

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

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Evidence of humic acid-aluminium-silicon complexes 1 2

under controlled conditions

- 3
- Patricia Merdy^{a*}, Jean-Dominique Meunier^b, Fabio Ziarelli^c, Yves Lucas^a 4
- 5
- 6 ^a Université de Toulon, Aix Marseille Univ, CNRS, IM2NP, 83041 Toulon CEDEX 9, 7 France
- ^b CEREGE, CNRS, Aix-Marseille Univ, IRD, INRAE, 13545 Aix-en-Provence, France 8
- ^c Aix Marseille Univ, CNRS, Centrale Marseille, FSCM, FR1739, 13013, Marseille, 9 France
- 10 11
- 12 *Corresponding author (merdy@univ-tln.fr)
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HIGHLIGHTS 14

- 15
- First evidence of OM-metal-Si complex impacting environmental 16 • 17 dynamics
- Si alone actually interacts with humic acid (HA), but weakly 18 •
- With both Si and Al, HA-Al-Si complex with bridging Al and Al-O-Si bond 19 •
- 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)

24 **GRAPHICAL ABSTRACT**

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23



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 Al³⁺ 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, ²⁹Si 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 AI, however, a ternary complex HA-AI-Si forms, likely with AI 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 towards plants and probably also exists with other metals, such as Fe or Mn, and 46 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 authors pointed out that carbon-silicon bond formation is unknown in nature. 65 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 (H₄SiO₄). 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 Si(OH)₄ by 100 K₂C₂O₄. Potentiometric titration experiments were performed by Ohman et al.

101 (1991) in homogeneous solutions of Si(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, and dissolved Si, under different conditions of concentration and pH. We have 113 114 considered the presence of Al³⁺ 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 ²⁹Si 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

An HA solution at 120 mg L⁻¹ was prepared from a commercial powder (Humic 122 Acid, Alfa Aesar, 41747). Si and Al stock solutions were prepared from Na2SiO3 123 124 (Carlo Erba Reagenti, 373908) and Al(NO₃)₃.9H₂O (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 mol L⁻¹ according to concentrations given in Table 1. This concentration range includes the 128 129 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 10 ⁻²	8 10 ⁻³	6 10 ⁻³	3 10 ⁻³	1 10 ⁻³	8 10 ⁻⁴	6 10 ⁻⁴	3 10 ⁻⁴	1 10 ⁻⁴	8 10 ⁻⁵	6 10 ⁻⁵	3 10 ⁻⁵	1 10 ⁻⁵	1 10 ⁻⁶	0

140 141

142 *2.2. Fluorescence spectroscopy*

143

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

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-

Al and HA-Si-Al), whose Si and Al concentrations varied from 10⁻² to 10⁻⁶ M, which
were adjusted to pH 4, 7 and 9 using HCl solutions (0.1 M, HCl Trace Metal Grade
37% v/v from Fisher Scientific) and/or NaOH (0.1M, Crystals from Sigma-Aldrich).
The solutions were diluted by a factor of 10 before fluorescence measurement.
Preliminary experiments were carried out to avoid inner screen effect, using a
sample dilution followed by checking the proportional signal intensity response
(data not shown).

166The measurement was performed using a Hitachi model F-4500167spectrophotometer, equipped with a 450 W xenon lamp. Sample solutions were168placed in 1 cm x 1 cm quartz cells. The excitation window was set at 5 nm and the169emission window at 10 nm. The excitation wavelengths ranged from 200 nm to170500 nm, and emission wavelengths from 250 nm to 600 nm, with a 5 nm step at a171scan 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

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

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

199 was quantified using a Thermo Flash 2000 Elemental Analyzer in NC mode200 (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 enough solids on the filter could be analyzed in solid-state infrared. 211

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 (2.10⁻⁴ 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, Fisher Scientific) (Kennedy and Powell, 1986). 222

223

224 2.6. Colloid size distribution

225

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

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233 2.7. Solid-state NMR of ²⁹Si

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

All solid-state NMR spectra were obtained on a Bruker Avance-400 MHz NMR 239 spectrometer operating at ²⁹Si resonance frequency of 79.5 MHz. About 20 mg of 240 241 samples were placed in zirconium dioxide rotors with a 4-mm outer diameter and spun at a Magic Angle Spinning rate of 10 kHz in a commercial Bruker Double 242 243 Channel probe. ²⁹Si CPMAS experiments were performed with the Cross 244 Polarization (CP) technique (Schaefer and Stejskal, 1976) using a ramped 1H-pulse 245 starting at 100% power and decreasing to 50% during the contact time (5 ms) in 246 order to circumvent Hartmann-Hahn mismatches (Peersen et al., 1993; Cook et 247 al., 1996). To improve the resolution, a dipolar decoupling GT8 pulse sequence 248 (Gerbaud et al., 2003) was applied during the acquisition time.

