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Effect of natural organic matter on thallium and silver speciation

Loïc A. Martin^{1,2}, Caroline Simonucci², Sétareh Rad³, and Marc F. Benedetti^{1*}

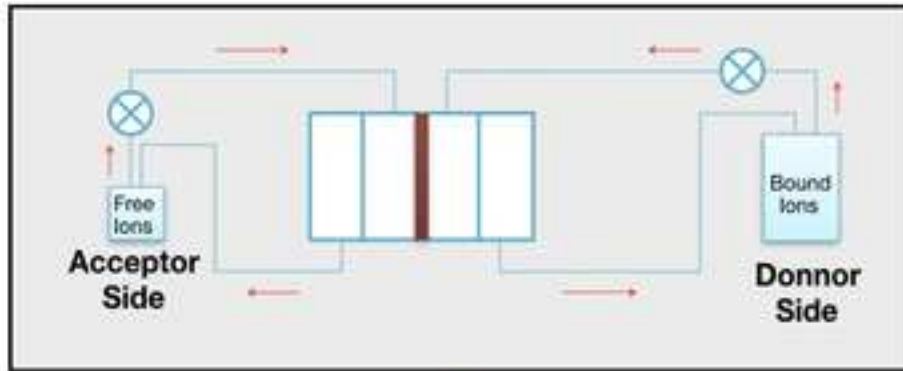
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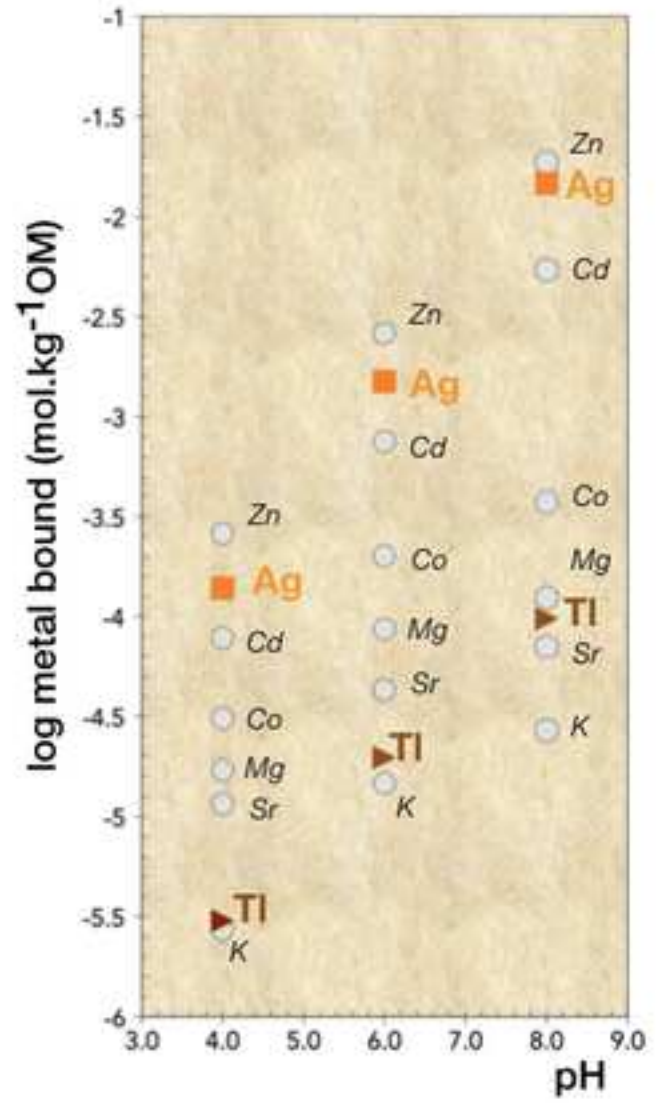
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Donnan membrane detection



Silver and **Thallium** ions compete with divalent cations between pH 7 and 8.



