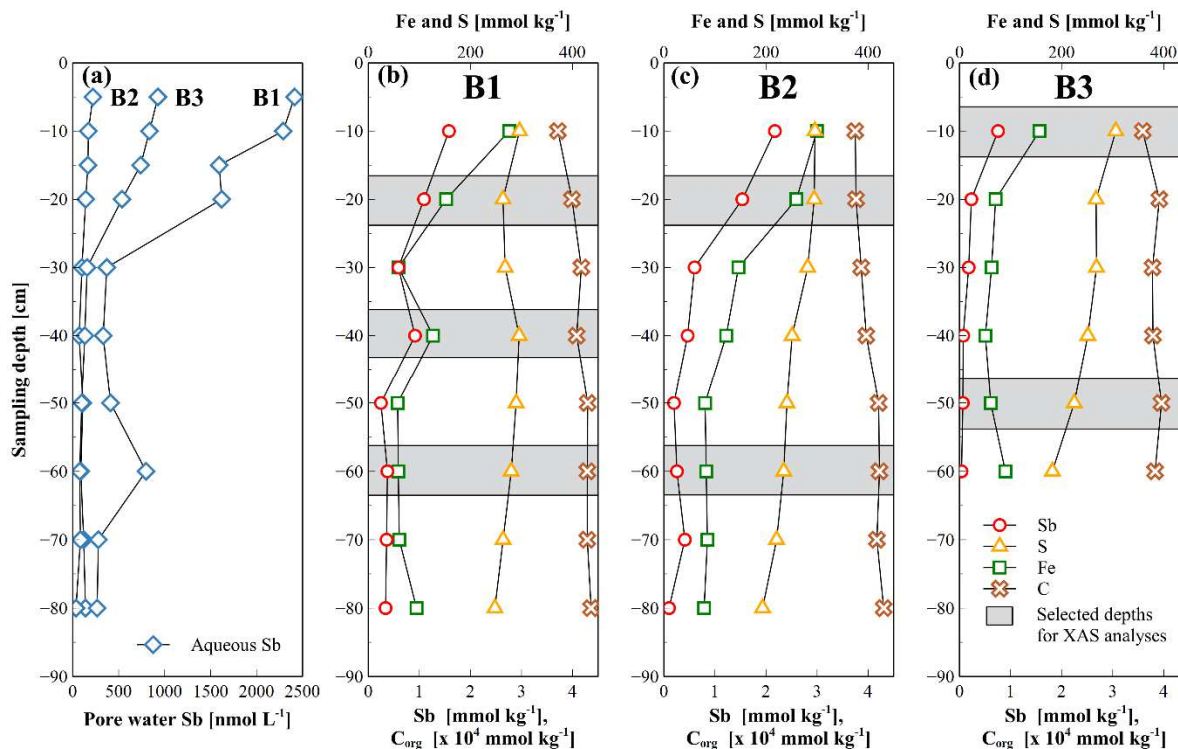
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618 Figure 1: Vertical element distributions in peat samples for sampling points B1-B3. Total aqueous
 619 Sb concentrations (a) and down core contents of Sb, S, Fe, and C_{org} for sampling points B1-B3,
 620 respectively (b-d). Element contents are given on dry-weight basis. Total C represents organic C
 621 (C_{org}) only as absence of carbonates was tested with 10% HCl. Depth resolution for aqueous Sb:
 622 0-20 cm: 5 cm; 20-80 cm: 10 cm. Solid-phase element distribution resolution: 10 cm, whereby e.g.
 623 10 cm depth means an integrated sample from 0-10 cm. At sampling location B3, solid-phase
 624 sampling was only possible down to 60 cm. Please note that the scales differ between upper and
 625 lower x-axes.

