

Complexation of arsenite, arsenate, and monothioarsenate with oxygen-containing functional groups of natural organic matter: An XAS study

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1 **Complexation of arsenite, arsenate, and monothioarsenate to alcoholic**
2 **functional groups of natural organic matter: Insights from X-ray**
3 **absorption spectroscopy**

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17 **TOC Art**

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20 **ABSTRACT**

21 This study investigated the potentiality of arsenite (As(III)), arsenate (As(V)), and
22 monothioarsenate (MTAs(V)) complexation to alcoholic groups of natural organic matter
23 (NOM). The extent of complexation was highest for As(III), followed by MTAs(V) and As(V).
24 Complexation was higher at pH 7.0 than at pH 4.5 for As(III) and As(V), vice versa for
25 MTAs(V) due to partial transformation to As(III) at pH 4.5. Conditional distribution coefficients
26 were considerably lower than those for complexation through organic thiol groups, but
27 comparable to those for ternary complexation through Fe³⁺ bridging. EXAFS modelling of the
28 As K-edge spectra revealed monodentate and bidentate complexation of the AsO₃ pyramid but
29 tridentate complexation of the AsO₄ and the AsSO₃ tetrahedra to alcoholic groups of peat. The
30 higher denticity and an observed longer As-C interatomic distance in As(V)- and MTAs(V)-
31 treated peat - as compared to As(III)-treated peat - is attributed to electrostatic repulsion between
32 negatively charged peat and As species. This study implies that complexation through alcoholic
33 groups of NOM can be an additional or alternative mode of As sorption and depending on acidity
34 of the functional NOM groups, As(V) species can have a higher mobility than arsenite in NOM-
35 rich environments.

36 *Keywords.* Arsenic; biogeochemistry; sorption; peat; EXAFS

37

38 INTRODUCTION

39 Over the last four decades, the natural and anthropogenic occurrences of elevated
40 concentrations of arsenic (As) in surface waters, groundwaters, and agricultural soils have been
41 highlighted as a potential environmental concern in many parts of the world.¹⁻³ It is estimated
42 that only in Southeast Asia more than 100 million of people are at risk of chronic As toxicity
43 from drinking water and food consumption.⁴ Therefore, it is necessary to characterize different
44 biogeochemical processes that regulate the mobility of As in the aquatic and terrestrial
45 ecosystems.

46 Formation and inter-conversion of different As species determine the extent of its mobility in the
47 environment.¹ Two most commonly reported inorganic As species are penta-valent arsenate
48 (As(V)) and tri-valent arsenite (As(III)) which predominate under strongly oxidizing conditions
49 and moderately oxidizing to moderately reducing conditions, respectively.¹ After recent
50 advances in analytical speciation technique, it has become evident that under anoxic sulfidic
51 conditions thiolated penta-valent As species, so-called thioarsenates ($H_xAsS_nO_{4-n}^{3-x}$; $n = 1-4$; x
52 $= 1-3$), can also be formed in significant quantities under diverse natural settings.⁵⁻¹¹ Extent of
53 sorption of these As species onto different mineral matters, specially metal oxyhydroxides in
54 soils and sediments is identified as one of the key regulating processes for their mobility in the
55 environment.^{1,12-14} Recently, a series of studies have highlighted the potentiality of natural
56 organic matter (NOM) as an alternative or additional sorbent for As and its regulatory role in the
57 As mobilization and transport process in the surface and sub-surface environments.¹⁵⁻²¹

58 Natural organic matter, being the decomposition product of animal, plant and soil biomass is
59 abundant in aquatic and terrestrial ecosystems.¹⁶ It has a complex structure with a variety of
60 functional groups, such as carboxylic, alcoholic, esteric, quinone, amino, nitroso, thiol, hydroxyl
61 etc., which are mostly negatively charged at near-neutral pH.¹⁶ Several mechanisms for the
62 binding of As(V) and As(III) to NOM have been put forward. One spectroscopically well
63 characterized mechanism is the formation of ternary complexes through polyvalent metal cation
64 (e.g. Fe^{3+} , Al^{3+} , Ca^{2+} , etc.) bridging between negatively charged or neutral As species and
65 negatively charged NOM (As-M-NOM; M represents polyvalent metal cations).^{17,22-26} Another
66 mechanism is the binary complexation by direct binding of As species to the specific functional
67 group of NOM. The most prominent site for such binary complexation can be organic thiol
68 groups ($-SH$).^{21,27} Langner et al.²¹ by using X-ray absorption spectroscopy (XAS) have found

69 almost 100% of As(III) to be bound to thiol groups in the deep peat layer of a minerotrophic peat
70 bog (*Gola di Lago*). A follow-up study has shown that As(III) binding by thiol group can be
71 competitive to its binding by ferrihydrite.²⁸ Recently, Catrouillet et al.^{29,30} have developed a
72 geochemical model for As(III) complexation to NOM by thiol group and via Fe²⁺ and Fe³⁺
73 bridging. Liu and Cai,³¹ on the other hand, have reported two types of binding sites (strong and
74 weak sites) to be involved during binary complexation of As(III) with Aldrich Humic Acid
75 (AHA); although, they did not attempt to characterize the binding sites.

76 Few studies have highlighted that alcoholic (-OH) groups (aliphatic and/or aromatic, specially
77 phenol), a highly abundant functional group in NOM,³² can also be a potential binding site for
78 binary complexation of As species to NOM. For example, Buschmann et al.¹⁸ in a dialysis
79 experiment found that 26% As(III) and 62% As(V) of total spiked concentrations bound to AHA
80 and estimated that under environmentally relevant conditions at least 10% As(V) should be
81 bound to dissolved organic carbon (DOC) in aquatic environments. They hypothesized that OH⁻
82 ligand exchange reaction between As species and alcoholic groups of NOM could be the
83 underlying mechanism of such bindings; although, they did not present any spectroscopic
84 evidence in support of their hypothesis. Lenoble et al.³³ have investigated the interaction of
85 As(III) and As(V) to Suwanee River Humic Acid (SRHA) in the absence and presence of Ca²⁺
86 by fluorescence spectroscopy. Based on sorption data and fluorescence quenching phenomena of
87 SRHA they concluded the formation of only a binary complex for As(III) and a mixture of
88 binary and Ca²⁺ bridged ternary complexes for As(V). They have determined the stability
89 constant of these complexes assuming monodentate binding to alcoholic group of SRHA,
90 without further effort to characterize the type of functional group involved in the complexation
91 and mode of binding. Evidence of As-O-C bond formation by ligand exchange reaction between
92 alcoholic group of NOM and As species is given by Hoffmann et al.²⁶ and Guénet et al.³⁴ During
93 modelling of As K edge EXAFS spectra of the samples obtained by equilibrating As(III) with Fe
94 spiked peat Hoffmann et al.²⁶ had to include C in addition to Fe for the second shell. They have
95 determined coordination numbers (CN) of 1.5 to 2.0 for C at the distance of 2.70 to 2.77 Å from
96 the As. However, they have mentioned that due to signal contribution from Fe backscatterer at
97 similar distance, the CN of C must be treated with caution. They have further estimated that at
98 least 27% of total As(III) was bound to phenolic groups, in addition to ternary complexation via
99 Fe³⁺ bridging. Similarly, Guénet et al.³⁴ have provided XAS based evidence for the complexation

