



HAL
open science

Evidence of humic acid-aluminium-silicon complexes under controlled conditions

Patricia Merdy, Jean-Dominique Meunier, Fabio Ziarelli, Yves Lucas

► **To cite this version:**

Patricia Merdy, Jean-Dominique Meunier, Fabio Ziarelli, Yves Lucas. Evidence of humic acid-aluminium-silicon complexes under controlled conditions. *Science of the Total Environment*, 2022, 829, pp.154601. 10.1016/j.scitotenv.2022.154601 . hal-03967824

HAL Id: hal-03967824

<https://hal.science/hal-03967824>

Submitted on 1 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

1 **Evidence of humic acid-aluminium-silicon complexes**
2 **under controlled conditions**

3

4 Patricia Merdy^{a*}, Jean-Dominique Meunier^b, Fabio Ziarelli^c, Yves Lucas^a

5

6 ^a Université de Toulon, Aix Marseille Univ, CNRS, IM2NP, 83041 Toulon CEDEX 9,
7 France

8 ^b CEREGE, CNRS, Aix-Marseille Univ, IRD, INRAE, 13545 Aix-en-Provence, France

9 ^c Aix Marseille Univ, CNRS, Centrale Marseille, FSCM, FR1739, 13013, Marseille,
10 France

11

12 *Corresponding author (merdy@univ-tln.fr)

13

14 **HIGHLIGHTS**

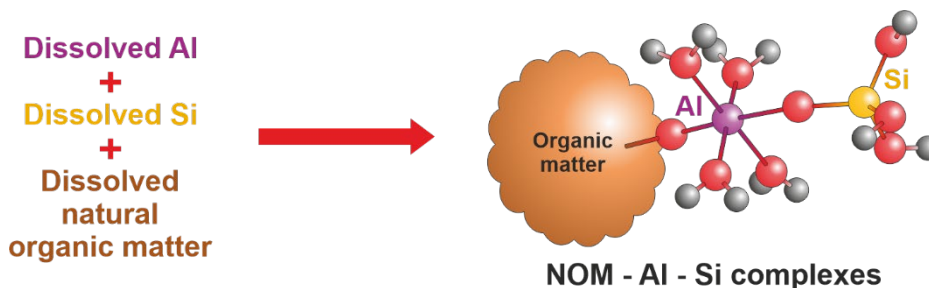
15

- 16
- 17 • First evidence of OM-metal-Si complex impacting environmental dynamics
 - 18 • Si alone actually interacts with humic acid (HA), but weakly
 - 19 • With both Si and Al, HA-Al-Si complex with bridging Al and Al-O-Si bond
 - 20 • Si promotes the maintenance of both Al and HA in solution
 - 21 • Such complexes likely exist with other metals (Fe, Mn) and metalloids (As,
22 Ge)

23

24 GRAPHICAL ABSTRACT

25



26

27

28 ABSTRACT

29

30 The chemistry of silicon (Si), the second most abundant element in soil after
31 oxygen, is not yet fully understood in the soil-water-plant continuum. Although Si
32 is widely accepted as an element that has little or no interaction with natural
33 organic matter, some data seems to show the opposite. To identify a potential
34 interaction between natural organic matter and Si, batch experiments were
35 achieved at various pH and Si concentrations, involving also Al^{3+} as a common ion
36 in soil and using humic acid (HA) as a typical model for natural organic matter.
37 Several complementary techniques were used to characterize the possible
38 complexes formed in the dissolved or solid phases: molecular fluorescence
39 spectroscopy, ^{29}Si solid-state NMR, Fourier transform infrared spectroscopy,
40 quantification of Si, Al and organic carbon, and nanoparticle size distribution.
41 These tools revealed that humic acid indeed interacts, but weakly, with Si alone.
42 In the presence of Al, however, a ternary complex HA-Al-Si forms, likely with Al as
43 the bridging atom. The presence of Si promotes the maintenance of both Al and
44 DOM in solution, which is likely to modify the result or the kinetics of
45 pedogenesis. Such complexes can also play a role in the control of Al toxicity
46 towards plants and probably also exists with other metals, such as Fe or Mn, and
47 other metalloids such as As.

48

49 Keywords

50 Silicon, Humic acid, Complexation, Spectroscopy, Nanocolloids, Sorption sites

51 1. Introduction

52

53 Silicon-carbon interaction is a subject of interest in many disciplines. The
54 synthesis of organosilicon compounds has given rise to products of daily use such
55 as silicone or silsesquioxanes with many applications in industrial chemistry,
56 agriculture and medicine (Larina, 2021). It has long been known that life is able to
57 manipulate silicon for various purposes, for example forming sponge spicules,
58 diatom frustules or plant phytoliths (Perry, 2015). Plants have several types of
59 membrane transport proteins (Ma and Yamaji, 2015), and the polymerization of
60 silica is carried out thanks to enzymes such as silicatein in sponges (Cha et al.,
61 1999; Shimizu and Morse, 2018) or to small peptides such as silaffins in diatoms
62 (Otzen, 2012). Recently, it has been shown that carbon-silicon bonds can be
63 formed by biocatalysis carried out by bacteria modified by direct evolution, which
64 increases the capacities of living systems (Kan et al., 2016). However, these latter
65 authors pointed out that carbon-silicon bond formation is unknown in nature.

66 In the terrestrial ecosystem, the biogeochemical cycle of Si is largely
67 documented and presents mostly inorganic chemical reactions (Schaller et al.,
68 2021). The weathering of primary or secondary silicate minerals is the primary
69 source of dissolved Si. Among secondary silicate minerals, phytoliths from plant Si
70 recycling (Lucas et al., 1993) play a key role due to their high solubility (Cornelis et
71 al., 2011; Keller et al., 2012). Soluble Si in soils is mostly in the form of bioavailable
72 orthosilicic acid (H_4SiO_4). It is indeed this species which is absorbed by the roots
73 (Jones and Handreck, 1967) and which is found in the xylemic sap of plants
74 (Mitani et al., 2005). It precipitates in the plant tissue in biogenic opal, forming
75 phytoliths. If the soil solution is oversaturated with Si, for example due to
76 evaporation or freezing, the orthosilicic acid rapidly precipitates in the form of
77 clay minerals or, where dissolved Al is not available, in the form of hydrated opal
78 or siliceous gel (Sommer et al., 2006), with possible transitional formation of
79 polymerized silicic acid species (Wonish et al., 2008). The existence of natural
80 organosilicon compounds in the soil-water-plant continuum is a subject of
81 controversy. Some studies suggested the existence of such compounds
82 (Kolesnikov and Gins, 2001; Inanaga et al., 1995; Matychenkov et al., 2016;
83 Bennett et al., 1991; Bennett, 1991) while others did not find evidence of them
84 (Peggs and Bowen, 1984; Exley, 1998; Viers et al., 1997; Viers et al., 2000). Recent
85 studies motivated by the growing concern for the treatment of polluted sites or
86 effluents have empirically shown the impact of the Si-organic matter association
87 on the dynamics of metals or metalloids, without mechanistic processes having
88 been identified (Li and al., 2019; Ma et al., 2021; Zhao et al., 2022).

89 In the present study, we are questioning the nature of interactions between
90 natural organic matter and Si in the form of orthosilicic acid. In particular, we
91 wonder if the complexation of Si by ligands of natural organic matter would
92 increase the overall Si solubility in the soil solution. While interactions between
93 dissolved organic molecules and Si have been shown to exist, leading to
94 accelerated dissolution of quartz, it is mainly adsorption processes that have been
95 mentioned (Bennet, 1991). Studies on complexation between Si and natural
96 organic matter in solution are very few and seem to show, or to hypothesize, the
97 absence of complexation between Si and organic molecules, or the presence of
98 weak complexes when they exist. For example, the study by Poulson (1997) could
99 not prove the existence of an oxalate-Si complex after titration of $\text{Si}(\text{OH})_4$ by
100 $\text{K}_2\text{C}_2\text{O}_4$. Potentiometric titration experiments were performed by Ohman et al.
101 (1991) in homogeneous solutions of $\text{Si}(\text{OH})_4$ and catechol, showing the existence

102 above pH 7 of a hexacoordinated complex, SiL_3^{2-} , where L is the catechol ligand.
 103 Inanaga and Okasaka (1995) have shown that silicon can combine with lignin-
 104 carbohydrate complexes in cell walls of rice shoots, but the corresponding species
 105 has not been identified. Pokrovski and Schott (1998) reported that Si formed weak
 106 complexes in solution with simple organic ligands having carboxylic or phenolic
 107 functional groups. Kambalina et al. (2014), however, concluded after
 108 spectrophotometric measurements that Si does not form stable complexes with
 109 fulvic and humic acids in weak-acid media (pH 3-4).

110 In the present study, we used several complementary techniques to identify
 111 possible species in which Si is bound to natural organic matter. Batch tests were
 112 performed using humic acid (HA), taken as a model of natural soil organic matter,
 113 and dissolved Si, under different conditions of concentration and pH. We have
 114 considered the presence of Al^{3+} species in the systems, as aluminium is a very
 115 common element present in soil and highly reactive with Si. The products formed
 116 in the batch tests were analyzed by molecular fluorescence, IRTF and ^{29}Si solid-
 117 state NMR spectroscopies, along with Si, Al and organic carbon quantifications.
 118

119 2. Material and methods

120 2.1. Batch systems

121
 122 An HA solution at 120 mg L^{-1} was prepared from a commercial powder (Humic
 123 Acid, Alfa Aesar, 41747). Si and Al stock solutions were prepared from Na_2SiO_3
 124 (Carlo Erba Reagenti, 373908) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Merck, 1.01063.0500),
 125 respectively. Three systems were studied: HA-Si, HA-Al and HA-Si-Al. For each
 126 system, 15 solutions (S01 to S15) were prepared with an HA concentration equal
 127 to 120 mg L^{-1} and Si or Al concentrations varying from 0 to $10^{-2} \text{ mol L}^{-1}$ according
 128 to concentrations given in Table 1. This concentration range includes the
 129 concentrations range observed in most natural surface waters (soil solutions,
 130 rivers and lakes) for dissolved Si (Cornelis et al., 2011) and Al (Lindsay and
 131 Walthall, 2020). After component mixing, each solution was left to equilibrate for
 132 one week. Precipitation occurred in some of the solutions, these are indicated in
 133 the results section. All experiments with the associated measurements were
 134 repeated three times to ensure reliability.