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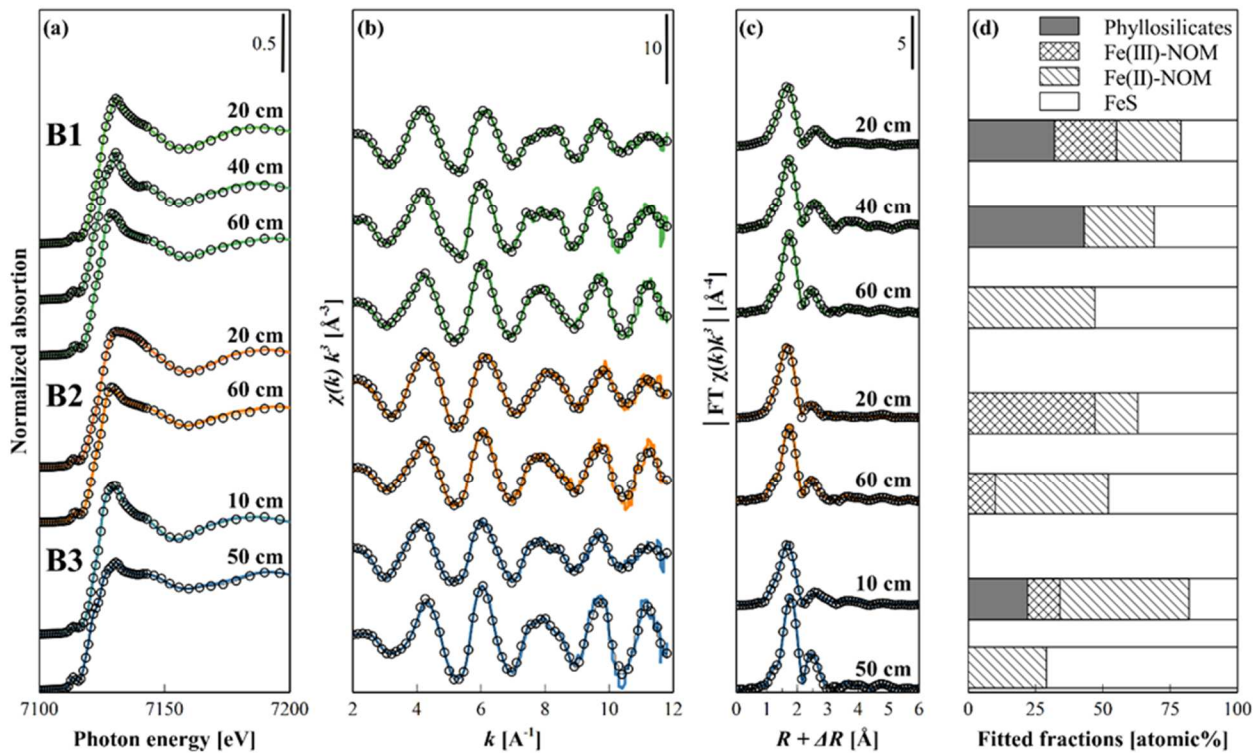
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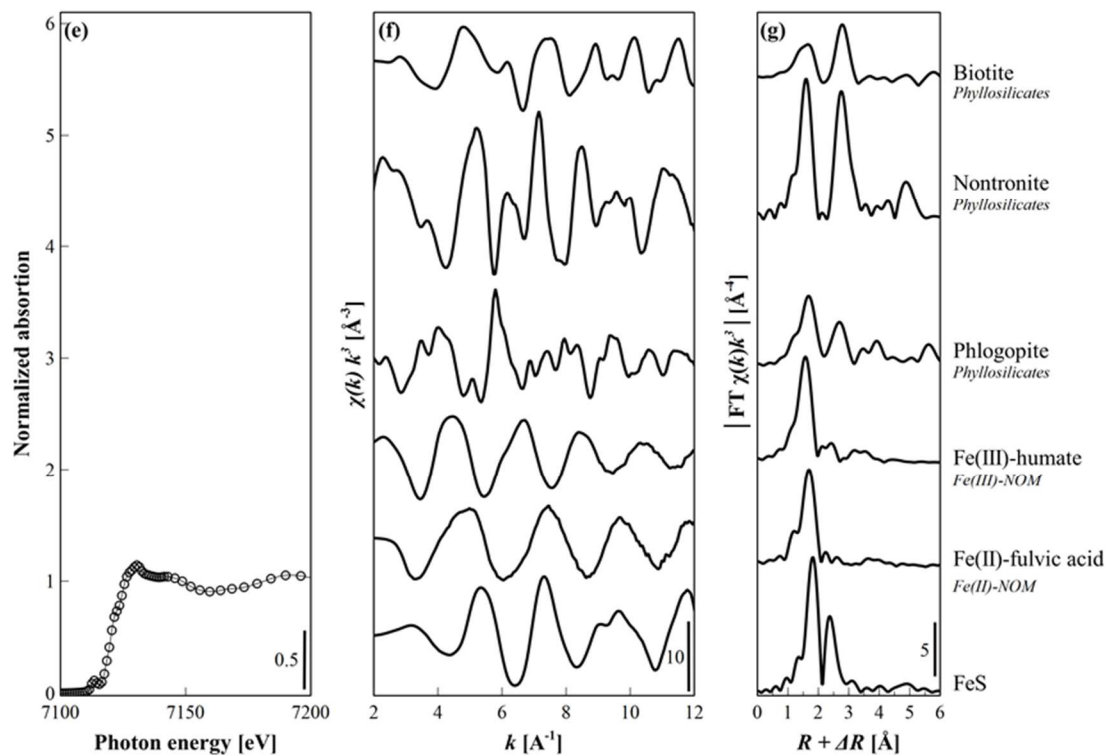
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Fe Samples