100 of As(V) and As(III) mixtures to alcoholic groups of organic matter, in addition to their bindings
101 to Fe nanoparticle aggregates in the size fraction of 5-0.2 μm during oxidation of reduced soil
102 suspension solution. However, to the best of our knowledge, so far it has never been attempted to
103 investigate the extent of As(III) and As(V) bindings to NOM by complexation exclusively to the
104 alcoholic group, with spectroscopic evidence of As-O-C bond formation. Unavailability of this
105 information obscures the potentiality of As(III) and As(V) bindings to NOM when polyvalent
106 metal cation content in the system is too low for ternary complexation and thiol group content in
107 NOM is not large enough to make significant thiol coordination. It is worth highlighting that the
108 complexation of thioarsenate to alcoholic group of NOM has never been tested at all.
109 The objective of the present study was to investigate the potentiality and determine the structural
110 parameters for ligand exchange binary complexation of different As species (including
111 thioarsenate) to alcoholic groups of NOM. The objective was accomplished by equilibrating
112 individual As species with low metal containing purified-peat (as a representative for NOM)
113 under anoxic conditions, followed by determining the local coordination environment (up to 4 \AA)
114 of As in the peat by As K edge XAS analysis. The findings of this study will help to better
115 constrain the geochemical model for simulating the interaction of As species with NOM in
116 aquatic and terrestrial environments. In general, this study will also develop our limited
117 understanding of neutral to oxyanionic species complexation to NOM, a topic that is not as
118 developed as metal cation complexation to NOM.¹⁸

119 MATERIALS AND METHODS

120 **Materials.** This study used low metal containing purified-peat as a model NOM compound.
121 Collection, purification, and characterization of this peat are presented in Besold et al.³⁵
122 Monothioarsenate (hereafter referred as MTAs(V)) was used as the representative of thioarsenate
123 species, since it is often reported as the major thioarsenic species formed under diverse natural
124 settings and is structurally analogous to the As(V).^{6,35-37} Because there is no commercial
125 standard, MTAs(V) was synthesized in the laboratory, with a purity of 90% (5% arsenate and 5%
126 arsenite).³⁵ All other chemicals of analytical grade, including As(III) and As(V) standards, were
127 purchased from Fluka, Alfa Aesar, or Sigma-Aldrich. All the glasswares used in this study were
128 acid-washed and dried before use.

129 **Sorption experiment.** An equilibrium-sorption experiment was conducted for individual As
130 species at pH 4.5 (± 0.3) and 7.0 (± 0.3). For this experiment, 0.2 g of dry peat was incubated with
131 variable concentrations (0 – 1000 μM) (0 – 4.6 mmol As/mol C) of each As species in an anoxic
132 background electrolytic solution of 30 mM NaCl in glass septum bottles capped and sealed with
133 butyl rubber stoppers and aluminum caps. Incubation was conducted for 96 h in an end over end
134 shaker in the dark under anoxic conditions ($p\text{O}_2 < 1$ ppm) at ambient temperature. The duration of
135 96 h was selected for incubation so that the results can be directly compared to the studies of
136 Hoffmann et al.^{26,27} which have used the same peat to investigate As(III) bindings through binary
137 organic thiol coordination and Fe^{3+} bridged ternary complex formation. To avoid microbial
138 activity, 0.15 mM NaN_3 (0.75 mmol/mol C) was added to the reaction medium. The desired pH
139 was adjusted with anoxic HCl and NaOH solution. After equilibration, the peat-solution slurry
140 was filtered through 0.2 μm nylon filter using a vacuum filtration unit inside the glove box. The
141 peat residue was freeze-dried, homogenized, and stored in the dark at ambient temperature inside
142 the glove box until analyses. The amount of As sorbed to peat was determined after microwave-
143 assisted digestion followed by quantification of As by inductively coupled plasma-mass
144 spectrometry (ICP-MS).³⁵ The conditional distribution coefficient (K_{OC}) (L/kg) of As was
145 determined as: $K_{\text{OC}} = C_{\text{P}}/C_{\text{S}}$, where C_{P} and C_{S} represent As concentration in peat ($\mu\text{g}/\text{kg}$) and As
146 concentration in solution ($\mu\text{g}/\text{L}$) after equilibration, respectively. C_{S} was determined by
147 subtracting the amount of As sequestered into peat from the solution.

148 **Arsenic K edge XAS analysis.** To determine the local coordination environment of As in the
149 peat after equilibration, As K edge (11867 eV) XAS analysis was performed at the Rossendorf
150 Beamline (ROBL) at the European Synchrotron Radiation Facility (ESRF), Grenoble, France
151 and at the beamline 11-2 of the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford,
152 USA. To aid the modelling of the sample spectra, triethoxyarsine ($(\text{C}_2\text{H}_5\text{O})_3\text{As}$) (TEA) was
153 measured as a reference standard at ROBL, ESRF. Samples were measured in fluorescence
154 mode, while the TEA standard was measured in transmission mode. Samples and the standard
155 were measured at about 15 K using a He cryostat to avoid beam damage and to minimize
156 thermal disorder in the structure. Details on beamline setup, sample preparation, analysis, data
157 reduction, and modelling are provided in the supporting information.