23 **Effect of natural organic matter on thallium and silver speciation**

24

25 Loïc A. Martin^{1,2,3}, Caroline Simonucci², Sétareh Rad⁴, and Marc F. Benedetti^{1*}

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34

35 **Abstract:** Natural organic matter (NOM) is known to play an important role in the transport and
36 binding of trace metal elements in aquatic and soil systems. Thallium is a pollutant for which the
37 extent of the role played by NOM is poorly known. Consequently, this study investigates thallium(I)
38 and its complexation to a purified humic substance as proxy for NOM. Experiments were performed
39 with the Donnan Membrane Technique to separate, [for the first time](#), the free Tl^+ ion from its
40 complexed form in the bulk solution. Various pH and concentrations were investigated at constant
41 ionic strength and constant NOM proxy concentrations in solution. Experimental results were
42 described with NICA-Donnan model. Thallium complexation was compared to silver complexation
43 using literature data and using the same NICA-Donnan formalism. [Parameters for these two cations](#)
44 [\(\$Tl^+\$ and \$Ag^+\$ \) are reported in this article, for the first time](#). Results display low thallium complexation
45 to the NOM proxy while silver competes with divalent cations for the NOM binding sites. Calculated
46 speciation for dissolved thallium highlights the dominance of free thallium (Tl^+) in solution whereas
47 Tl -NOM complexes contribute roughly 15 % to total $Tl(I)$ species in river and lake type waters.
48 Similar results are obtained for soil solutions, Tl -bound to NOM < 30 % of total, from UK soils with
49 different land use and geochemistry.

50 **Keywords:**

51 Thallium

52 Organic matter

53 Speciation

54 [NICA-Donnan model](#)

55 Soil

56 Water

57

58 -----

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60

61 **Introduction**

62 Thallium (Tl) is a trace element and a contaminant, mainly byproducts of extractives industries
63 and comes from ferrous and non-ferrous metal and coal mining (Cheam, 2001; Lis et al., 2003;
64 Peter and Viraraghavan, 2005; Casiot, et al., 2011; Campanella et al., 2017). Thallium occurs
65 in two oxidation states, Tl(I) and Tl(III) (Jacobson et al., 2005a; Peter and Viraraghavan, 2005).
66 Tl(I) exhibits either lithophile or chalcophile behavior that is determined by the geological
67 context (Prytulak et al., 2017). In the critical zone, Tl(I) is relatively soluble, mobile and
68 bioavailable (Jacobson et al., 2005a; Coup and Swedlund, 2015; Voegelin et al., 2015). Studies
69 demonstrated that Tl(I) is the most dominant and thermodynamically stable form in aquatic
70 systems and soils (Vink, 1993; Xiong, 2009; Casiot, et al., 2011). However, in some
71 environments Tl(III) is also found in variable amounts (Lin and Nriagu, 1999; Peacock and
72 Moon, 2012; Voegelin et al., 2015; Campanella et al., 2017). Tl(III) should be found mostly in
73 highly oxidative environments (Vink, 1993; Watanabe and Takahashi, 2015) but photochemical
74 reactions in surface waters (Karlsson et al., 2006) or microbiological processes (Twining et al.,
75 2003) could oxidize Tl(I) into Tl(III) under moderately oxidizing conditions. Stabilization by
76 humic substances was also witnessed at low pH and high redox potential values (i.e. $\text{pH} < 4$ $\text{Eh} >$
77 0.82 V in Watanabe and Takahashi, (2015)). Recent studies also highlighted the possible role
78 of Fe(III) or As(V) in the formation of Tl(III) compounds in acid mining drainage (Karlsson et
79 al., 2006; Campanella et al., 2018).

80 Processes driving Tl chemical speciation and mobility are well documented but some questions
81 remain open (Twining et al., 2003; Karlsson et al., 2006; Coup and Swedlund, 2015; Voegelin
82 et al., 2015; Casiot et al., 2017; Campanella et al., 2017; Campanella et al., 2018). Its interaction
83 with natural organic matter (NOM) is one of them (Jacobson et al., 2005a; Liu et al., 2011). It
84 is known that NOM plays an important part in the fate of metal ions and can control ion mobility,
85 concentration in soils and natural waters (Benedetti et al., 1995; Benedetti et al., 1996a). NOM
86 is a complex mixture of compounds but the most studied and the most reactive fractions are the
87 humic substances (HS) consisting of humic (HA) and fulvic (FA) acids (Benedetti et al., 1996a;
88 Koopal et al., 2005). Kaplan and Mattigod (1998) defined two stability constants for Tl(I)
89 binding onto FA with $\log K_{\text{Tl-Ful1}} = 4.83$ and $\log K_{\text{Tl-Ful2}} = 3.32$ (no units specified) to predict the