Fe References

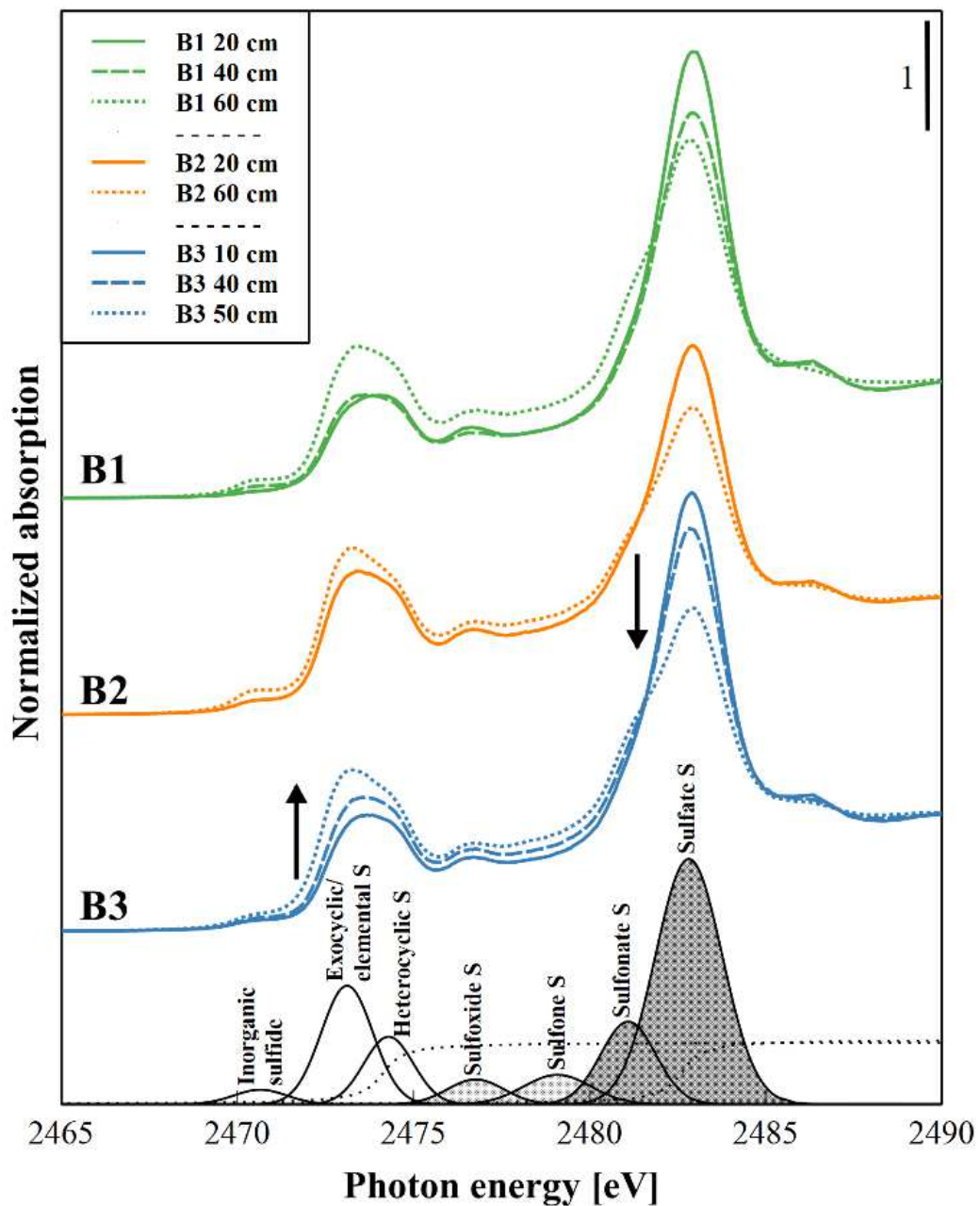


632 Figure 2: Normalized Fe *K*-edge XANES spectra (a, e), k^3 -weighted Fe *K*-edge EXAFS spectra (b,
633 f) and their corresponding Fourier-transform (FT) magnitudes (c, g) of selected peat samples and