158 RESULTS AND DISCUSSION

159 **Complexation of As species to peat.** Amounts of As sorbed to peat at different equilibrated
160 concentrations of the three As species at pH 4.5 and 7.0 are illustrated in Figure 1. Among the
161 three tested species, maximum sorption was observed for As(III), followed by MTAs(V) and
162 As(V). Earlier studies have reported higher sorption of As(V) to AHA and SRHA compared to
163 As(III);^{18,22,38} the possible reason for this inconsistency is discussed in the following section after
164 determination of the binding mechanism. The maximum sorption capacity of the peat was not
165 exhausted even with the highest equilibrated As(III) concentration of 1000 μM (4.6 mmol
166 As/mol C). In agreement with earlier studies,^{18,22,31,33,38} the sorption of As(III) and As(V) was
167 higher at pH 7.0. The pH effect was more prominent for As(III) compared to As(V). However,
168 for MTAs(V) the sorption was higher at pH 4.5, which can be attributed to the partial
169 transformation of MTAs(V) to As(III) at this pH, as reflected by the XANES spectra discussed in
170 the following section. The calculated $\log K_{\text{OC}}$ (L/kg) at pH 7.0 were 0.83 – 1.01 (mean: 0.90) for
171 As(III), 0.40 – 0.56 (mean: 0.47) for MTAs(V), and 0.34 – 0.41 (mean: 0.38) for As(V); at pH
172 4.5 corresponding values were 0.73 – 0.85 (mean: 0.78), 0.44 – 0.66 (mean: 0.52), and 0.31 –
173 0.38 (mean: 0.35). With experimental uncertainty, the $\log K_{\text{OC}}$ decreased with the increase of
174 equilibrated As concentration (more specifically with the increase of equilibrated As/NOM ratio
175 as the amount of NOM was fixed to 0.2 g) in the system for all three As species at both pH
176 (Figure SI-1). Although no explanation is offered, earlier studies have also reported similar
177 decreasing trend of distribution coefficients for As(V) and As(III) binding to NOM with
178 increasing As/NOM ratios.^{18,31} Hoffmann et al.^{26,27} have determined the $\log K_{\text{OC}}$ values at pH 7.0
179 by equilibrating 0.275 mmol As(III)/mol C of the same peat spiked with variable amount of S(-
180 II) and Fe^{3+} . The values for As(III) at pH 7.0 of the present study (0.83 – 1.01) are considerably
181 lower than the values (0 – 2.9) obtained after spiking with S(-II), but comparable to that (1.2 –
182 1.5) obtained after spiking with Fe^{3+} .

183 **EXAFS modelling and complexation mechanism.** Normalized As K edge XANES spectra of
184 peat after equilibration with As(III), As(V), and MTAs(V) at two pH together with various
185 reference standards are displayed in Figure SI-2. The E_0 of peat equilibrated with As(III) and
186 As(V) at both pH appeared at the respective position of As(III) (~11869 eV) and As(V)
187 (~11873 eV) reference standards, indicating no species transformation during equilibration.
188 Similarly, MTAs(V) was not transformed to other species at pH 7.0, indicated by the similar E_0

189 of the samples and reference standard at ~ 11871 eV. However, at pH 4.5 the spectra of the two
190 MTAs(V) treated peat samples showed two humps at the position of MTAs(V) and As(III)
191 standards, suggesting partial transformation of MTAs(V) to As(III) during equilibration at this
192 pH. Our earlier study³⁵ has shown that MTAs(V) can be transformed into As(III) at acidic pH in
193 the presence of S(-II) treated peat, which makes the transformation reaction kinetically feasible
194 by sorbing As(III) (product of transformation) from the solution. The present study suggests that
195 this acid-assisted transformation will be feasible in the presence of any sorbent that sorbs As(III)
196 more strongly than MTAs(V). Based on the findings from XANES spectra, EXAFS modelling
197 was performed for all analyzed peat samples equilibrated with As(III) and As(V) at two pH and
198 MTAs(V) at pH 7.0 only; for the two peat samples equilibrated with MTAs(V) at pH 4.5, linear
199 combination fit (LCF) analysis was performed.

200 To better constrain sample spectra during EXAFS modelling, the spectrum of TEA was modelled
201 first (Figure SI-3). The major peak at $R+\Delta R \sim 1.3$ Å in the FT is due to the nearest neighbor O of
202 the AsO₃ pyramid. This major peak was followed by a small FT peak at $R+\Delta R \sim 2.2$ Å, which
203 can be assigned to C in the second shell.^{26,39} Quantitative structural parameters of these two
204 shells were determined by shell-fit analysis. The final model for TEA included As-O and As-C
205 single-scattering (SS) paths and triangular As-O-C multiple-scattering (MS) path.
206 Parameterization (CN: path degeneracy or coordination number, R: interatomic distance or mean
207 half path length (bond length for first shell atom), and σ^2 : Debye – Waller parameter) of these
208 paths are presented in Table SI-1. Furthermore, the triangular As-O-O MS path within the AsO₃
209 pyramid (Table SI-1) was also tested, but finally discarded, since it did not improve the fit
210 significantly. The fitted R and σ^2 of the As-O and As-C paths were 1.78 Å and 0.0021 and 2.78
211 Å and 0.0059, respectively (Table SI-2), which are consistent with reported values.²⁶

212 The k^3 -weighted As K edge EXAFS spectra and their corresponding FT (magnitudes and real
213 parts) of the peat samples equilibrated with As(III) and As(V) at the two pH and MTAs(V) at pH
214 7.0 are shown in Figure 2. Qualitative Morlet wavelet transforms (WT) analysis of As K edge
215 EXAFS spectra of the samples did not indicate the presence of any heavy backscatterer in the
216 second or higher shell (Figure SI-4). Similar to TEA, FT of the k^3 -weighted EXAFS spectra of
217 As(III)-, As(V)-, and MTAs(V)-treated peat samples were characterized by two peaks: a major
218 peak at $R+\Delta R \sim 1.3$ Å corresponding to nearest neighbor O in the first shell and a small peak at