135
 136 **Table 1**

137 Si or Al concentrations in the HA-Si, HA-Al or HA-Si-Al systems. In the HA-Si-Al
 138 system, both Si and Al are at the given concentration.
 139

Suffix of the solution	S01	S02	S03	S04	S05	S06	S07	S08	S09	S10	S11	S12	S13	S14	S15
Concentration mol L^{-1}	$1 \cdot 10^{-2}$	$8 \cdot 10^{-3}$	$6 \cdot 10^{-3}$	$3 \cdot 10^{-3}$	$1 \cdot 10^{-3}$	$8 \cdot 10^{-4}$	$6 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$1 \cdot 10^{-4}$	$8 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$1 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	0

140
 141

142 2.2. Fluorescence spectroscopy

143
 144 Fluorescence spectroscopy is an interesting tool for studying complex molecules
 145 such as natural organic matter since it emits natural fluorescence under excitation
 146 and the fluorescence is sensitive to the physicochemical properties of the solution.
 147

148 2.2.1. *Fluorescence excitation-emission matrix (EEM)*

149

150 In EEM measurements the emission signal is registered on a wavelength range,
151 at every step of the range of an excitation wavelength, resulting in a three-
152 dimensional contour plot of fluorescence intensity as a function of excitation and
153 emission wavelengths, commonly called an excitation-emission matrix (EEM). The
154 maximum intensity peaks observed on an EEM can be related to fluorophores
155 defined by a pair of emission and excitation wavelengths (λ_{ex} , λ_{em}). The emission-
156 excitation coordinates of the peaks can reveal the origin of the organic matter
157 (terrestrial, marine, fresh water), as described by Coble (1996).

158 EEMs were obtained from two series of 12 samples for each system (HA-Si, HA-
159 Al and HA-Si-Al), whose Si and Al concentrations varied from 10^{-2} to 10^{-6} M, which
160 were adjusted to pH 4, 7 and 9 using HCl solutions (0.1 M, HCl Trace Metal Grade
161 37% v/v from Fisher Scientific) and/or NaOH (0.1M, Crystals from Sigma-Aldrich).
162 The solutions were diluted by a factor of 10 before fluorescence measurement.
163 Preliminary experiments were carried out to avoid inner screen effect, using a
164 sample dilution followed by checking the proportional signal intensity response
165 (data not shown).

166 The measurement was performed using a Hitachi model F-4500
167 spectrophotometer, equipped with a 450 W xenon lamp. Sample solutions were
168 placed in 1 cm x 1 cm quartz cells. The excitation window was set at 5 nm and the
169 emission window at 10 nm. The excitation wavelengths ranged from 200 nm to
170 500 nm, and emission wavelengths from 250 nm to 600 nm, with a 5 nm step at a
171 scan rate of 2400 nm min^{-1} for both. The photomultiplier was set to 700 V.

172

173 2.2.2. *Fluorescence quenching or enhancement*

174

175 This technique consists of following the change of the fluorescence intensity of
176 a fluorophore during the gradual addition of Si, Al or both together. For natural
177 organic matter such as HA, this change indicates the formation of a complex
178 between the fluorophore and the added compound (static quenching or
179 enhancement) (Luster et al., 1996). It allows calculation of the complexing
180 capacities and the apparent stability constants of the fluorescence ligand (Ryan
181 and Weber, 1982).

182 We recorded the fluorescence intensity of the HA fluorophore that had the
183 higher intensity without an added compound as a function of Si, Al or both
184 together at three pH (4, 7 and 9) adjusted with HCl and NaOH, which were
185 preferred over the usual buffers in order to avoid any impact on the fluorescence
186 signal (Merdy et al., 2020). During the fluorescence quenching experiment, it
187 checks should be made for the absence of solid precipitation after each addition
188 of Si or Al. This was done after equilibrating the solutions for at least three hours
189 by visual inspection of the solutions and by measuring the amount of residual
190 carbon in batch sample after filtration.

191

192 2.3. *Organic carbon analysis*

193

194 The batch samples were filtered through glass fiber filters (0.7 μm , GF/F
195 Whatman) previously treated at 450°C to get rid of any traces of organic carbon.
196 In the resulting filtrate, the dissolved organic carbon (DOC) concentration was
197 measured using a TOC-VCSH analyzer (Shimadzu) coupled to an ASI-V auto-
198 sampler (Shimadzu). The particulate organic carbon (POC) remaining on the filters

199 was quantified using a Thermo Flash 2000 Elemental Analyzer in NC mode
200 (ThermoScientific).

201

202 *2.4. Infrared spectroscopy*

203

204 The precipitates obtained after filtration of batch samples were analyzed by IR
205 spectroscopy in order to identify vibration frequencies that could clarify the
206 nature of the bonds between Si and HA in the solid phases . Infrared spectra were
207 recorded using a JASCO FT/IR-410 spectrometer over a range from 400 to 4000
208 cm^{-1} in steps of 1 cm^{-1} . The pellets used in the analysis were obtained using a
209 hydraulic press exerting a pressure of 5000 psi for approximately one minute.
210 They were prepared from KBr (powder, Sigma-Aldrich). Only samples presenting
211 enough solids on the filter could be analyzed in solid-state infrared.

212

213 *2.5. Si and Al quantification*

214

215 Dissolved Si was quantified using a DR2800 (Hach Lange) spectrophotometer.
216 An assay kit (Method 8186, Hach Lange) was used to apply a colorimetric method
217 based on the formation of the blue Cr-Si complex, a method adapted from
218 "Standard Methods for the Examination of Water and Wastewater" (Greenberg,
219 1992). Dissolved Al was quantified with a Shimadzu UV-1800 spectrophotometer
220 using the chromazurol S reagent ($2 \cdot 10^{-4} \text{ mol L}^{-1}$, powder, VWR) in hexamine buffer
221 (0.2 mol L^{-1} , powder, VWR) at pH 4.9, adjusted with HCl (37% v/v Trace Metal Grade,
222 Fisher Scientific) (Kennedy and Powell, 1986).

223

224 *2.6. Colloid size distribution*

225

226 The colloid size distribution was determined by Nano Tracking Analysis (NTA)
227 using a Malvern NS500 apparatus. This technique tracks individual colloidal
228 particles in the liquid and relates the rate of Brownian motion to the particle size.
229 The tracking of a sufficient number of particles allows particle size distribution and
230 concentration to be obtained. The NTA analysis was performed on samples whose
231 concentrations were 120 mg L^{-1} for HA, 10^{-3} M for Si and 10^{-3} M for Al.

232

233 *2.7. Solid-state NMR of ^{29}Si*

234

235 The solid-state NMR of ^{29}Si was used to supplement the data obtained by IR
236 spectroscopy. NMR spectra were determined on powders obtained after
237 centrifugation of a sufficiently large volume of batch solutions prepared at pH 7
238 using 120 mg L^{-1} of HA and $10^{-2} \text{ mol L}^{-1}$ Si or Al concentrations.

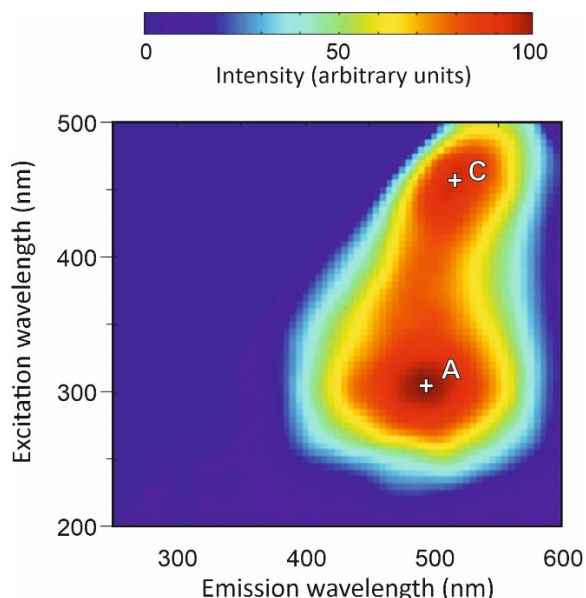
239

240 All solid-state NMR spectra were obtained on a Bruker Avance-400 MHz NMR
241 spectrometer operating at ^{29}Si resonance frequency of 79.5 MHz. About 20 mg of
242 samples were placed in zirconium dioxide rotors with a 4-mm outer diameter and
243 spun at a Magic Angle Spinning rate of 10 kHz in a commercial Bruker Double
244 Channel probe. ^{29}Si CPMAS experiments were performed with the Cross
245 Polarization (CP) technique (Schaefer and Stejskal, 1976) using a ramped 1H-pulse
246 starting at 100% power and decreasing to 50% during the contact time (5 ms) in
247 order to circumvent Hartmann-Hahn mismatches (Peersen et al., 1993; Cook et
248 al., 1996). To improve the resolution, a dipolar decoupling GT8 pulse sequence
(Gerbaud et al., 2003) was applied during the acquisition time.

249 To obtain a good signal-to-noise ratio, between 10^3 and 10^4 scans were
250 accumulated using a delay of 2.5 s. The ^{29}Si chemical shifts were referenced to
251 tetramethylsilane.
252