634 Fe references. Best linear combination fits of Fe *K*-edge EXAFS peat spectra (d). The Fe EXAFS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

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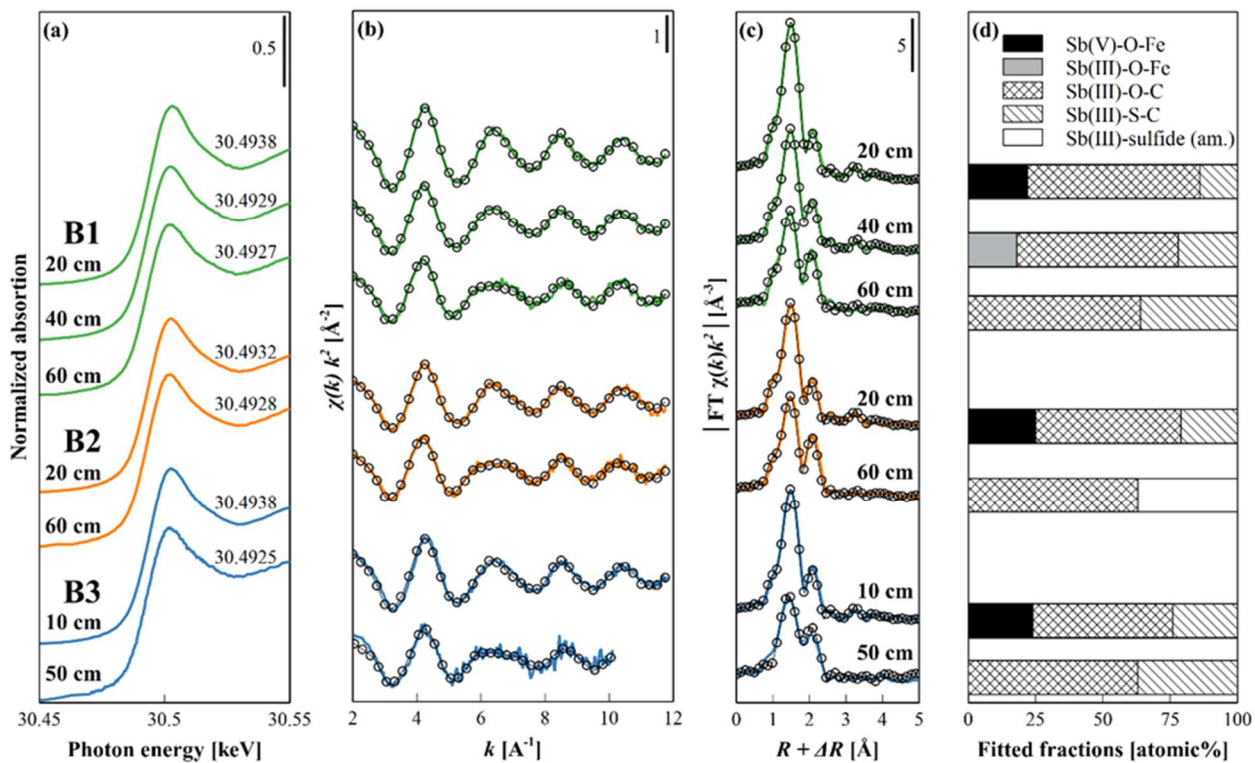
645