219 $R+\Delta R \sim 2.2 \text{ \AA}$ for As(III) (Figure 2A) and $\sim 2.3 \text{ \AA}$ for As(V) and MTAs(V) (Figure 2B,C)
220 corresponding to C in the second shell. For MTAs(V)-treated peat samples, an additional peak
221 appeared at $R+\Delta R \sim 1.8 \text{ \AA}$ (Figure 2C), which can be attributed to S in the first shell.³⁶
222 Accordingly, for all peat samples except #As(V)/4.5/500, inclusion of As-O and As-C SS paths
223 (Table SI-1) in the structural model was essential to fit the sample spectra. For the three
224 MTAs(V)-treated samples, additional As-S SS path (Table SI-1) was also necessary for the
225 fitting. For the sample #As(V)/4.5/500, despite the small FT peak at $R+\Delta R \sim 2.3 \text{ \AA}$ the addition
226 of As-C SS path to the model after As-O SS path and MS paths within the AsO_4 tetrahedra
227 (discussed latter) did not improve the fit significantly according to the F-Test, although it
228 decreased the R-factor. Although, the As-O-C MS path was essential to fit the TEA spectrum,
229 this MS path (constrained similarly as for TEA, Table SI-1) did not improve the fit significantly
230 for any samples according to the set criteria for the MS path. For the As(III)-treated peat samples
231 the triangular As-O-O MS path within the AsO_3 pyramid (Table SI-1) was tested and found to be
232 significant only for the sample #As(III)/7.0/150 by decreasing the $\text{red}\chi^2$ by 31% compared to the
233 model with only As-O SS path. However, for all As(V) treated samples, when three MS paths
234 within the AsO_4 tetrahedra, namely, triangular As-O-O, colinear As-O-As-O, and non-colinear
235 As-O-As-O (Table SI-1) were included together in the fit, decreased the $\text{red}\chi^2$ on average by
236 52% (38-69%). Similarly, addition of triangular As-O-O and colinear As-O-As-O MS paths
237 within the AsSO_3 tetrahedra (Table SI-1) decreased the $\text{red}\chi^2$ in the MTAs(V)-treated samples on
238 average by 30% (23-36%), compared to the model with only As-O and As-S SS paths.
239 Therefore, the final fit model included As-O and As-C SS paths for As(III)-treated samples
240 (additional triangular As-O-O MS path for #As(III)/7.0/150); As-O and As-C (except
241 #As(V)/4.5/500) SS paths and three MS paths within the AsO_4 tetrahedra for As(V)-treated
242 samples, and As-O, As-S, and As-C SS paths and two MS paths within the AsSO_3 tetrahedra for
243 MTAs(V)-treated samples. The final fits are displayed in Figure 2 and EXAFS parameters are
244 listed in Table 1.

245 In the As(III)-treated peat samples the average $R_{\text{As-O}}$ was $1.79 \pm 0.01 \text{ \AA}$ (\pm std. dev.) (range: 1.78
246 – 1.80 \AA), consistent with the reported As-O bond lengths in the AsO_3 pyramid.^{39,40} For As-C
247 path, the fitted $R_{\text{As-C}}$ was $2.73 \pm 0.01 \text{ \AA}$ ($2.73 - 2.74 \text{ \AA}$) with CN of 1.7 ± 0.6 (1.0 – 2.4). Despite
248 similar oxidation state of As, the fitted $R_{\text{As-C}}$ was relatively longer in TEA (2.78 \AA) compared to
249 that in peat, which can be attributed to the liquid state of the TEA standard. The fitted $R_{\text{As-C}}$

250 values suggest that the AsO₃ pyramids were complexed to peat probably through alcoholic
251 groups (aliphatic and/or aromatic) instead of carboxylic group because, in case of complexation
252 through carboxylic groups, shorter R_{As-C} values (2.58 – 2.68 Å) are expected due to possible
253 hydrogen bonding between the H atom of the As(III) and the carbonyl O of the carboxyl
254 group.^{26,39} The fitted R_{As-C} and CN_{As-C} values in peat are consistent with the values (R: 2.70 –
255 2.77 Å, CN: 1.5 – 2.0) determined by Hoffmann et al.²⁶ for the Fe-spiked peat equilibrated with
256 As(III) (0.275 mmol As(III)/mol C) at the pH of 7.0, 8.4, and 8.8. They have determined
257 relatively longer R_{As-C} at pH ≥8.4 compared to that at pH 7.0; no such difference was observed in
258 the studied pH range (4.5 to 7.0) of the present study. To determine the exact mode of binding, in
259 the next step we fixed the CN_{As-C} to either 1.0 (Figure SI-5) or 2.0 (Figure SI-6) in the fit model,
260 while keeping the fit strategy for the rest of the parameters unchanged. Results show that for the
261 sample #As(III)/7.0/150 redχ² was decreased further when CN_{As-C} was fixed to 1.0 (Table SI-3
262 vs. Table 1), while for the sample #As(III)/7.0/1000, #As(III)/4.5/1000, and #As(III)/4.5/500,
263 redχ² was decreased when CN_{As-C} was fixed to 2.0 (Table SI-4 vs. Table 1). For the sample
264 As(III)/7.0/100, redχ² was increased in both cases; however, the increment was more when CN_{As-}
265 _C was fixed to 2.0 (Tables-SI-3 and 4 vs. Table 1). Therefore, we conclude that irrespective of
266 pH when equilibrated As(III) concentration is low (≤150 μM; 0.69 mmol As(III)/mol C) each
267 AsO₃ pyramid gets complexed to one alcoholic group of peat (monodentate, Figure 3A);
268 whereas, when equilibrated As(III) concentrations is high (≥500 μM; 2.3 mmol As(III)/mol C)
269 the preferential binding mode is the complexation of each AsO₃ pyramid to two alcoholic groups
270 (bidentate, Figure 3B).