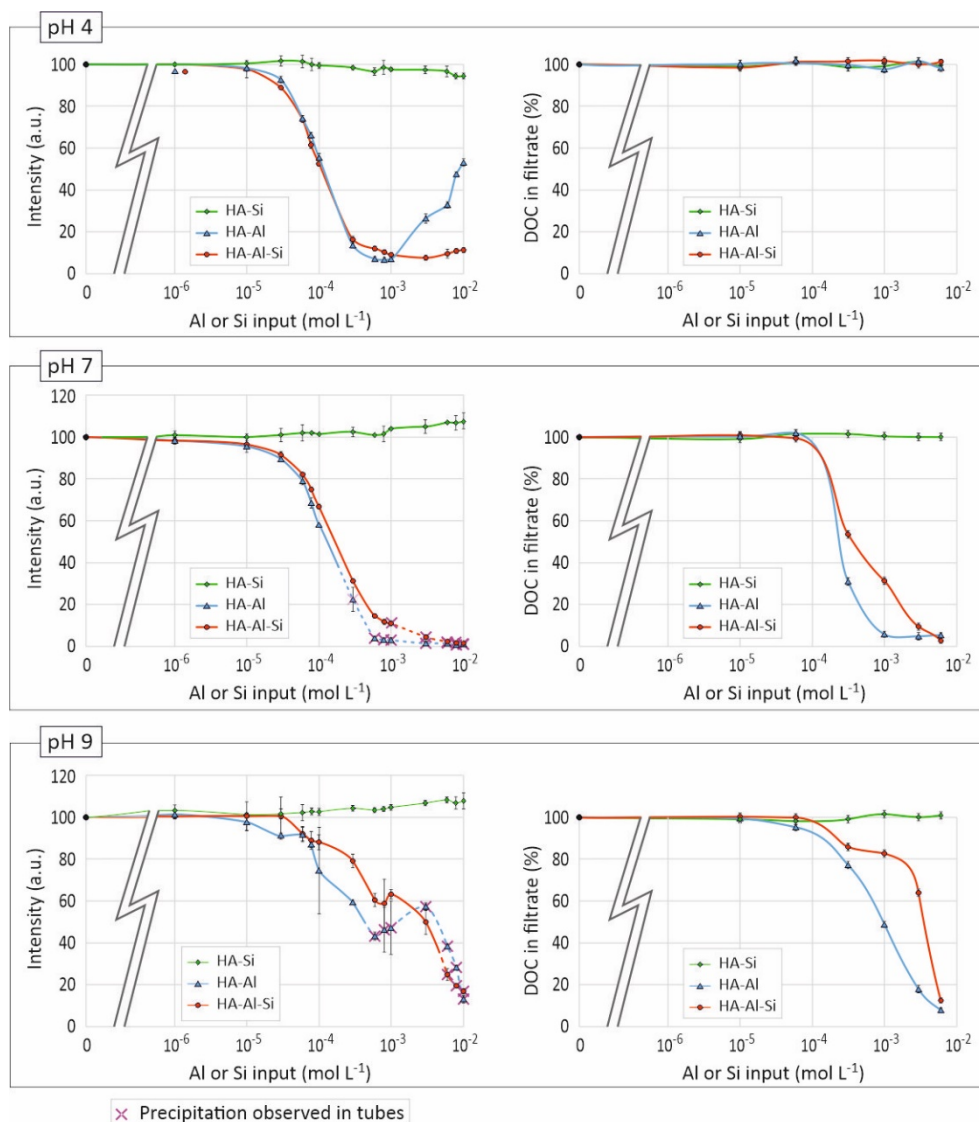
253 3. Results and discussion

254 3.1. Fluorescence spectroscopy and precipitations in the different systems 255



256
257 **Fig. 1.** Fluorescence excitation-emission matrix of the humic acid used in this
258 study.

259
260 The 3D fluorescence signal of the HA used in our experiments is shown in Fig.
261 1. It indicated two peaks identified by their emission and excitation wavelengths
262 at their maximum intensities. One (peak A) corresponds to fulvic-like molecules at
263 ($\lambda_{\text{ex}} = 305\text{nm}$ and $\lambda_{\text{em}} = 495 \text{ nm}$) and the other (peak C) to humic-like molecules at
264 ($\lambda_{\text{ex}} = 460\text{nm}$ and $\lambda_{\text{em}} = 520 \text{ nm}$) (Coble, 1996; Fellman, 2008; Ohno et Bro, 2006).
265 The same spectrum was obtained at pH 4 and pH 9. It is typical of what was
266 recorded elsewhere (Coble, 1996; Parlanti et al., 2002). The ability of natural
267 organic matter, especially humic substances, to interact with metals is attributed
268 to the presence of various functional groups such as amines, carboxyl, hydroxyl,
269 phenolic or carbonyl. Metal ions or other complexing molecules are able to
270 quench the fluorescence of organic ligands when they complex to these functional
271 groups (Gauthier et al., 1986; Elkins and Donald, 2002; Provenzano et al., 2004).
272 They can, in some cases, enhance the fluorescence intensity (Merdy et al., 2020 ;
273 Manoharan et al., 2014).
274



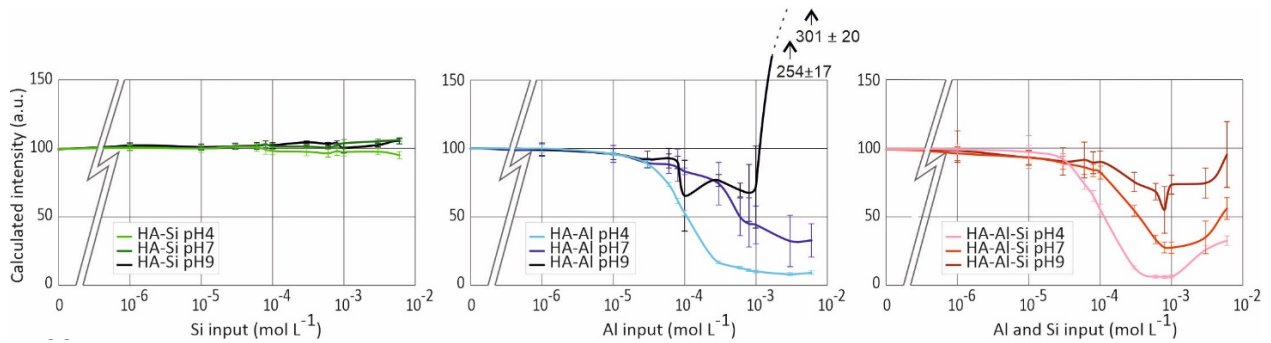
275
 276 **Fig. 2.** Representation of the fluorescence intensity (no unit) of the different
 277 systems at different pHs as a function of the concentration of Si or Al (in mol L⁻¹).
 278 Fluorescence intensity and DOC % were normalized to their value in the pure HA
 279 solution (S15).

280
 281 The left side of Fig. 2 shows the results of the quenching experiments, and the
 282 right side shows the measurement of organic carbon in the filtrates at each point
 283 of the experiment, which makes it possible to quantify any precipitation of
 284 organic matter. When carbon precipitation occurred, the fluorescence intensity
 285 I_{calc} was calculated assuming that the DOC remaining in solution had the same
 286 fluorescence properties as the DOC at the start of quenching:

287
$$I_{calc} = I_{obs} \frac{DOC_{init}}{DOC_{batch}}$$

288 Where I_{obs} and DOC_{batch} are the fluorescence intensity and the DOC
 289 concentration of the batch sample after filtration, respectively, and DOC_{init} is the
 290 DOC concentration at the beginning of the quenching experiment. The results are
 291 shown in Fig. 3.

292

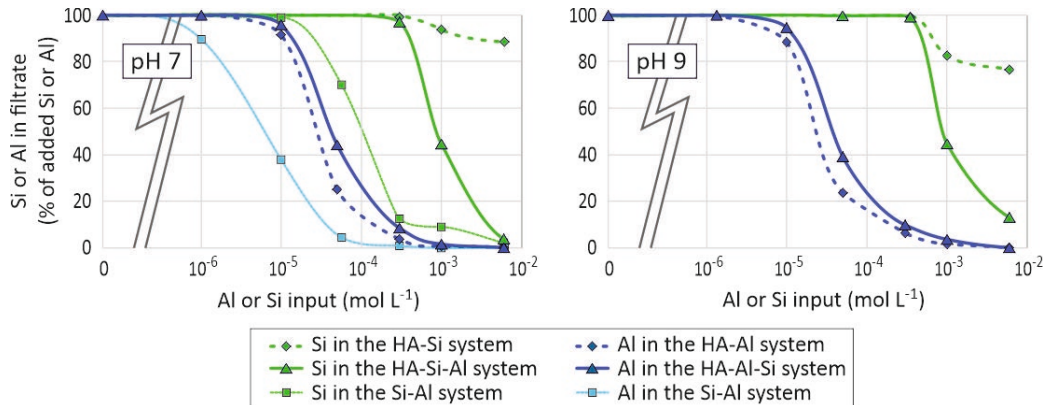


294 **Fig. 3.** Fluorescence intensity referred to the amount of DOC remaining in
 295 solution.

296

297 **In the HA-Si system,** the fluorescence intensity remained almost constant
 298 whatever the pH when the Si concentration increased to 10^{-4} mol L $^{-1}$. Starting
 299 from this concentration, there was a slight and reproducible fluorescence increase
 300 at pH 7 and 9 and a slight and reproducible decrease at pH 4. No DOC precipitation
 301 occurred so these observations were not related to the removal of fluorophores
 302 from the solution. There is globally no strong fluorescence quenching or
 303 enhancement effect. This indicates negligible interactions between Si and HA at
 304 concentrations lower than $1 \cdot 10^{-4}$ mol L $^{-1}$, which is consistent with the literature
 305 (Pokrovski and Schott, 1998), and slight direct interactions beyond this
 306 concentration under the experimental conditions. Although this was not visible in
 307 the experimental vials, precipitation of Si occurred when added Si was greater
 308 than 10^{-4} and $3 \cdot 10^{-4}$ mol L $^{-1}$ at pH 7 and 9, respectively (Fig. 4) (no data for pH 4).
 309 In the absence of Al, precipitation of Si likely occurred as a species whose solubility
 310 was intermediate between quartz and amorphous SiO $_2$ (Fig. 5), such as opal-a or
 311 opal-CT (Scheinost, 2005). According to Dietzel (2000), monosilicic acid is the
 312 largely dominant species of Si in solution up to pH 9.8 The possibility of
 313 condensation of monosilicic acid into polysilicic acid, which would have led to an
 314 increase in the binding capacity of dissolved Si, can therefore be ruled out for
 315 these experiments.

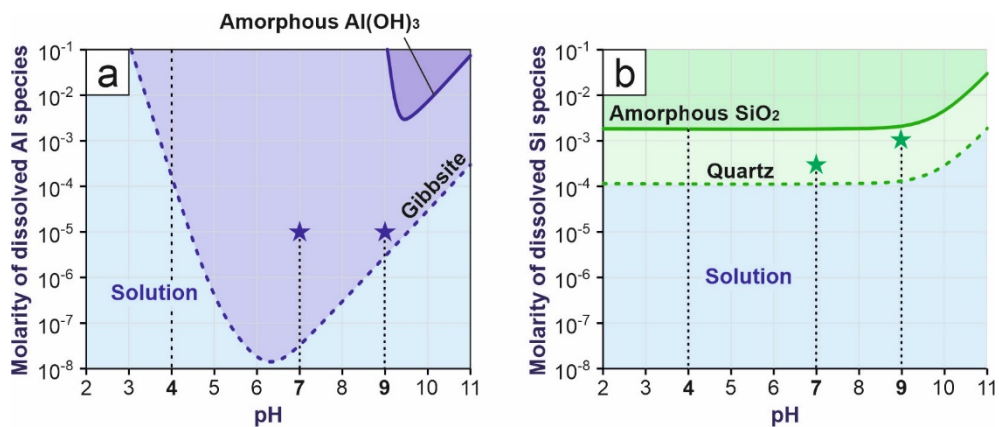
316



317

318 **Fig. 4.** Si or Al remaining in solution in the different systems at pH 7 and pH 9.