90 impact of NOM on thallium speciation. According to these calculations up to 67% of Tl(I) is
91 bound to organic compounds in bog water despite its very low pH that should not favor Tl(I)
92 binding to NOM (Kaplan and Mattigod, 1998). Thus, NOM could play a non-negligible part in
93 Tl(I) speciation. However, Jacobson et al., (2005a) reported poor Tl(I) complexation within a
94 peat soil. Liu et al. (2011) also studied Tl(I) binding using two purified humic acids and their
95 results also suggested weak Tl(I) interactions with these NOM proxies. However, these studies
96 used very high Tl(I) concentrations, which are mostly relevant for highly polluted sites (i.e.
97 issued from mining activities (Campanella et al., 2017; Casiot et al., 2017)). Investigations made
98 at lower concentration of Tl(I) will allow a better understanding of NOM role on Tl(I) speciation
99 in the critical zone. It is also assumed that Tl(I) chalcophile behavior accounts for Tl(I)
100 complexation to NOM through interactions with the S-rich functional groups of the NOM, such
101 as thiols (Jacobson et al., 2005a, 2005b). However, Tl(I) affinity to sulfur-containing organic
102 compounds, such as cysteine for instance, is still under investigation while no data were found
103 regarding thiol (Garcia Bugarin et al., 1989; Gharib and Shamel, 2009; Rodriguez Mercado et
104 al., 2013)

105 The role of S-rich compounds, such as thiol groups, is often raised when metal complexation
106 to humic substances (HS) is studied (Skylberg et al., 2006; Aiken et al., 2011) and there are
107 evidences of S-binding for Hg(II) or As(III) (Haitzer et al., 2002; Skylberg et al., 2006; Aiken
108 et al., 2011; Catrouillet et al., 2015). *These divalent or trivalent cations cannot really be*
109 *compared to Tl(I). Whereas silver, as Ag(I), can (Jacobson et al., 2005a , 2005b), both Ag(I)*
110 *and Tl(I) are soft, non-essential monovalent cations, (Smith et al., 2002; Pearson, 1968) with*
111 *both chalcophilic and lithophilic behaviors (Pearson, 1968; Jacobson et al., 2005a, 2005b;*
112 *Aiken et al., 2011). Moreover, Ag(I) has high affinity for thiolate (Smith et al., 2002; Kleja et*
113 *al., 2016) and Ag-S binding in NOM compounds was already mentioned in a previous study*
114 *(Kleja et al., 2016). Another remaining question is the abundance of S-rich functional group,*
115 *especially thiol group, and how to quantify it in NOM (Valravamurthy et al., 1997; Aiken et al.,*
116 *2011; Manceau and Nagy, 2012; Rao et al., 2014).*

117 In this study, the main objective is to evaluate the importance and strength of Tl complexation
118 by a NOM proxy. In order to do that, complexation of Tl(I) with a purified humic acid (HA) is
119 investigated at multiple pH and concentrations. Experimentations are conducted with Donnan
120 Membrane Technique (Temminghoff et al., 2000) to determine the amount of ion bound to the
121 NOM proxy. These observations are used to calibrate the NICADonnan model to predict Tl(I)
122 behavior during complexation. In addition, Tl(I) results are compared to Ag(I) literature data
123 (Sikora and Stevenson, 1988) and the potential role of S-rich functional groups is discussed.

124 Ag(I) specific parameters for NICA-Donnan model are not yet available, thus data of Ag(I)
125 sorption to various HA is described with NICA-Donnan model for the first time in this study
126 (Sikora and Stevenson, 1988; Chen et al., 2012; Kleja et al. 2016). Finally, the role of NOM
127 Tl(I) cycle is also investigated by revisiting existing data from natural waters (Kaplan and
128 Mattigod, 1998) and simulating Tl(I) speciation in soil solutions under different geochemical
129 contexts.

130

131 **1 Materials and methods**

132 **1.1 Experimental approach**

133 Donnan Membrane Technique (DMT) was first described by Temminghoff et al. (2000).
134 Additional developments were performed to fully constrain the kinetics aspect of the technique
135 (Weng et al., 2005) and to adapt the geometry of the cells (Kalis et al., 2006; Kalis et al., 2007).
136 In this study, the DMT device, used for the experiments, is similar to the one used in Kalis *et*
137 *al.* (2006, 2007) and its design shown in Appendix A (Fig. S1). Prior to experiments with humic
138 acids, the time to reach Donnan equilibrium for Tl(I) was evaluated. Experiments with only free
139 Tl(I) ions in a 50 mmol/L KNO₃ background electrolyte were performed and showed that
140 equilibrium was reached after 24 hr (Appendix A, Fig. S3).