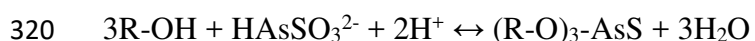
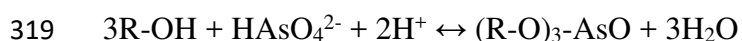
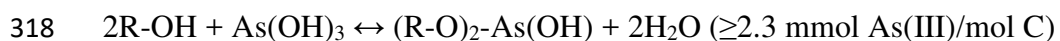
271 Because of higher oxidation state of As, in the As(V)-treated peat the R_{As-O} was considerably
272 shorter (1.69 ± 0.01 Å, 1.68 – 1.69 Å) compared to the R_{As-O} in the As(III)-treated peat samples.
273 These fitted R_{As-O} values are similar to the reported As-O bond lengths within the AsO₄
274 tetrahedra.⁴¹ The fitted R_{As-C} and CN_{As-C} were 2.83 ± 0.01 Å (2.82 – 2.84 Å) and 3.2 ± 0.2 (3.0 –
275 3.4), respectively, comparatively higher than that in the As(III)-treated peat samples. When
276 CN_{As-C} was set to 3.0 in the model (Figure SI-7), redχ² was decreased on average by 6% for all
277 the samples (Table SI-5 vs. Table 1), suggesting that each AsO₄ tetrahedra was attached to three
278 alcoholic groups of the peat (Figure 3C). It is worth mentioning that even in the sample
279 #As(V)/4.5/500, although fit improvement because of inclusion of the As-C path in the model
280 was not statistically significant, the fitted R_{As-C} (2.79 Å) and CN_{As-C} (2.3) were comparable to

281 other samples and $\text{red}\chi^2$ was decreased by 5% when $\text{CN}_{\text{As-C}}$ was set to 3.0 (Table SI-6). Guénet et
282 al.³⁴ have determined comparable $R_{\text{As-C}}$ (2.85-2.86 Å), but relatively smaller $\text{CN}_{\text{As-C}}$ (1.7 – 2.1)
283 for the mixture of As(V) and As(III) in the 5 – 0.2 μm size fraction during oxidation of the
284 reduced soil suspension. The smaller $\text{CN}_{\text{As-C}}$ may be result from the presence of As(III) in the
285 system; however, in that case a shorter $R_{\text{As-C}}$ is also expected. A more probable alternative
286 explanation is that this can be due to the low As-organic carbon ratio (~0.04 mmol As/mol C) in
287 the solution at the starting of oxidation of the reduced soil suspension. This reason will implicate
288 that similar to As(III), at the low concentration of As(V), each AsO_4 tetrahedra will probably be
289 attached to a lower number (<3.0) of alcoholic groups. Similar to As(III) treatment, there was no
290 effect of change in the equilibrium pH on the fitted EXAFS parameters for the As(V) treatment
291 (Table 1).

292 In the MTAs(V)-treated peat, the fitted $R_{\text{As-O}}$ was 1.72 ± 0.01 Å (1.71 – 1.72 Å), relatively
293 longer than $R_{\text{As-O}}$ in As(V)-treated peat but shorter than As(III)-treated peat. The $R_{\text{As-S}}$ was
294 determined as 2.10 ± 0.02 Å (2.08 – 2.11 Å), indicating S was double bonded to As.³⁶ Suess et
295 al.³⁶ have determined $R_{\text{As-O}}$ and $R_{\text{As-S}}$ in pure MTAs(V) standard by EXAFS modelling as 1.70 Å
296 and 2.13 Å, respectively. Despite same oxidation state of As, relatively longer $R_{\text{As-O}}$ in the
297 AsSO_3 tetrahedra compared to that in the AsO_4 tetrahedra in peat can be attributed to the less
298 positive partial charge on the central As atom because of replacement of the double bonded O
299 with double bonded S, which is less electronegative. For As-C path, the fitted R and CN were
300 2.80 ± 0.02 Å (2.78 – 2.82 Å) and 3.0 ± 0.4 (2.6 – 3.4), respectively, similar to the values
301 obtained for As(V)-treated peat. Again, fixing of $\text{CN}_{\text{As-C}}$ to 3.0 (Figure SI-8) decreased the $\text{red}\chi^2$
302 on average by 6% for all the samples (Table SI-7 vs Table 1), suggesting each AsSO_3 tetrahedra
303 was attached to three alcoholic groups of the peat (Figure 3D). To the best of our knowledge this
304 is the first study that determines the local coordination environment of As when MTAs(V) is
305 complexed to NOM. Since the number of alcoholic group in the peat equilibrated with all three
306 As species was the same, the higher $\text{CN}_{\text{As-C}}$ in the As(V)- and MTAs(V)-treated peat (CN 3)
307 explains why the extent of sorption of these two As species was less compared to As(III) (CN 1-
308 2) (Figure 1). Furthermore, increase of $\text{CN}_{\text{As-C}}$ with the increase of equilibrated As concentration
309 (clearly identified for As(III) system) was probably the reason for decreased log K_{OC} with the
310 increase of As/NOM ratio (Figure SI-1). The LCF analysis of the two peat samples equilibrated
311 with MTAs(V) at the pH 4.5 (Figure SI-9) indicated they were a mixture of almost equal

312 proportion (Table SI-8) of MTAs(V) (44 – 58%) and As(III) (44 – 60%) complexed to peat with
313 the above determined coordination environments.

314 Above presented modelling of the As K edge EXAFS data of peat equilibrated with different As
315 species has identified two types of complex to be formed for As(III) and one each for As(V) and
316 MTAs(V) (Figure 3), with the following reaction stoichiometry:



321 The formation of ester of As(III) and As(V) acid with alcohol is well known.^{42–44} The underlying
322 mechanism for this esterification is the nucleophilic attack by the alcoholic group to the partially
323 positively charged As atom in the As species.¹⁸ An increase of nucleophilicity of the alcoholic
324 group and a partial positive charge on the As atom increases the rate and thereby extent of
325 complex formation. Since the nucleophilicity of the alcoholic group increases with an increase of
326 pH, it is expected that the extent of complex formation between As species and the alcoholic
327 group will be more at higher pH, which explains the higher sorption of As(III) and As(V) at pH
328 7.0 compared to 4.5 in the present study (Figure 1). Few earlier studies have reported that
329 complexation of As(III) and As(V) to NOM is optimum around near-neutral pH,^{18,22} because at
330 high pH alcoholic group experiences competition with hydroxyl ion from the reaction medium
331 for the nucleophilic attack to the As center. Among the three tested As species, partial positive
332 charge on the central As atom is highest in the As(V), followed by MTAs(V) and As(III);
333 because in As(V) there is an additional O, double bonded to As compared to As(III) and in
334 MTAs(V) this double bonded O is replaced by the less electronegative S. Therefore, considering
335 the partial positive charge on an As atom the expected order of the extent of complexation for the
336 three As species would be As(V) > MTAs(V) > As(III). In agreement with this expected order
337 earlier studies have reported higher sorption of As(V) compared to As(III) to AHA and
338 SRHA.^{18,22,38} However, in the present study with peat this order is found to be exactly opposite,
339 which can be potentially explained by the electrostatic repulsion between peat and As species.