319



320
321
322
323
324
325
326

Fig. 5. Stability domain of amorphous Al(OH)₃ and gibbsite (a) and of amorphous SiO₂ and quartz (b). Blue and green stars indicate the Al or Si concentration at which precipitation began at the given pH in the HA-Al and HA-Si systems, respectively. Solubility products taken from the PHREEQC database (Johnson et al., 2000) and Furrer et al. (1991).

327
328
329
330
331
332
333
334
335
336
337
338
339

In the HA-Al system, an apparent fluorescence quenching was observed at any pH for Al input higher than 10⁻⁶ mol L⁻¹. DOC precipitation, however, occurred at Al input greater than 10⁻⁴ and 10⁻⁵ mol L⁻¹ at pH 7 and 9, respectively (Fig. 2). Such precipitation was expected given the flocculating power on DOC by Al species in solution at sufficiently high concentration, as demonstrated by several studies (Nierop et al., 2002; Masion et al., 2000; Sadrnourmohamadi and Gorczyca, 2015), or by DOC adsorption on newly precipitated Al hydroxides (Heckman et al., 2013). Aluminium precipitation, however, occurred at Al input greater than 3.10⁻⁶ mol L⁻¹ at pH 7 and 9 (Fig. 3), when no DOC precipitation was observed between 3.10⁻⁶ and 3.10⁻⁵ mol L⁻¹, so that HA adsorption on Al hydroxides was not the main process. In the absence of Si, precipitation of Al likely occurred as species whose solubility was intermediate between gibbsite and amorphous Al(OH)₃ (Fig. 5), such as Al₁₃ gel (Jolivet, 2000).

340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360

After correction of the precipitated DOC, fluorescence quenching was confirmed at pH 4 and 7 over the entire concentration range (Fig. 3). At pH 9, the fluorescence quenching observed at Al input of between 10⁻⁵ and 10⁻³ mol L⁻¹ was followed by a fluorescence enhancement at greater Al input. The fluorescence enhancement effect on natural organic matter complexed with Al had already been observed (Blaser et al., 1999; Sharpless and McGown, 1999; Elkins et al., 2002). Elkins et al. (2002) considered Al to be unique compared to other metal ions such as Cu, Co, Mn, Pb, which have a propensity to quench the fluorescence; Al would be different due to its high charge density. Other studies showed a quenching phenomenon of natural organic matter upon Al ion addition, such as Shotyky and Sposito (1988) on leaf litter aqueous extract at $\lambda_{ex} = 440$ nm and $\lambda_{em} = 525$ nm at pH = 4.0, 4.5, and 5.0. More recent studies tried to identify the processes responsible for quenching or enhancement of the fluorescence signal, such as that of Yan et al. (2013). If the quenching of fulvic acid signals was dominating at higher emission wavelengths and increasing total Fe(III) concentrations, the pattern observed with Al(III) was much more complex with both quenching and enhancement phenomena observed in different areas of the spectra. Basically, at low concentrations, the authors mentioned that the interactions took place with phenolic groups of the fulvic acid, and then weakly binding carboxylic groups. After saturation of the complexing sites, metallic ions keep interacting with fulvic acids through non-specific Donnan gel electrostatic

361 interactions. The specific pattern observed for Al(III) ions at pH 6 was not fully
362 understood by these authors and could be explained, according to them, by
363 discrete subsets of natural organic matter fluorophores. This last assumption
364 could apply here, where the transition from quenching to enhancement when
365 added Al increased could be explained by the precipitation of a subset of
366 fluorophores, the fluorophores remaining in solution having higher quantum
367 yields. Greater ionic strength when Al input increased may also have resulted in Al
368 decomplexation from fluorophores. Because of the precipitation of both Al and
369 organic matter, however, the verification of this hypothesis would require
370 dedicated studies.

371 **In the HA-Si-Al system**, the evolution of fluorescence is close to that of the HA-
372 Al system, but the DOC precipitation is lower than in the latter for Si or Al inputs
373 between 10^{-4} and $8 \cdot 10^{-3} \text{ mol L}^{-1}$. There was no fluorescence enhancement, but it
374 was observed after correction of the precipitated DOC that the quenching was
375 maximum for Si or Al inputs around $10^{-3} \text{ mol L}^{-1}$ and decreased when metal
376 concentrations increased. The presence of Si changed the behavior of the system
377 compared to the presence of Al alone. For metal input greater than $8 \cdot 10^{-4} \text{ mol L}^{-1}$,
378 both quenching (at pH 4 and 7) and enhancement (at pH 9) became less intense in
379 the HA-Si-Al system, unlike what was observed in the HA-Al system.

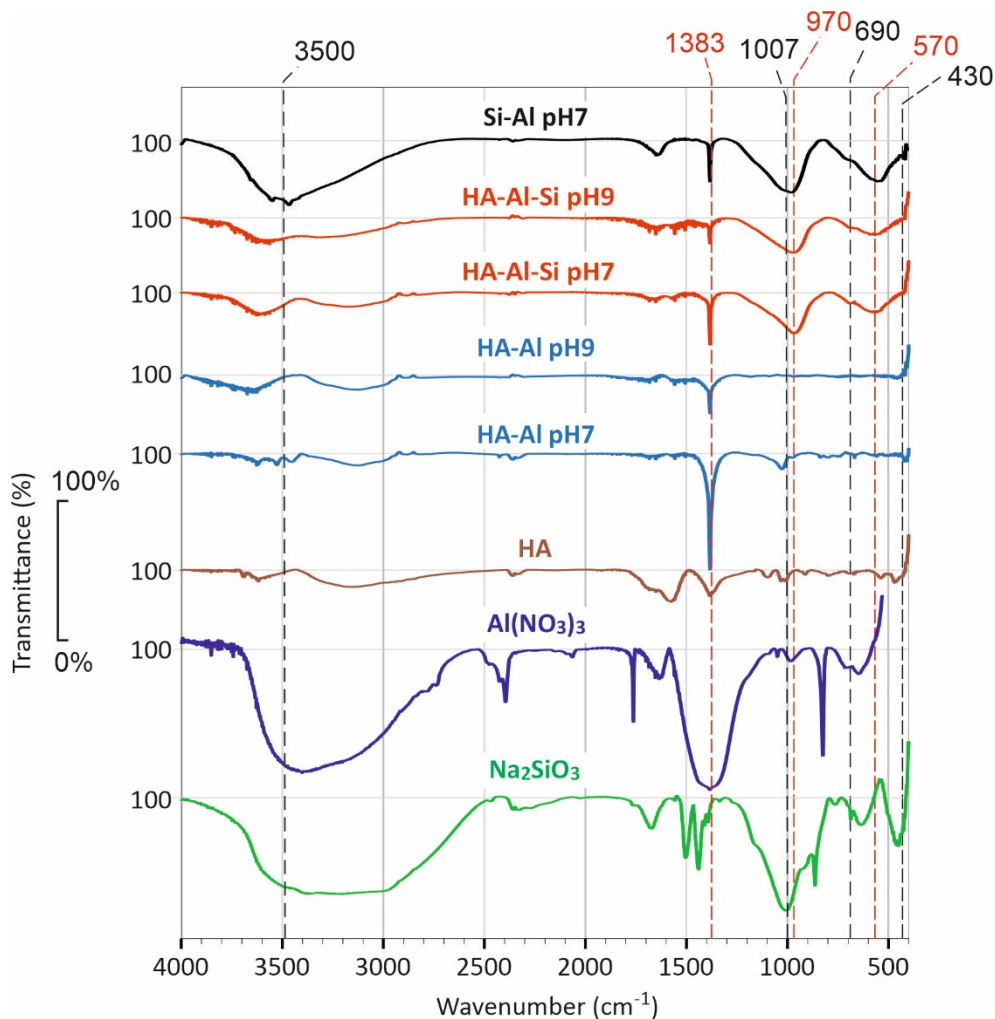
380 In order to evaluate the role of HA in the precipitation of Al and Si, we
381 measured the Si and Al remaining in solution in a Si-Al system without HA at pH 7,
382 using the same batch protocol as for the quenching measurements; the results
383 are shown in Fig. 4. It can be seen that with increasing inputs of Si and Al, the
384 presence of HA delayed precipitation of both Al and Si. This can be explained by
385 the formation of HA-Al complexes, which delayed the precipitation of Al
386 hydroxides and aluminosilicates. However, precipitation of DOC (Fig. 2) and Al
387 (Fig. 4) was lower in the HA-Si-Al system than in the HA-Al system for amounts of
388 added metal less than $8 \cdot 10^{-3} \text{ mol L}^{-1}$, at pH 7 as well as at pH 9. The presence of Si
389 therefore favored the maintenance of both DOC and Al in solution. Consequently,
390 the supposition of DOC and Al removal by precipitation of minerals and
391 subsequent HA adsorption cannot explain the experimental observation, and the
392 process of DOC flocculation by Al^{3+} species is at least slowed down by dissolved
393 silicon.

394 At this stage of the study, our hypothesis to explain our data is the formation
395 of a ternary complex between HA, Al and Si. At pH of around 5.5 to 7.5, Al^{3+} in its
396 octahedral first hydration shell is more likely than Si^{4+} in its tetrahedral first
397 hydration shell to form an inner sphere complex with a reactive nucleophilic site
398 of the NOM (Jolivet et al., 2000). Indeed, Al^{3+} has a much higher affinity than Si^{4+}
399 with HA. It is therefore very likely that Al play facts as a bridge between NOM and
400 a Si species, with an Al-O-Si bond.

401

402 *3.2. IR spectroscopy*

403



404
405 **Fig. 6.** IR spectra of the solid phases collected on the membrane filters in the
406 different systems.
407

408 The IR spectra of Na_2SiO_3 and of the different solids precipitated from batches
409 are given in Fig. 6. The IR spectrum of Na_2SiO_3 was similar to that obtained by
410 Yahya et al. (2015). The Si-O vibration frequency can be seen at 1007 cm^{-1} (Halasz
411 et al., 2007). The broad band around $3000\text{--}3800\text{ cm}^{-1}$ observed in most spectra is
412 characteristic of an OH bond elongation in Si-OH, Al-OH and water. The 1387 cm^{-1}
413 frequency observed where Al was present corresponds to N-O bonds in NO_3^-
414 (Klopprogge, 2001). The two bands at 740 and 830 cm^{-1} correspond to deformation
415 modes of nitrate (Ruiz Madronero and Rodriguez Paéz, 2010).