To obtain a good signal-to-noise ratio, between 10³ and 10⁴ scans were

accumulated using a delay of 2.5 s. The ²⁹Si 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





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 $(\lambda_{ex} = 305$ nm and $\lambda_{em} = 495$ nm) and the other (peak C) to humic-like molecules at $(\lambda_{ex} = 460$ nm and $_{\lambda em} = 520$ nm) (Coble, 1996; Fellman, 2008; Ohno et Bro, 2006). 264 265 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 groups (Gauthier et al., 1986; Elkins and Donald, 2002; Provenzano et al., 2004). 271 272 They can, in some cases, enhance the fluorescence intensity (Merdy et al., 2020; 273 Manoharan et al., 2014).



275

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

280

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

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

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









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).

326 327 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 328 329 Al input greater than 10⁻⁴ and 10⁻⁵ mol L⁻¹ at pH 7 and 9, respectively (Fig. 2). Such 330 precipitation was expected given the flocculating power on DOC by Al species in 331 solution at sufficiently high concentration, as demonstrated by several studies 332 (Nierop et al., 2002; Masion et al., 2000; Sadrnourmohamadi and Gorczyca, 2015), 333 or by DOC adsorption on newly precipitated Al hydroxides (Heckman et al., 2013). 334 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 3.10⁻⁶ 335 336 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 337 338 solubility was intermediate between gibbsite and amorphous Al(OH)₃ (Fig. 5), such 339 as Al₁₃ gel (Jolivet, 2000).

After correction of the precipitated DOC, fluorescence quenching was 340 341 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 342 343 followed by a fluorescence enhancement at greater Al input. The fluorescence 344 enhancement effect on natural organic matter complexed with Al had already 345 been observed (Blaser et al., 1999; Sharpless and McGown, 1999; Elkins et al., 346 2002). Elkins et al. (2002) considered Al to be unique compared to other metal 347 ions such as Cu, Co, Mn, Pb, which have a propensity to quench the fluorescence; 348 Al would be different due to its high charge density. Other studies showed a 349 quenching phenomenon of natural organic matter upon Al ion addition, such as 350 Shotyk and Sposito (1988) on leaf litter aqueous extract at λ_{ex} = 440 nm and λ_{em} = 525 nm at pH = 4.0, 4.5, and 5.0. More recent studies tried to identify the 351 352 processes responsible for quenching or enhancement of the fluorescence signal, 353 such as that of Yan et al. (2013). If the quenching of fulvic acid signals was 354 dominating at higher emission wavelengths and increasing total Fe(III) 355 concentrations, the pattern observed with Al(III) was much more complex with 356 both quenching and enhancement phenomena observed in different areas of the 357 spectra. Basically, at low concentrations, the authors mentioned that the 358 interactions took place with phenolic groups of the fulvic acid, and then weakly 359 binding carboxylic groups. After saturation of the complexing sites, metallic ions keep interacting with fulvic acids through non-specific Donnan gel electrostatic 360

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 10⁻³ 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 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 10⁻⁴ 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-AI complexes, which delayed the precipitation of AI 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 added metal less than 8 10⁻³ mol L⁻¹, at pH 7 as well as at pH 9. The presence of Si 388 389 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 process of DOC flocculation by Al³⁺ species is at least slowed down by dissolved 392 393 silicon.

At this stage of the study, our hypothesis to explain our data is the formation of a ternary complex between HA, AI and Si. At pH of around 5.5 to 7.5, Al³⁺ in its octahedral first hydration shell is more likely than Si⁴⁺ in its tetrahedral first hydration shell to form an inner sphere complex with a reactive nucleophilic site of the NOM (Jolivet et al., 2000). Indeed, Al³⁺ has a much higher affinity than Si⁴⁺ with HA. It is therefore very likely that AI play facts as a bridge between NOM and a Si species, with an Al-O-Si bond.