340 Considering the pKa values of the three As species, at the studied pH range (4.5 and 7.0) the
341 predominant species for As(III) should be neutral H_3AsO_3 , whereas for As(V) and MTAs(V) it
342 should be negatively charged $\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$ and $\text{H}_2\text{AsSO}_3^-/\text{HAsSO}_3^{2-}$, respectively.^{1,45}
343 Possibly, because of higher acidity of the functional groups, the studied peat is more negatively
344 charged than AHA and SRHA at a specific pH. Therefore, compared to AHA and SRHA, when
345 As(V) and MTAs(V) were equilibrated with peat the effect of electrostatic repulsion between
346 more negatively charged peat and negatively charged As species predominated over the effect of
347 higher partial positive charge on the As center in these two species, resulting in lower sorption.
348 On the other hand, since the predominant As (III) species at the studied pH was neutral, the
349 electrostatic repulsion between negatively charged peat and neutral As species would be low,
350 resulting in higher complexation, despite lower partial positive charge on the As center. This
351 electrostatic repulsion can also explain the more prominent pH effect for As(III) complexation
352 compared to As(V) complexation to peat (Figure 1). During change of pH from 4.5 to 7.0 the
353 effect of increased nucleophilicity of the alcoholic group was largely offset by the increased
354 electrostatic repulsion between the negatively charged peat and As(V) species; whereas, for
355 As(III) this offset was small because of involvement of the neutral species in the complexation.
356 Furthermore, this electrostatic repulsion was also probably responsible for the increased $R_{\text{As-C}}$
357 and $\text{CN}_{\text{As-C}}$ in As(V)- and MTAs(V)-treated peat compared to that in As(III)-treated peat (Table
358 1). It is worth recalling that in the study of Hoffmann et al.²⁶ the $R_{\text{As-C}}$ in Fe-spiked peat
359 equilibrated with As(III) was longer at $\text{pH} \geq 8.4$ than at $\text{pH} 7.0$, which can also be due to the
360 formation of predominantly negatively charged H_2AsO_3^- species at these pH, which are close to
361 the pKa1 of H_3AsO_3 (9.2),¹ resulting in increased electrostatic repulsion. Despite electrostatic
362 repulsion, the driving force for complexation of the As species to alcoholic group of NOM has
363 been attributed to the stability gained by donation of the negative charge of the alkoxide ion (R-
364 O⁻) to the partially positively charged As atom and/or additional chelation and hydrogen bonding
365 with nearby functional group.¹⁸

366 **Environmental implication.** This study shows that alcoholic groups of NOM can be an
367 alternative or additional binding site for the binary complexation of different As species to
368 NOM. Although the extent of binding is considerably less compared to the binary complexation
369 through organic thiol groups, it is comparable to the binding through Fe^{3+} bridged ternary
370 complex formation. This study implies that NOM can still be a potential sorbent for different As

371 species in systems that are deficient in polyvalent metal cations for ternary complex formation
372 and where organic thiol group content in NOM is not high enough to make significant thiol
373 coordination. Such conditions may prevail in anoxic sulfur deficient ombrotrophic peat bogs, in
374 paddy soils, or aquifer sediments in Bangladesh and West Bengal, India, where the extent of As
375 toxicity to the local inhabitants is most severe. However, similar complexation in the aqueous
376 phase may increase the mobility of As species, but decrease their toxicity by decreasing free ion
377 concentration. This study further implies that the determination of acidity of the functional
378 groups in NOM is essential to assess the mobility of different As species in NOM-rich
379 environments. When the acidity of the functional groups is high, complexation of As(III) is more
380 compared to As(V) and MTAs(V) and vice versa. Therefore, in systems, where NOM is the
381 predominant sorbent for As species, depending on acidity of the functional groups of NOM,
382 As(V) can have a higher mobility than As(III); this is contrasting to the general assumption often
383 made of arsenate being more mobile than arsenite in the environment.¹

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397 **SUPPORTING INFORMATIONS**

398 Additional tables, figures, and analytical methods.

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- 521
- 522

523 **TABLE CAPTIONS**

524 **Table 1:** EXAFS parameters determined by shell-fit analysis of the As K edge EXAFS spectra
525 of the peat equilibrated with different concentrations of As(III) and As(V) at pH 4.5 and 7.0 and
526 MTAs(V) at pH 7.0 only.

527

528 **Table 1:** EXAFS parameters determined by shell-fit analysis of the As K edge EXAFS spectra of the peat equilibrated with different
 529 concentrations of As(III) and As(V) at pH 4.5 and 7.0 and MTAs(V) at pH 7.0 only.

As species	Sample label	k-range	As-O			As-S			As-C			ΔE_0^a (eV)	R-factor ^b (%)	red χ^2 ^c
			CN ^d	R ^e (Å)	σ^{2f} (Å ²)	CN	R (Å)	σ^2 (Å ²)	CN	R (Å)	σ^2 (Å ²)			
As(III)	7.0/1000	2.2-13.0	3.0^g	1.80(0 ^h)	0.0022(3)				1.7(4)	2.74(3)	0.0059ⁱ	0.9(6)	1.5	362
	7.0/150	2.2-9.5	3.0	1.78(0)	0.0023(3)				1.0(3)	2.73(4)	0.0059	1.6(7)	0.6	60
	7.0/100	2.2-11.0	3.0	1.79(0)	0.0031(3)				1.4(3)	2.73(3)	0.0059	1.4(6)	1.0	62
	4.5/1000	2.2-12.0	3.0	1.80(0)	0.0010(4)				2.1(5)	2.73(3)	0.0059	1.1(7)	1.7	144
	4.5/500	2.2-12.0	3.0	1.80(1)	0.0006(4)				2.4(5)	2.74(3)	0.0059	1.4(8)	2.2	122
As(V)	7.0/1000	2.2-12.5	4.0	1.69(0)	0.0016(4)				3.2(10)	2.84(2)	0.0059	1.7(8)	1.7	407
	7.0/500	2.2-12.5	4.0	1.69(1)	0.0009(5)				3.4(14)	2.82(3)	0.0059	1.3(11)	3.4	372
	7.0/250	2.2-12.0	4.0	1.68(1)	0.0011(4)				3.1(11)	2.82(3)	0.0059	2.1(9)	2.3	110
	4.5/1000	2.2-12.5	4.0	1.69(1)	0.0017(4)				3.0(10)	2.82(4)	0.0059	0.9(9)	2.1	315
	4.5/500	2.2-12.0	4.0	1.68(1)	0.0006(5)							-0.8(9)	3.2	260
MTAs(V)	7.0/1000	2.2-12.5	3.0	1.71(0)	0.0034(4)	1.0	2.08(1)	0.0042(9)	2.6(5)	2.78(2)	0.0059	1.0(6)	0.7	171
	7.0/150	2.2-10.5	3.0	1.72(1)	0.0045(5)	1.0	2.10(1)	0.0048(10)	2.9(5)	2.82(2)	0.0059	1.6(7)	0.6	60
	7.0/100	2.2-10.0	3.0	1.72(1)	0.0031(5)	1.0	2.11(1)	0.0027(11)	3.4(7)	2.81(2)	0.0059	1.0(9)	0.8	33