416 In the HA spectrum, the C=O vibration band from the carboxylic functional
417 group appeared at 1700 cm^{-1} and 1400 cm^{-1} where the $-\text{COOH}$ group is partially
418 converted into its salt form $-\text{COO}^-$. A definite assignment of bands around 1600
419 cm^{-1} is still unsure: according to Stevenson (1971), it could be assigned to
420 aromatic C=C stretch vibration, H-bonded C=O of quinones or H-bonded and
421 conjugated ketones of the type β -diketones ($-\text{CO}-\text{CH}_2-\text{CO}-$). The C-O stretch of
422 alcohol, polysaccharide-like substances and/or aliphatic ether appeared at 1000
423 and 1100 cm^{-1} (Rodriguez, 2011; Stevenson, 1971). It should be noted that C-O
424 stretching and O-H deformation of carboxylic groups could also explain the
425 absorption near 1100 or 1200 cm^{-1} .

426 The two bands of HA at 1600 and 1700 cm^{-1} disappeared almost entirely after
427 Al was added to HA. The same observation can be made for the 1100 cm^{-1} band.

428 These ascertainties seem to indicate that Al was binding to carboxylic groups
429 but also to alcohol and ether groups of HA.

430 We have to be careful with the band at 1650 cm^{-1} present in Na_2SiO_3 and
431 $\text{Al}(\text{NO}_3)_3$ since it could be attributed to deformation vibration of the O-H bond
432 from water (Myronyuk et al., 2016).

433 The HA-Si-Al ternary system IR spectrum was similar to that obtained by Rouff
434 et al. (2012) on the same type of system. Interestingly, the HA-Si-Al and HA-Al
435 spectra exhibited a clear difference: a band at 1007 cm^{-1} was observed in the HA-
436 Al system while another one was observed at 970 cm^{-1} in the HA-Si-Al system,
437 showing that the complexes HA-Si-Al and HA-Al were not the same, which
438 strongly suggests that Si takes part in the ternary complex. In fact, the band at 970
439 cm^{-1} was attributed to the elongation of the Si-O bond and the band at 1007 cm^{-1}
440 could supposedly be associated with Al-O vibration, with oxygen coming from HA.

441 The band from 400 to 800 cm^{-1} comes from the elongations of the Si-O-Al and
442 Si-O-Si stretching bonds. The 630 cm^{-1} of the Al-O band (Nakamoto, 1962)
443 observed for the Na_2SiO_3 sample shifted towards 570 cm^{-1} in the Si-Al and HA-Si-Al
444 systems. This shift could indicate that Al complexed to an aluminosilicate oxygen
445 or an HA oxygen. Additionally, this band is indicative of an imogolite-like structure
446 observed in natural allophane and imogolite, with a peak at 570 cm^{-1} and a
447 shoulder at 690 cm^{-1} and 430 cm^{-1} . This pattern is the signature of the Si and Al
448 association.

449 As a conclusion, the IR spectra indicated Al with Si association on one hand and
450 HA with Al association on the other. The differences between HA-Al and HA-Si-Al
451 at 1000 cm^{-1} and 970 cm^{-1} suggest the presence of an HA-Al-Si ternary complex.

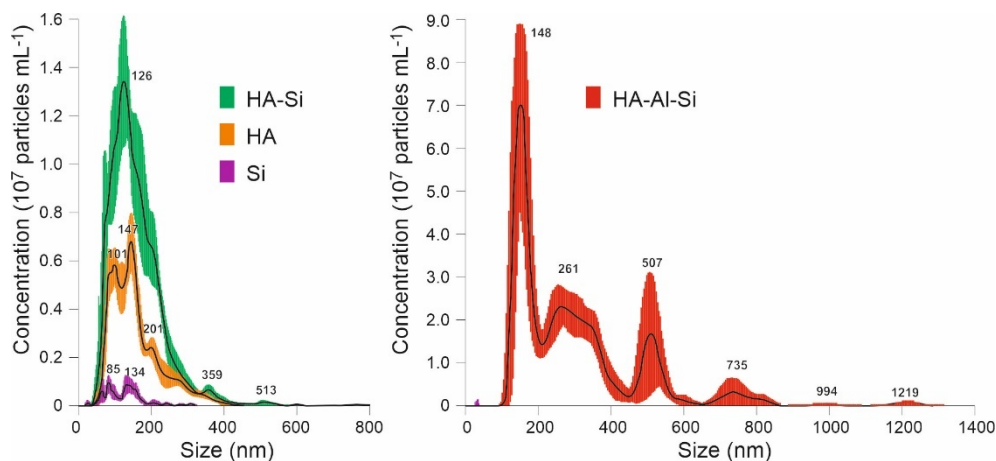
452

453 3.3. Colloid size distribution

454

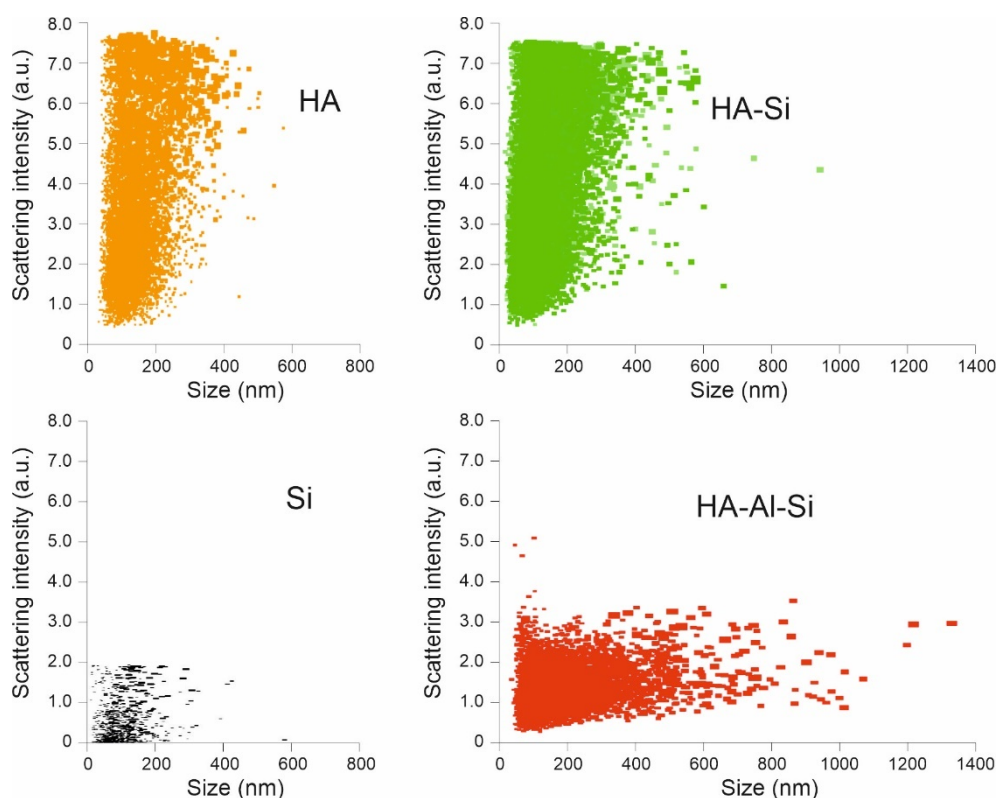
455 The colloid size distribution was determined by Nano Tracking Analysis on
456 solutions with 120 mg L^{-1} HA and $10^{-3}\text{ mol L}^{-1}$ of Si and/or Al. The size distributions
457 are given in Fig. 7, particle scattering intensities are given in Fig. 8 and statistics of
458 the size distribution are given in Table 2.

459



460

461 **Fig. 7.** Particles size distribution obtained by Nano Tracking Analysis. Error bars
 462 indicate ± 1 standard error of the mean.
 463



464 **Fig. 8.** Particle scattering intensity represented as a function of size distribution in
 465 the systems HA, HA-Si, Si and HA-Al-Si.
 466
 467

468 **Table 2**
 469 **Statistics of the size distribution.**

Solution	Concentration of total particles (particles mL ⁻¹)	Mean (nm)	Mode (nm)
Si	$7.9 \cdot 10^7 \pm 0.8 \cdot 10^7$	134 ± 2	116 ± 17
HA	$7.9 \cdot 10^8 \pm 3.2 \cdot 10^8$	158 ± 3	124 ± 12
HA-Si	$1.7 \cdot 10^9 \pm 0.07 \cdot 10^9$	158 ± 3	119 ± 8
HA-Al-Si	$9.1 \cdot 10^9 \pm 0.3 \cdot 10^9$	289 ± 45	213 ± 72

470
 471
 472 The Si solution showed a small concentration of small colloidal particles, which
 473 may be silica precipitates. The HA solution showed particles in the same size range
 474 but with a concentration one order of magnitude higher. Comparison of the size
 475 distribution shows that when Si was added to HA, the size of the particles did not
 476 change significantly but their number increased. There was, therefore, very
 477 probably an interaction between dissolved Si and HA that favored the formation
 478 of small colloids. This assumption is supported by the fact that the small particles
 479 of very low scattering intensity which were observed in the Si solution (Fig. 8)
 480 were no longer observed in the HA-Si solution. This can be explained because
 481 dissolved Si, interacting with HA, was no longer available for silica precipitation.
 482 The HA-Al-Si solution showed particles larger and more numerous than in the
 483 HA-Si solution, which is consistent with the results obtained in fluorescence
 484 spectroscopy. As for the HA-Si solution, the small particles of very low scattering

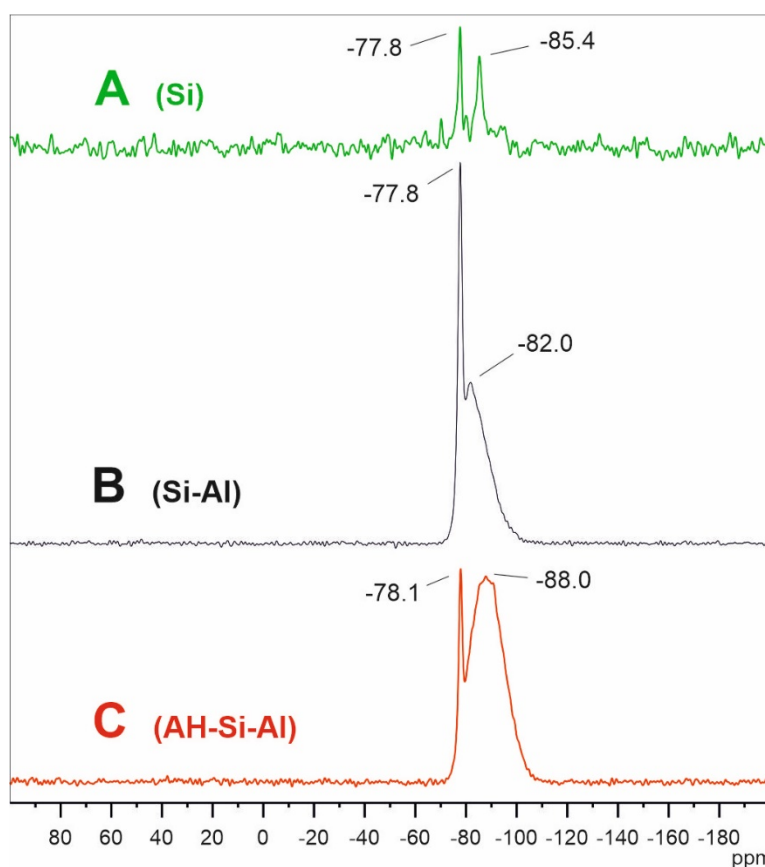
485 intensity characteristic of the Si solution were not observed. The particle
486 scattering intensity in the HA-Al-Si solution was lower than in the HA and the HA-
487 Si solution. This indicates different form and/or structure factors, which remain to
488 be determined.