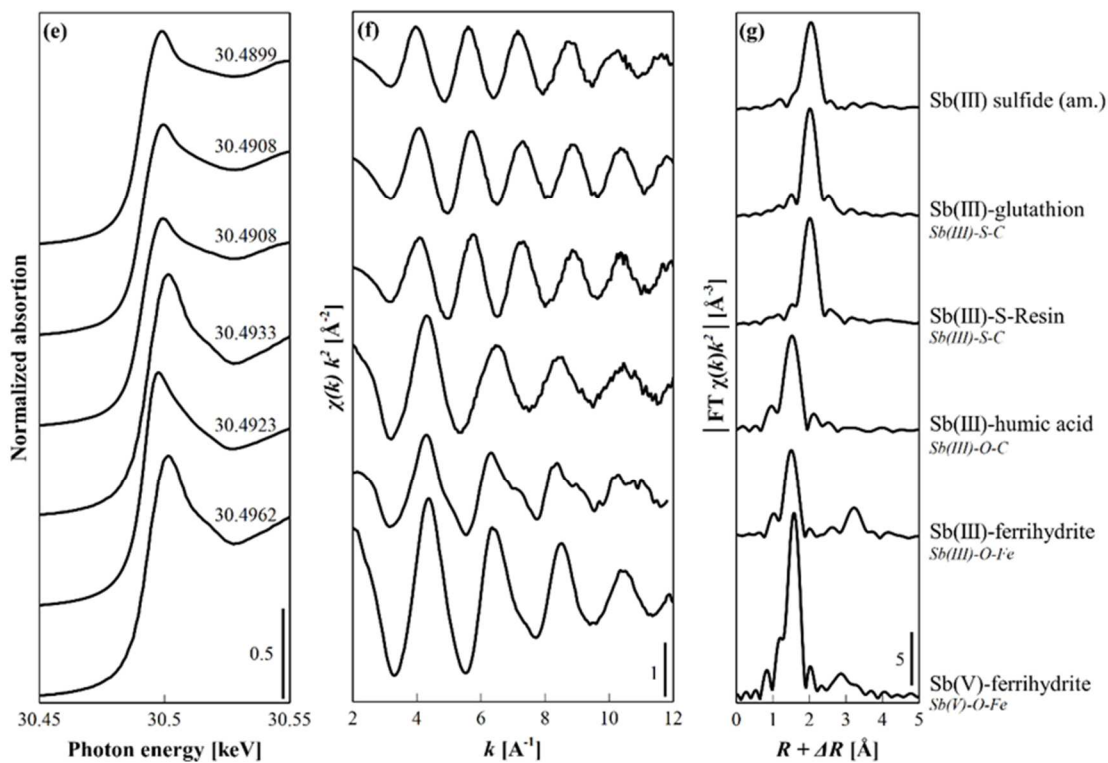
646
 647 Figure 3: Sulfur solid-phase speciation of selected peat samples from sampling points B1-B3. The
 648 normalized S *K*-edge XANES spectra of peat are plotted as a function of sampling depth. Spectral
 649 decomposition is illustrated as an example for sample B3 50 cm (with offset from the other
 650 spectra). The two arctan functions are shown as dotted lines and the Gaussian functions as straight
 651 lines correspond to reduced S (oxidation states -II to + I; no shading): inorganic (mono) sulfide,

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

Sb Samples



Sb References



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

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