530 ^aEnergy-shift parameter, was the same for all paths. ^bR-factor = $\sum_i(\text{data}_i - \text{fit}_i)^2 / \sum_i \text{data}_i$. ^cred χ^2 = $(N_{\text{idp}}/N_{\text{pts}}) \sum_i ((\text{data}_i - \text{fit}_i)/\epsilon_i)^2 (N_{\text{idp}} -$
 531 $N_{\text{var}})^{-1}$, where N_{idp} : the number of independent points in the model fit, N_{pts} : the total number of data points, N_{var} : the number of
 532 variables in the fit, ϵ_i : the uncertainty in the i^{th} data point. ^dCoordination number (path degeneracy). ^eInteratomic distance or mean half
 533 path length (bond distance for atom in the first-shell). ^fDebye – Waller parameter. ^gValues in bold were fixed in the fit. ^hValues in
 534 parenthesis represent uncertainty in the last significant figure of the fitted parameters. ⁱThis value was determined by fitting the TEA
 535 (reference standard) spectrum. Various multiple scattering paths (see text for details) were included in the fit and constrained in terms
 536 of three single scattering paths (Table SI-1). Passive amplitude reduction factor (S_0^2) was set to 1.0 for shell-fit analysis of all the
 537 samples.

538

539

540 **FIGURE CAPTIONS**

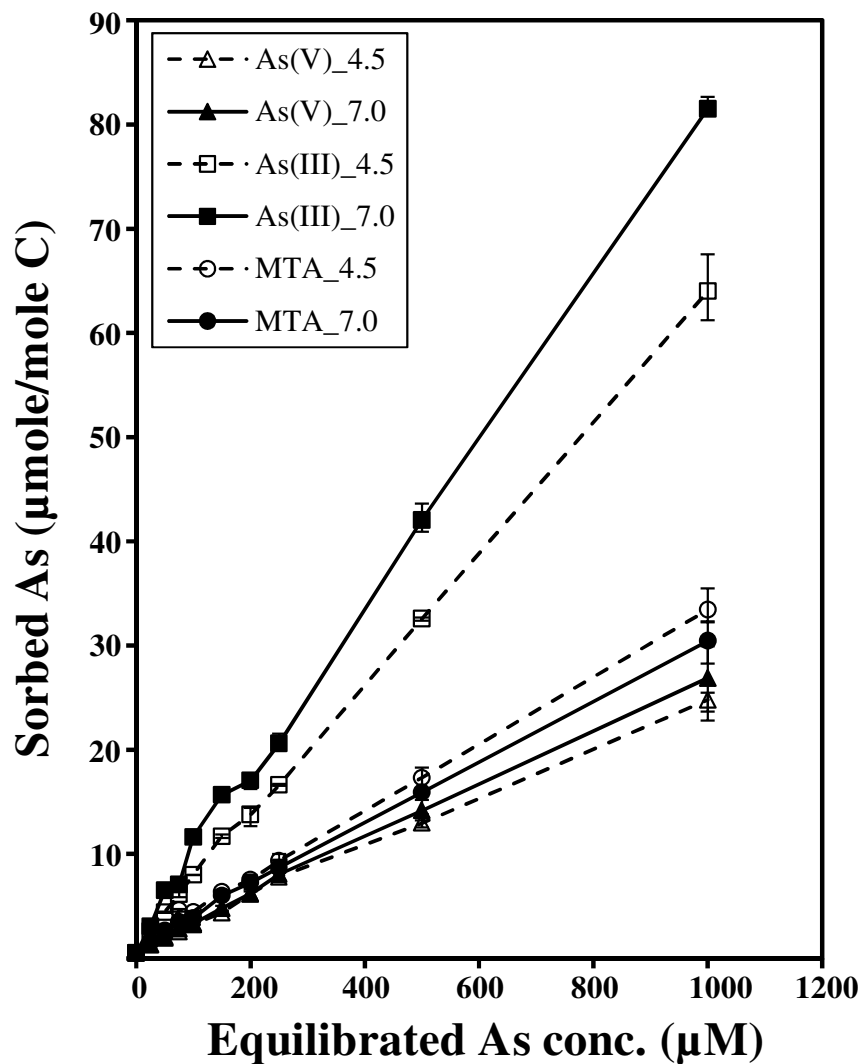
541 Figure 1: Sorption of three As species to peat at different equilibrated concentrations at pH 4.5
542 and 7.0. Symbol and replicate represent average and range of the three replicates.

543 Figure 2: k^3 -Weighted As K edge EXAFS spectra and magnitude and real part of the Fourier
544 transforms (FT) of (A) As(III), (B) As(V), and (C) MTAs(V). Grey lines and red dots represent
545 data and model fit, respectively. Sample labels represent equilibrated pH and As concentration.