489 Silica scattered little light compared to HA. It was therefore differentiable
490 when it was isolated. On the other hand, whether or not it was in the presence of
491 Si, the light scattering of HA remained the same, again confirming the absence of
492 interactions or the little interaction between HA and Si. In contrast, signals
493 specific to isolated silica particles no longer existed in the ternary system,
494 suggesting that Si was involved in complexes.

495

496 3.4. Solid-state NMR of ^{29}Si

497



498

499 **Fig. 9.** ^{29}Si Solid State NMR spectra of the particles precipitated in the batch
500 solutions at pH7 (HA 120 mg L^{-1} , Si and Al $10^{-2} \text{ mol L}^{-1}$)

501

502 Fig. 9 A shows the typical ^{29}Si NMR signal of the SiO_3 compound at -77 ppm and
503 a narrow signal at -85 ppm, indicating a partial condensation of a Si-O-Si group
504 (Jones et al., 2005). Fig. 9 B shows, in addition to the signal of free SiO_3 , a broad
505 signal at -82 ppm characteristic of a Si-O-Al bond (2). The addition of HA (Fig. 9 C)
506 causes a shift in the complexation signal of the Si-O-Al group probably due to the
507 interaction with the organic substance. It should be noted that the signal for the
508 Si-O-Al complex has a higher intensity than in the case of aluminium alone. Since
509 the ^{29}Si technique used has been optimized for a semi-quantitative regime, it can
510 be concluded that the presence of HA favored the formation of the Si-O-Al bond
511 compared to the Si-Al system, which supports the assumption given above. The
512 data acquired does not, however, allow the size of the compounds complexed

513 with HA to be determined. They may be complexes of reduced size with one Al
514 and one Si only, or nanocolloids of aluminosilicates.

515 Liu et al. (2011) indirectly evidenced Fe-bridged As-Fe-DOM complexes, which
516 are likely due to the same type of interaction as described here. Dupuis et al.
517 (1982), studying the effect of fulvic acid on Si-Mg colloids, obtained results
518 suggesting the presence of FA-Mg-Si complexes. More broadly, this type of
519 interaction is likely to exist with other metals than Al, such as Fe or Mn, and other
520 metalloids than Si, such as As or Ge.

521

522 *3.5. Implications in the soil-water-plant continuum*

523

524 The presence of HA-Al-Si complexes suggested by our study may appear, at a
525 first glance, to contradict previous studies, such as those of Viers et al. (1997,
526 2000). These authors studied rivers in Cameroon and concluded that Si does not
527 complex with humic substances because (1) there was no correlation between
528 dissolved Si (DSi) and dissolved organic carbon (DOC) when a correlation was
529 observed between DOC and dissolved Al (DAI), and (2) after separation of
530 dissolved and colloidal fractions by ultrafiltration, 100% of Al was found in the
531 colloidal fraction while Si was predominantly in the dissolved fraction. We argue
532 that these observations are not demonstrative, given the high level of DSi (8-18
533 mg L⁻¹) compared to DAI (<0.2 mg L⁻¹) in the studied rivers. If only a minor fraction
534 of Si was complexed with HA and Al, it has no weight in the correlation and is
535 included in the small amount of Si observed in the colloidal fraction.

536 On the other hand, the presence of HA-Al-Si complexes suggested by our study
537 is in agreement with the assumptions put forward to interpret the experiments of
538 Merdy et al. (2021). These authors showed, in laboratory column percolations of
539 podzolic horizons, that certain types of organic matter can promote the transfer
540 of Al and DOM through kaolinitic materials and presume the existence of DOM-Al-
541 Si complexes. There is also a parallel between our results, in which Si in solution
542 binds to organic matter via a bridging Al, and earlier results from Bartoli (1985),
543 which presented compelling evidence that an organic matter, alanine, binds to a
544 silica surface via a bridging Al. This type of complex certainly plays a role in soil
545 processes other than mineral-solution relationships. Li et al. (2020) showed, for
546 example, that such complexes are probably involved in phytoliths cycling, and
547 therefore Si cycling, in soils.

548 The identification of DOM-Al-Si complexes may also have some impact on the
549 knowledge of Al-Si interactions in plant biology. Aluminum is recognized as toxic
550 to plants, but Si has been proven to alleviate its deleterious effect (Hodson and
551 Evans, 2020). The mechanisms are not fully elucidated but one hypothesis is that
552 Al and Si, which have a strong affinity in soil solution, may combined to form
553 insoluble hydroxylaluminosilicates (HAS) (Beardmore et al., 2016). Therefore, the
554 formation of HAS may have the ability to attenuate the root uptake of Al. As
555 Hodson and Evans (2020) mentioned, equilibrium with respect to HAS is assumed,
556 but it may not be the case. Our results suggest another Al sequestration
557 mechanism, that does not require equilibrium with HAS: the formation of DOM-
558 Al-Si complexes. Such complexes can, of course, lead to the formation of HAS if
559 the DOM is destroyed by microorganisms. However, more research is needed to
560 explore this hypothesis.

561

562 **4. Conclusion**

563

564 Until now, interaction between Si and organic matter was considered non-
565 existent or very weak; our fluorescence experiments confirmed that HA-Si
566 interactions exist but are weak. Through several complementary techniques,
567 however, we have shown that stronger HA-Si interactions exist but in the
568 presence of an intermediate ion such as Al³⁺ by the formation of a ternary
569 complex HA-Al-Si with bridging Al and an Al-O-Si bond. Such DOM-Al-Si complexes
570 can play an important role in pedogenesis wherever dissolved organic matter
571 (DOM) is abundant, such as in the surface horizons of most soils or horizons in
572 which podzolic processes occur. The presence of Si significantly promotes the
573 maintenance of both Al and DOM in solution, which is likely to modify the result
574 or the kinetics of the processes of dissolution/precipitation of minerals, therefore
575 of pedogenesis.

576 These results pave the way for further studies, both at the molecular level to
577 better specify the structure of the complexes, and at the macroscopic scale to
578 determine their equilibrium and kinetic constants. In addition, the type of
579 interaction shown here with Al and Si probably also exists with other metals, such
580 as Fe or Mn, and other metalloids, such as As.

581

582 **Acknowledgments**

583 The authors thank Cyril Neytar for his participation in the laboratory work.

584

585 **Funding**

586 This work was funded by the French ANR program BioSiSol ANR-14-CE01-0002.

587

588 **References**

589

590 Bartoli F., 1985. Crystallochemistry and surface properties of biogenic opal. *J. Soil*
591 *Sci.* 36, 335–350. doi:10.1111/j.1365-2389.1985.tb00340.x

592 Beardmore, J., Lopez, X., Mujika, J.I., Exley, C., 2016. What is the mechanism of
593 formation of hydroxyaluminosilicates? *Sci. Rep.* 6, 30913.

594 <https://doi.org/10.1038/srep30913>.

595 Bennett, P.C., 1991. Quartz dissolution in organic-rich aqueous systems. *Geochim.*
596 *Cosmochim. Acta* 55, 1781-1797. [https://doi.org/10.1016/0016-](https://doi.org/10.1016/0016-7037(91)90023-X)
597 [7037\(91\)90023-X](https://doi.org/10.1016/0016-7037(91)90023-X).

598 Bennett, P.C., Siegel, D.I., Hill, B.M., Glaser, P.H., 1991. Fate of silicate minerals in
599 a peat bog. *Geology* 19, 328-331. [https://doi.org/10.1130/0091-](https://doi.org/10.1130/0091-7613(1991)019<0328:FOSMIA>2.3.CO;2)
600 [7613\(1991\)019<0328:FOSMIA>2.3.CO;2](https://doi.org/10.1130/0091-7613(1991)019<0328:FOSMIA>2.3.CO;2)

601 Blaser, P., Heim, A., Luster, J., 1999. Total luminescence spectroscopy of NOM-
602 typing samples and their aluminium complexes. *Environ. Int.* 25, 285–293.
603 [https://doi.org/10.1016/S0160-4120\(98\)00106-8](https://doi.org/10.1016/S0160-4120(98)00106-8).

604 Bro, R., 1997. PARAFAC. Tutorial and applications. *Chemom. Intell. Lab. Sys.* 38,
605 149-171. [https://doi.org/10.1016/S0169-7439\(97\)00032-4](https://doi.org/10.1016/S0169-7439(97)00032-4).

606 Cha, J.N., Shimizu, K., Zhou, Y., Christiansen, S.C., Chmelka, B.F., Stucky, G.D.,
607 Morse, D.E., 1999. Silicatein filaments and subunits from a marine sponge

608 direct the polymerization of silica and silicones in vitro. PNAS, 96, 361–365.
609 <http://www.jstor.org/stable/46816>

610 Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater
611 using excitation-emission matrix spectroscopy. *Mar. Chem.*, 51, 325-346.
612 [https://doi.org/10.1016/0304-4203\(95\)00062-3](https://doi.org/10.1016/0304-4203(95)00062-3).

613 Cook, R.L., Langford, C.H., Yamdagni, R., Preston, C.M., 1996. A modified cross-
614 polarization magic angle spinning ¹³C NMR procedure for the study of humic
615 materials. *Anal. Chem.* 68, 3979– 3986. <https://doi.org/10.1021/ac960403a>.

616 Cornelis, J.T., Delvaux, B., Georg, R.B., Lucas, Y., Ranger, J., Opfergelt, S. 2011.
617 Tracing the origin of dissolved silicon transferred from various soil-plant
618 systems towards rivers: a review. *Biogeosci.* 8, 89-112.
619 <https://doi.org/10.5194/bg-8-89-2011>.