141

142 **1.2 Reagents and chemicals**

143 In order to have Tl(I) at the beginning of all experiments, the source of thallium is a Tl(I)NO₃
144 salt (99.9%, Sigma Aldrich). Tl(I) should be the only stable thallium species under our
145 experimental conditions (Vink, 1993; Xiong, 2009; Campanella et al., 2017; Casiot et al., 2017).
146 Tl(I) oxidation to Tl(III) happens in highly acidic conditions or on mineral surfaces which
147 stabilize Tl(III), either on vacant sites or as oxides like Tl₂O₃ (Watanabe and Takahashi, 2015;
148 Campanella et al., 2017; Prytulack et al., 2017). Consequently, free Tl(III) should not be present
149 in our solutions because of the chosen conditions i.e. pH > 4 and moderate Eh. Background
150 electrolyte solutions were prepared with KNO₃ (VWR Chemical) and Ca(NO₃)₂ (VWR
151 Chemical) dissolved in ultrapure water (milli Q, Millipore). pH was adjusted with distilled 0.1
152 mol/L HNO₃ and 0.5 mol/L NaOH (VWR Chemical). A peat purified humic acid from the Mogi
153 river region of Ribeirão Preto, São Paulo State, Brazil was used in all experiments. Detailed of
154 purification procedures and chemical compositions are described in Botero et al. (2017).
155 Thallium calibration standards were diluted from a thallium ICP standard solution (TraceCERT[®],
156 Sigma Aldrich). Chemical blanks were analyzed with HR-ICP-MS Element 2 (Thermo
157 Scientific) and no thallium was detected.

158

159 **1.3 Tl isotherms.**

160 Experiments were performed at room temperature ($23 \pm 1^\circ\text{C}$) open to atmosphere with a unique
161 concentration of soluble HA. Previous studies reported low Tl(I) complexation to humic acid
162 (Jacobson et al., 2005; Liu et al., 2011). Then, 150 mg/L was used during experiments (pH and
163 concentration isotherms) to maximize Tl complexation to humic acid and to derive NICA-
164 Donnan parameters for Tl^+ . The effects of Tl(I) concentration and pH were tested. For sorption
165 edge experiments pH ranged from 3.98 to 7.89 ± 0.05 and the total Tl(I) initial concentration
166 was 200 pmol/L. In the case of concentration isotherms, the pH was fixed at 7.35 ± 0.05 and
167 initial concentrations ranged from 20 pmol/L to 2.0 $\mu\text{mol/L}$. The use of this range of
168 concentrations was reported for Tl in the literature for freshwater (pristine and polluted). 20
169 pmol/L correspond to Tl concentration in most of the world big rivers (Kaplan and Mattigod,
170 1998; Nielsen et al., 2005) and 2.0 $\mu\text{mol/L}$ is close to the highest Tl values measured in polluted
171 rivers in mining areas (Casiot et al., 2011; Campanella et al., 2017). The background electrolyte
172 in the donor and acceptor sides was KNO_3 50 mmol/L. DMT were run in duplicates for each
173 experimental data point.

174 Prior to isotherm experiments, all cells, bottles and beakers used for the donor solution were
175 washed with Suprapur HNO_3 (Merck) 2% and ultrapure water (milliQ). The cation exchange
176 membrane (551652U, VWR Chemicals) was prepared by successive washing as in previous
177 studies (Temminghoff et al., 2000; Weng et al., 2005; Kalis et al., 2006; Chen et al., 2012). At
178 each pH or concentration steps, two new DMT cells were added in the donor solution whereas
179 the two at equilibrium with the solution conditions were removed from the later and both
180 acceptor and donor solutions were sampled. The donor solution corresponded to the sample
181 with Tl(I) ions, HA and the background electrolyte while the acceptor solution was the one
182 inside the DMT device and contained the electrolyte and also the free Tl(I) ions after the Donnan
183 equilibrium was reached in 24 hr (Appendix A, Fig. S3). Preliminary modeling suggested that
184 only free Tl(I) ions were stable in the acceptor solution (Appendix A, Table S1). Every
185 dissolved species in solution were sum up in Appendix A (Table S2). For more details on the
186 experimental design readers are invited to refer to supporting information (Appendix A, Fig. S1
187 and S2). Finally, collected samples were acidified to $\text{pH} \sim 1$ with distilled HNO_3 2%, diluted
188 when necessary and stored for further analysis.