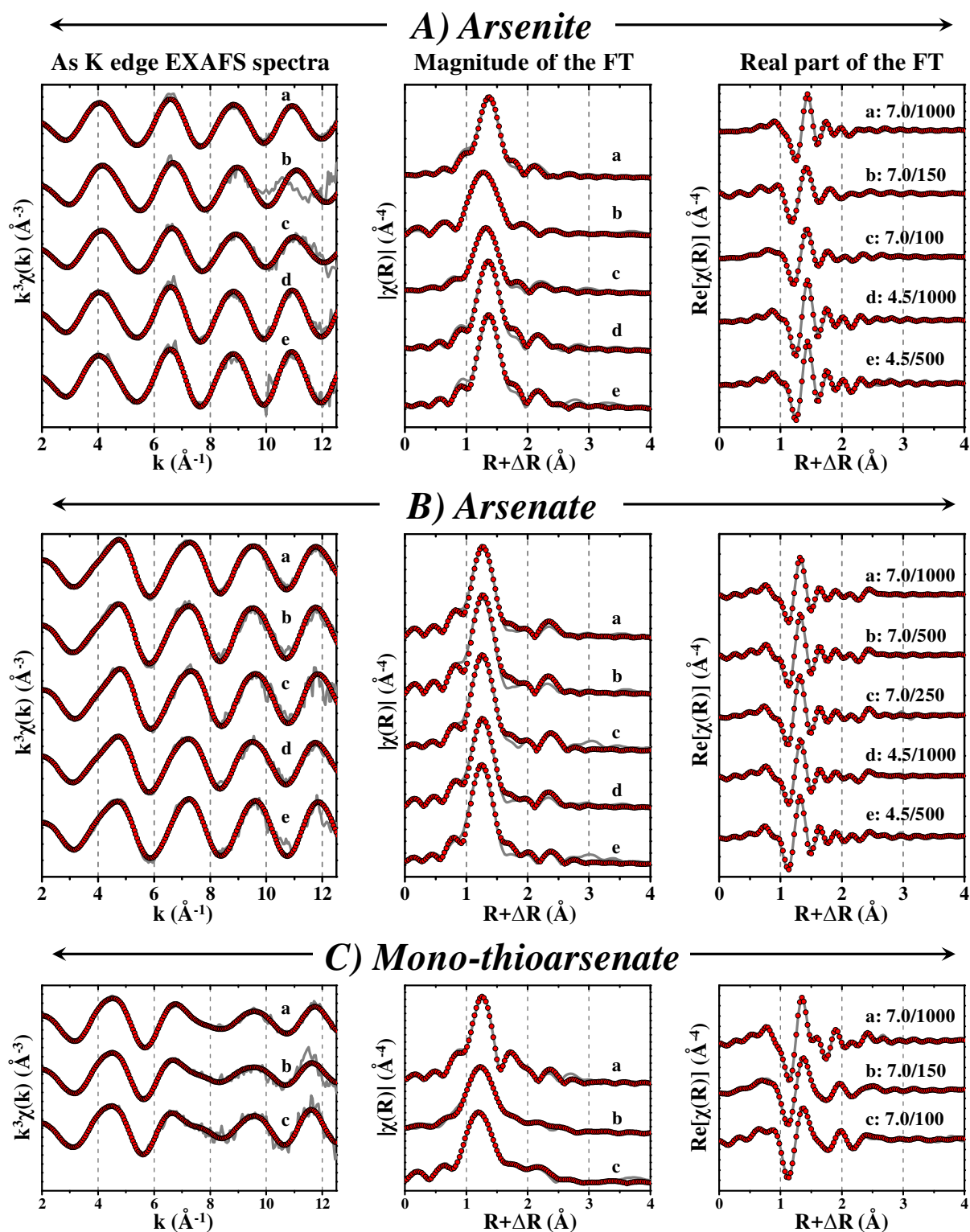
546 Figure 3: Schematic presentation of complexes of the three As species with alcoholic group (for
547 simplicity shown as phenol) of peat identified in the present study: (A) monodentate binding of
548 As(III) at ≤ 0.69 mmol As(III)/mol C, (B) bidentate binding As(III) at ≥ 2.3 mmol As(III)/mol,
549 (C) tridentate binding of As(V), and (D) tridentate binding of MTAs(V). Color code of the
550 sphere: purple – As, blue – O, yellow – S, and black – C.

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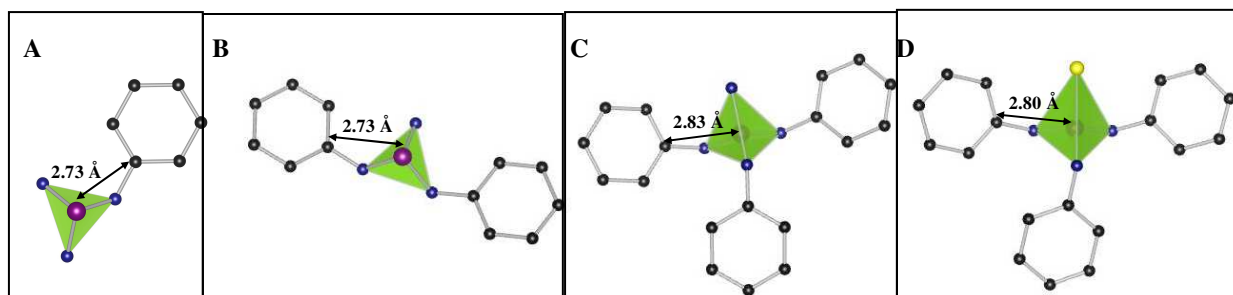


553
 554 **Figure 1:** Sorption of three As species to peat at different equilibrated concentrations at pH 4.5
 555 and 7.0. Symbol and replicate represent average and range of the three replicates.
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559 **Figure 2:** k^3 -Weighted As K edge EXAFS spectra and magnitude and real part of the Fourier
 560 transforms (FT) of (A) As(III), (B) As(V), and (C) MTAs(V). Grey lines and red dots represent
 561 data and model fit, respectively. Sample labels represent equilibrated pH and As concentration.
 562



563
 564 **Figure 3:** Schematic presentation of complexes of the three As species with alcoholic group (for
 565 simplicity shown as phenol) of peat identified in the present study: (A) monodentate binding of
 566 As(III) at ≤ 0.69 mmol As(III)/mol C, (B) bidentate binding As(III) at ≥ 2.3 mmol As(III)/mol,
 567 (C) tridentate binding of As(V), and (D) tridentate binding of MTAs(V). Color code of the
 568 spheres: purple – As, blue – O, yellow – S, and black – C.

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