620 Dietzel, M., 2000. Dissolution of silicates and the stability of polysilicic acid.
621 *Geochim. Cosmochim. Acta* 64, 3275-3281. [https://doi.org/10.1016/S0016-](https://doi.org/10.1016/S0016-7037(00)00426-9)
622 [7037\(00\)00426-9](https://doi.org/10.1016/S0016-7037(00)00426-9)

623 Dupuis, Th., Jambu, P., Dupuis, J., 1982. Etude expérimentale de l'action des
624 acides fulviques sur les gels silico-magnésiens et les silicates magnésiens. *Sci.*
625 *Sol* 4, 241-252.

626 Elkins, K.M., Nelson, D.J., 2002. Spectroscopic approaches to the study of the
627 interaction of aluminum with humic substances. *Coordin. Chem. Rev.* 228, 205-
628 225. [https://doi.org/10.1016/S0010-8545\(02\)00040-1](https://doi.org/10.1016/S0010-8545(02)00040-1).

629 Fellman, J.B., D'Amore, D.V., Hood, E., Boone, R.D., 2008. Fluorescence
630 characteristics and biodegradability of dissolved organic matter in forest and
631 wetland soils from coastal temperate watersheds in southeast Alaska.
632 *Biogeochem.* 88, 169-184. <https://doi.org/10.1007/s10533-008-9203-x>.

633 Furrer, G., Ludwig, C., Schindler, P., 1991. On the chemistry of the Keggin Al₁₃
634 polymer: I. Acid-base properties. *J. Coll. Interf. Sci.* 149, 56-67.
635 [https://doi.org/10.1016/0021-9797\(92\)90391-X](https://doi.org/10.1016/0021-9797(92)90391-X).

636 Gauthier, T.D., Shane, E.C., Guerin, W.F., Seitz W.R., Grant C.L., 1986.
637 Fluorescence quenching method for determining equilibrium constants for
638 polycyclic aromatic hydrocarbons binding to dissolved humic materials.
639 *Environ. Sci. Technol.* 20, 1162-1166.

640 Gerbaud, G., Ziarelli, F., Caldarelli, S., 2003. Increasing the robustness of
641 heteronuclear decoupling in magic-angle sample spinning solid-state NMR,
642 *Chem. Phys. Lett.* 377, 1-5. [https://doi.org/10.1016/S0009-2614\(03\)01056-X](https://doi.org/10.1016/S0009-2614(03)01056-X).

643 Greiser, S., Gluth, G.J.G., Sturmb, P., Jäger, C., 2018. ²⁹Si{²⁷Al}, ²⁷Al{²⁹Si} and
644 ²⁷Al{¹H} double-resonance NMR spectroscopy study of cementitious sodium
645 aluminosilicate gels (geopolymers) and gel-zeolite composites. *RSC Advances* 7,
646 4164 – 4171. <https://doi.org/10.1039/C8RA09246J>.

647 Halasz, I., Agarwal, M., Li, R., Miller, N., 2007. Vibrational spectra and dissociation
648 of aqueous Na₂SiO₃ solutions. *Catal. Lett.* 117, 34-42.
649 <https://doi.org/10.1007/s10562-007-9141-6>.

650 Heckman, K., Grandy, A.S., Gao, X., Keiluweit, M., Wickings, K., Carpenter, K.,
651 Chorover, J., Rasmussen, C., 2013. Sorptive fractionation of organic matter and
652 formation of organo-hydroxy-aluminum complexes during litter
653 biodegradation in the presence of gibbsite. *Geoch. Cosmoch. Acta* 121, 667-
654 683. <https://doi.org/10.1016/j.gca.2013.07.043>.

655 Hodson, M.J., Evans, D.E., 2020. Aluminium–silicon interactions in higher plants:
656 an update. *J. Exp. Bot.* 71, 6719–6729. <https://doi.org/10.1093/jxb/eraa024>.

657 Inanaga, S., Okasaka, A., Tanaka, S., 1995. Does silicon exist in association with
658 organic compounds in rice plant? *Soil Sci. Plant Nutr.* 41, 111-117.
659 <https://doi.org/10.1080/00380768.1995.10419564>.

660 Inanaga, S., Okasaka, A., 1995. Calcium and silicon binding compounds in cell wall
661 of rice shoots. *Soil Sci. Plant Nutr.* 41, 103-110.
662 <https://doi.org/10.1080/00380768.1995.10419563>.

663

664 Johnson, J., Anderson, F., Parkhurst, D.L., 2000. Database thermo.com.V8.R6.230,
665 Rev 1.11. Lawrence Livermore National Laboratory, Livermore, California.

666 Jolivet, J.P., Henry, M., Livage, J., 2000. Metal oxide chemistry and synthesis : from
667 solution to solid state. John Willey, Chichester.

668 Jones, L.H.P, Handreck, K.A., 1967. Silica in soils, plants and animals. *Adv. Agron.*
669 19, 107-149. [https://doi.org/10.1016/S0065-2113\(08\)60734-8](https://doi.org/10.1016/S0065-2113(08)60734-8).

670 Jones, A.R., Winter, R., Greaves, G.N., Smith, I.H., 2005. ²³Na, ²⁹Si, and ¹³C MAS
671 NMR investigation of glass-forming reactions between Na₂CO₃ and SiO₂. *J.*
672 *Phys. Chem. B* 109, 23154-23161. <https://doi.org/10.1021/jp053953y>.

673 Kambalina, M., Mazurova, I., Skvortsova, L., Guseva, N., An, V., 2014. Study of
674 aqueous chemical forms of silicon in organic-rich waters. *Procedia Chem.* 10,
675 36-42. <https://doi.org/10.1016/j.proche.2014.10.008>.

676 Kan, S.B.J, Lewis, R.D., Chen, K., Arnold, F.H., 2016. Directed evolution of
677 cytochrome c for carbon-silicon bond formation: bringing silicon to life. *Science*
678 354, 1048-1051. <https://doi.org/10.1126/science.aah6219>.

679 Keller, C., Guntzer, F., Barboni, D., Labreuche, J., Meunier, J. D., 2012. Impact of
680 agriculture on the Si biogeochemical cycle: input from phytolith studies. *C. R.*
681 *Geosci.* 344, 739-746. <https://doi.org/10.1016/j.crte.2012.10.004>.

682 Kennedy, J.A., Powell, H.K.J., 1986. Colorimetric determination of aluminium (III)
683 with chrome azurol S and the reactivity of hydrolysed aluminium species. *Anal.*
684 *Chim. Acta* 184, 329-333. [https://doi.org/10.1016/S0003-2670\(00\)86501-0](https://doi.org/10.1016/S0003-2670(00)86501-0).

685 Klopogge, J.T., Ruan, H., Frost, R.L., 2001. Near-infrared spectroscopic study of
686 basic aluminum sulfate and nitrate. *J. Mat. Sci.* 36, 603-607.
687 <https://doi.org/10.1023/A:1004860118470>.

688 Kolesnikov, M.P., Gins, V.K., 2001. Forms of silicon in medicinal plants. *Appl.*
689 *Biochem. Microbiol.* 37, 524-527. <https://doi.org/10.1023/A:1010262527643>.

690 Larina, L.I., 2021. Chapter One - Organosilicon azoles: Structure, silylotropy and
691 NMR spectroscopy, in: Scriven, E.F.V., Ramsden, C.A. (Eds.), *Advances in*
692 *Heterocyclic Chemistry Volume 133*, Academic Press, London, pp. 1-63.
693 <https://doi.org/10.1016/bs.aihch.2019.08.001>.

694 Li, J., Zheng, L., Wang, S-L., Wu, Z., Wu, W., Niazi, N.K., Shaheen, S.M., Rinklebe, J.,
695 Bolan, N., Ok, Y.S., Wang, H. (2019). Sorption mechanisms of lead on silicon-
696 rich biochar in aqueous solution: Spectroscopic investigation. *Sci. Tot. Env.* 672,
697 572-582.

698 Lindsay, W.L., Walthall, P.M., 2020. The solubility of aluminum in soils, in: Sposito,
699 G. (Ed.), *The environmental chemistry of aluminum*, CRC Press, pp. 333-361.

700 Liu, G., Fernandez, A., Cai, Y., 2011. Complexation of arsenite with humic acid in
701 the presence of ferric iron. *Environ. Sci. Technol.* 45, 3210-3216.
702 <https://doi.org/10.1021/es102931p>.

703 Lucas, Y., Luizao, F.J., Chauvel, A., Rouiller, J., Nahon, D., 1993. The relation
704 between biological activity of the rainforest and mineral composition of the
705 soils. *Science* 260, 521-523. <https://doi.org/10.1126/science.260.5107.521>.

706 Luster, J., Lloyd, T., Sposito, G., Fry, I.V., 1996. Multi-wavelength molecular
707 fluorescence spectrometry for quantitative characterization of copper(II) and

708 aluminum(III) complexation by dissolved organic matter. *Environ. Sci. Technol.*
709 30: 1565-1574. <https://doi.org/10.1021/es950542u>.

710 Ma, J.F., Yamaji, N., 2015. A cooperative system of silicon transport in plants.
711 *Trends Plant Sci.* 20, 435-442. <https://doi.org/10.1016/j.tplants.2015.04.007>

712 Ma, C., Ci, K., Zhu, J., Sun, Z., Liu, Z., Li, X., Zhu, Y., Tang, C., Wang, P., Liu, Z.
713 (2021). Impacts of exogenous mineral silicon on cadmium migration and
714 transformation in the soil-rice system and on soil health. *Sci. Tot. Env.* 759,
715 143501. <https://doi.org/10.1016/j.scitotenv.2020.143501>

716 Manoharan, V., Ravindran, A., Anjali, C.H., 2014. Mechanistic insights into
717 interaction of humic acid with silver nanoparticles. *Cell Biochem. Biophys.* 68,
718 127–131. <https://doi.org/10.1007/s12013-013-9699-0>.

719 Masion, A., Vilg -Ritter, A., Rose, J., Stone, W.E.E., Teppen, B.J., Rybacki, D.,
720 Bottero, J.Y., 2000. Coagulation-flocculation of natural organic matter with Al
721 salts: speciation and structure of the aggregates. *Environ. Sci. Technol.* 34,
722 3242-3246. <https://doi.org/10.1021/es9911418>

723 Matychenkov, I.V., Khomyakov, D.M., Pakhnenko, E.P., Bocharnikova, E.A.,
724 Matychenkof, V.V., 2016. Mobile Si-rich compounds in the soil–plant system
725 and methods for their determination. *Moscow Univ. Soil Sci. Bull.* 71, 120–128.
726 <https://doi.org/10.3103/S0147687416030054>

727 Merdy, P., Neytard, C., Meunier, J.D., Lucas, Y., 2020. PDMPO: a specific silicon or
728 silica, pH sensitive fluorescent probe? *RSC Advances* 10, 31003-31011.
729 <https://doi.org/10.1039/D0RA05108J>].