401

402 *3.2. IR spectroscopy*



404 Wavenumber (cm⁻¹)
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 Na₂SiO₃ and of the different solids precipitated from batches 409 are given in Fig. 6. The IR spectrum of Na₂SiO₃ was similar to that obtained by 410 Yahya et al. (2015). The Si-O vibration frequency can be seen at 1007 cm⁻¹ (Halasz et al., 2007). The broad band around 3000-3800 cm⁻¹ observed in most spectra is 411 412 characteristic of an OH bond elongation in Si-OH, Al-OH and water. The 1387 cm⁻¹ 413 frequency observed where AI was present corresponds to N-O bonds in NO₃⁻ 414 (Kloprogge, 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 group appeared at 1700 cm⁻¹ and 1400 cm⁻¹ where the –COOH group is partially 417 418 converted into its salt form –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 (-CO-CH₂-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 stretching and O-H deformation of carboxylic groups could also explain the 424 425 absorption near 1100 or 1200 cm⁻¹.

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

These ascertainments seem to indicate that AI was binding to carboxylic groupsbut 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 Al(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 et al. (2012) on the same type of system. Interestingly, the HA-Si-Al and HA-Al 434 435 spectra exhibited a clear difference: a band at 1007 cm⁻¹ was observed in the HA-Al system while another one was observed at 970 cm⁻¹ in the HA-Si-Al system, 436 437 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.

The band from 400 to 800 cm⁻¹ comes from the elongations of the Si-O-Al and 441 442 Si-O-Si stretching bonds. The 630 cm⁻¹ of the Al-O band (Nakamato, 1962) 443 observed for the Na₂SiO₃ 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.

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

452

453 *3.3. Colloid size distribution*

454

The colloid size distribution was determined by Nano Tracking Analysis on solutions with 120 mg L⁻¹ HA and 10⁻³ mol L⁻¹ of Si and/or Al. The size distributions are given in Fig. 7, particle scattering intensities are given in Fig. 8 and statistics of the size distribution are given in Table 2.





461 **Fig. 7.** Particles size distribution obtained by Nano Tracking Analysis. Error bars

462 indicate ±1 standard error of the mean.





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

467

468 **Table 2**

469 Statistics of the size distribution.

Solution	Concentration of total particles	Mean	Mode
	(particles mL ⁻¹)	(nm)	(nm)
Si	$7.9 \ 10^7 \pm 0.8 \ 10^7$	134 ± 2	116 ± 17
HA	$7.9 \ 10^8 \pm 3.2 \ 10^8$	158 ± 3	124 ± 12
HA-Si	$1.7 \ 10^9 \pm 0.07 \ 10^9$	158 ± 3	119 ± 8
HA-Al-Si	$9.1\ 10^9\pm0.3\ 10^9$	289 ± 45	213 ± 72

470

471

472 The Si solution showed a small concentration of small colloidal particles, which may be silica precipitates. The HA solution showed particles in the same size range 473 474 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 change significantly but their number increased. There was, therefore, very 476 477 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-AI-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-AI-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 Si, the light scattering of HA remained the same, again confirming the absence of 491 492 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 ²⁹Si

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498

Fig. 9. ²⁹Si Solid State NMR spectra of the particles precipitated in the batch
solutions at pH7 (HA 120 mg L⁻¹, Si and Al 10⁻² mol L⁻¹)

Fig. 9 A shows the typical ²⁹Si NMR signal of the SiO₃ compound at -77 ppm and 502 503 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 SiO₃, 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 ²⁹Si 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

with HA to be determined. They may be complexes of reduced size with one Aland one Si only, or nanocolloids of aluminosilicates.

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

521

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

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524 The presence of HA-AI-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 AI (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-AI-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 hydroxyaluminosilicates (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.

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-AI-Si with bridging AI and an AI-O-Si bond. Such DOM-AI-Si complexes can play an important role in pedogenesis wherever dissolved organic matter 570 571 (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 AI 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.

576These results pave the way for further studies, both at the molecular level to577better specify the structure of the complexes, and at the macroscopic scale to578determine 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
- as Fe or Mn, and other metalloids, such as As.
- 581

584

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