730 Merdy, P., Lucas, Y., Coulomb, B., Melfi, A.J., Montes, C.R., 2021. Soil organic
731 carbon mobility in equatorial podzols: soil column experiments. *Soil* 7, 585-
732 594. <https://doi.org/10.5194/soil-7-585-2021>

733 Mitani, N., Ma, J.F., Iwashita, T., 2005. Identification of the silicon form in xylem
734 sap of rice (*Oryza sativa* L.). *Plant Cell Physiol.* 46, 279–283.
735 <https://doi.org/10.1093/pcp/pci018>.

736 Myronyuk, I.F., Mandzyuk, V.I., Sachko, V.M., Gun'ko, V.M., 2016. Structural and
737 morphological features of disperse alumina synthesized using aluminum
738 nitrate nonahydrate. *Nanoscale Res. Lett.* 11,153.
739 <https://doi.org/10.1186/s11671-016-1366-0>.

740 Nakamoto, K., 1962. Infrared spectra of inorganic and coordination compounds,
741 John Wiley & Inc., New York - London.

742 Nierop, K.G.J.J., Jansen, B., Verstraten, J.M., 2002. Dissolved organic matter,
743 aluminium and iron interactions: precipitation induced by metal/carbon ratio,
744 pH and competition. *Sci. Tot. Env.* 300, 201-211.
745 [https://doi.org/10.1016/S0048-9697\(02\)00254-1](https://doi.org/10.1016/S0048-9697(02)00254-1).

746 Ohman, L.O., Nordin, A., Sedeh, F.I., Sjöberg, S., 1991. Equilibrium and structural
747 studies of silicon(IV) and aluminium(III) in aqueous solution. 28. Formation of
748 soluble silicic acid-ligand complexes as studied by potentiometric and solubility
749 measurements. *Acta Chem. Scand.* 45, 335-341.

750 Ohno, T., Bro, R., 2006. Dissolved organic matter characterization using multiway
751 spectral decomposition of fluorescence landscapes. *Soil Sci. Soc. Am. J.* 70,
752 2028-2037. <https://doi.org/10.2136/sssaj2006.0005>.

753 Otzen, D., 2012. The role of proteins in biosilicification. *Scientifica*, 2012, ID
754 867562. <https://doi.org/10.6064/2012/867562>

755 Parlanti, E., Morin, B., Vacher, L., 2002. Combined 3D-spectrofluorimetry, high
756 performance liquid chromatography and capillary electrophoresis for the
757 characterization of dissolved organic matter in natural waters. *Org. Geochem.*
758 33, 221–236.

759 Peersen, O.B., Wu, X., Kustanovich, I., Smith, S.O., 1993. Variable-amplitude cross-
760 polarization MAS NMR. *J. Magn. Reson.* 104, 334–339.
761 <https://doi.org/10.1006/jmra.1993.1231>.

762 Perry, C.C., 2015. An overview of silica in biology: its chemistry and recent
763 technological advances, in: Müller, W.E.G., Grachev, M.A. (Eds.), *Biosilica in*
764 *Evolution, Morphogenesis, and Nanobiotechnology*, *Progress in Molecular and*
765 *Subcellular Biology, Marine Molecular Biotechnology* 47, 295-313. DOI:
766 10.1007/978-3-540-88552-8,

767 Pokrovski, G.S., Schott, J., 1998. Experimental study of the complexation of silicon
768 and germanium with aqueous organic species: implications for germanium and
769 silicon transport and Ge/Si ratio in natural waters. *Geochim. Cosmochim Acta*
770 62, 3413-3428. [https://doi.org/10.1016/S0016-7037\(98\)00249-X](https://doi.org/10.1016/S0016-7037(98)00249-X).

771 Poulson, S.R., Drever, J.I., Stillings, L.L., 1997. Aqueous Si-oxalate complexing,
772 oxalate adsorption onto quartz, and the effect of oxalate upon quartz
773 dissolution rates. *Chem. Geol.* 140, 1-7. [https://doi.org/10.1016/S0009-](https://doi.org/10.1016/S0009-2541(96)00177-5)
774 [2541\(96\)00177-5](https://doi.org/10.1016/S0009-2541(96)00177-5)

775 Provenzan, M.R., D'Orazio, V., Jerzykiewicz, M., Senesi, N., 2004. Fluorescence
776 behaviour of Zn and Ni complexes of humic acids from different sources .
777 *Chemosphere* 55, 885-892.
778 <https://doi.org/10.1016/j.chemosphere.2003.11.040>.

779 Rouff, A.A., Phillips, B.L., Cochiara, S.G., Nagy, K.L., 2012. The Effect of dissolved
780 humic acids on aluminosilicate formation and associated carbon sequestration.
781 *Appl. Env. Soil Sci.* 2012, ID 430354. <https://doi.org/10.1155/2012/430354>.

782 Ruiz Madroñero, C.V., Rodríguez Paéz, J.E., 2010. Sodium aluminates obtained
783 from the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ -NaOH system using the controlled precipitation
784 method. *Ingeniería e Investigación* 30, 16-24.

785 Ryan, D.K., Weber, J.H., 1982. Fluorescence quenching titration for determination
786 of complexing capacities and stability constants of fulvic acid. *Anal. Chem.* 54,
787 986-990.

788 Sadrnourmohamadi, M., Gorczyca, B., 2015. Removal of dissolved organic carbon
789 (DOC) from hgh DOC and hardness water by chemical coagulation: relative
790 importance of monomeric, polymeric, and colloidal aluminum species.
791 *Separation Sci. Technol.* 50, 2075-2085.
792 <https://doi.org/10.1080/01496395.2015.1014494>.

793 Schaefer, J., Stejskal, E.O.R., 1976. Carbon-13 nuclear magnetic resonance of
794 polymers spinning at magic angle. *J. Am. Chem. Soc.* 98, 1031– 1032.

795 Schaller, J., Puppe, D., Kaczorek, D., Ellerbrock, R., Sommer, M., 2021. Silicon
796 cycling in soils revisited. *Plants* 10, 295.
797 <https://doi.org/10.3390/plants10020295>.

798 Scheinost, A.C., 2005. Metal oxides, in: Hillel D. (Ed.), *Encyclopedia of soils in the*
799 *environment*. Elsevier, Oxford, pp. 428-438. [https://doi.org/10.1016/B0-12-](https://doi.org/10.1016/B0-12-348530-4/00194-6)
800 [348530-4/00194-6](https://doi.org/10.1016/B0-12-348530-4/00194-6).

801 Sharpless, C.M., McGown, L.B., 1999. Effects of aluminium-induced aggregation
802 on the fluorescence of humic substances. *Env. Sci. Technol.* 33, 3264–3270.
803 <https://doi.org/10.1021/es981332v>.

804 Shimizu, K., Morse, D.E., 2018. Silicatein: a unique silica-synthesizing catalytic triad
805 hydrolase from marine sponge skeletons and its multiple applications.
806 *Methods Enzymol.* 605, 429-455. <https://doi.org/10.1016/bs.mie.2018.02.025>

807 Shotyk, W., Sposito, G., 1988. Fluorescence quenching and aluminum
808 complexation by a chestnut leaf litter extract. *Soil Sci. Soc. Am, J.* 52, 1293–
809 1297. <https://doi.org/10.2136/sssaj1988.03615995005200050014x>.

810 Sommer, M., Kaczorek, D., Kuzyakov, Y., Breuer, J., 2006. Silicon pools and fluxes
811 in soils and landscapes – a review. *J. Plant Nutr. Soil Sci.* 169, 310–329.
812 <https://doi.org/10.1002/jpln.200521981>

813 Stevenson, F.J., Goh, K.M., 1971. Infrared spectra of humic acids and related
814 substances. *Geochim. Cosmochim. Acta* 85, 471-485.
815 [https://doi.org/10.1016/0016-7037\(71\)90044-5](https://doi.org/10.1016/0016-7037(71)90044-5).

816 Viers, J., Dupré, B., Polvé, M., Schott, J., Dandurand, J. L., Braun, J.J., 1997.
817 Chemical weathering in the drainage basin of a tropical watershed (Nsimi-
818 Zoetele site, Cameroon): comparison between organic poor and organic rich
819 waters. *Chem. Geol.* 140, 181-206. [https://doi.org/10.1016/S0009-
820 2541\(97\)00048-X](https://doi.org/10.1016/S0009-2541(97)00048-X).

821 Viers, J., Dupré, B., Braun, J.-J., Deberdt, S., Angeletti, B., Ngoupayou, J.N.,
822 Michard, A., 2000. Major and trace element abundances, and strontium
823 isotopes in the Nyong basin rivers (Cameroon): constraints on chemical
824 weathering processes and elements transport mechanisms in humid tropical
825 environments. *Chem. Geol.* 169, 211-241. [https://doi.org/10.1016/S0009-
826 2541\(00\)00298-9](https://doi.org/10.1016/S0009-2541(00)00298-9).

827 Wonisch, H., Gérard, F., Dietzel, M., Jaffrain, J., Nestroy, O., Boudot, J.-P., 2008.
828 Occurrence of polymerized silicic acid and aluminum species in two forest soil
829 solutions with different acidity. *Geoderma* 144, 435–445.
830 <https://doi.org/10.1016/j.geoderma.2007.11.022>.

831 Yahya, Z., Abdullah, M.M.A.B., Hussin, K., Ismail, K.N., Razak, R.A., Sandu, A.V.,
832 2015. Effect of solids-to-liquids, Na₂SiO₃-to-NaOH and curing temperature on
833 the palm oil boiler ash (Si+Ca) geopolymerisation system. *Materials* 8, 2227-
834 2242. <https://doi.org/10.3390/ma8052227>.

835 Yan, M., Benedetti, M.F., Korshin, G.V., 2013. Study of iron and aluminum binding
836 to Suwannee River fulvic acid using absorbance and fluorescence
837 spectroscopy: Comparison of data interpretation based on NICA-Donnan and
838 Stockholm humic models. *Water Res.* 47, 5439-5446.
839 <https://doi.org/10.1016/j.watres.2013.06.022>.

840 Zhao, K., Yang, Y., Peng, H., Zhang, L., Zhou, Y., Zhang, J., Du, C., Liu, J., Lin, X.,
841 Wang, N., Huang, H., Luo, L. (2022). Silicon fertilizers, humic acid and their
842 impact on physicochemical properties, availability and distribution of heavy
843 metals in soil and soil aggregates. *Sci. Tot. Env.* 153483.
844 <https://doi.org/10.1016/j.scitotenv.2022.153483>.

845