189

190 **1.4 Measurements of cations in solution.**

191 Thallium was measured with an HR-ICP-MS Element 2 (Thermo scientific, USA) installed in
 192 a clean room with a solution of ^{115}In (5 ppb) as internal standard. For each sample, 9
 193 measurements were done (3 x 3 runs, Appendix A, Table S3). Then, the average was used as
 194 concentration value and the standard deviation was used as measurement error. Concentrations
 195 were corrected from signal drift with the internal standard. Certified materials TM23.4 and
 196 TM24.4 (Environment Canada) validated Tl(I) analysis (Appendix A, Table S4). Limits of
 197 quantification (LOQ) ranged from 2.5 pmol/L to 7.5 pmol/L for Tl(I). Major cations (K^+ and
 198 Na^+) were analyzed with an ICP-AES (ICAP 6200, Thermo scientific, USA). More details of
 199 HR-ICP-MS measurement for thallium can be found in Appendix A (Table S3).

200

201 **1.5 Modeling.**

202 This experimental approach was combined with NICA-Donnan modeling within ECOSAT
 203 software (Keiser and Van Riemsdijk, 1994). Here, metal ions binding to humic substances (HS,
 204 mix of humic and fulvic acids) was assumed to occur through specific interactions between
 205 cations and reactive organic moieties of the NOM and by nonspecific Coulombic binding to
 206 any residual negative charge (Benedetti et al., 1995; Benedetti et al., 1996a) The model merges
 207 the Non-ideal Competitive Adsorption (NICA) isotherm model with the Donnan model. The
 208 first (NICA isotherm) describes competitive binding of protons and cations to NOM including
 209 binding site heterogeneity and the second (Donnan model) details the electrostatic interactions
 210 within the structure of humic substances considered as a water-permeable gel (Benedetti et al.,
 211 1996a; Benedetti et al., 1996b) The model accounts for binding site heterogeneity by including
 212 two different groups of binding sites each with a continuous affinity distribution: type 1 and 2,
 213 corresponding to low affinity and high affinity sites, respectively (Benedetti et al., 1995). The
 214 model equation is (Eq. 1):

$$215 \quad Q_i = \frac{n_{i,1}}{n_{H,1}} Q_{\max 1,H} \frac{(\tilde{K}_{i,1} c_i)^{n_{i,1}}}{\sum_i (\tilde{K}_{i,1} c_i)^{n_{i,1}}} \frac{[\sum_i (\tilde{K}_{i,1} c_i)^{n_{i,1}}]^{p_1}}{1 + [\sum_i (\tilde{K}_{i,1} c_i)^{n_{i,1}}]^{p_1}} + \frac{n_{i,2}}{n_{H,2}} Q_{\max 2,H} \frac{(\tilde{K}_{i,2} c_i)^{n_{i,2}}}{\sum_i (\tilde{K}_{i,2} c_i)^{n_{i,2}}} \frac{[\sum_i (\tilde{K}_{i,2} c_i)^{n_{i,2}}]^{p_2}}{1 + [\sum_i (\tilde{K}_{i,2} c_i)^{n_{i,2}}]^{p_2}}$$

216 (1)

217 where the amount of bound ion i , Q_i (mol/kg) at solution concentration c_i (mol/L) is given by
 218 the sum of two identical binding expressions, the first one for low affinity type of site (subscript
 219 1) and the second one for high affinity type of site (subscript 2) distributions. Four parameters
 220 describe intrinsic heterogeneity of HS ($Q_{\max 1,H}$, $Q_{\max 2,H}$, p_1 and p_2) and four ion specific
 221 parameters ($\tilde{K}_{i,1}$, $\tilde{K}_{i,2}$, $n_{i,1}$ and $n_{i,2}$) portray ion binding. p_1 and p_2 define the width of the affinity
 222 distributions and condense the intrinsic heterogeneity of HS. $Q_{\max 1,H}$ and $Q_{\max 2,H}$ (mol/kg) are

223 the maximum proton binding capacity of HS. $\tilde{K}_{i,1}$ and $\tilde{K}_{i,2}$, are the median values of the affinity
224 distributions for ion i , and $n_{i,1}$ and $n_{i,2}$ express the non-idealities of the ion-binding for each
225 distribution. For further NICA-Donnan theory, the reader has to refer to the following studies
226 (Benedetti et al., 1995; Benedetti et al., 1996a and b; Kinniburgh et al., 1996; Milne et al., 2001;
227 Koopal et al., 2005; Milne et al., 2003).

228 Input data were total concentrations of K and Tl, or Ag in solution, pH and ionic strength.
229 Tl and K ($\tilde{K}_{i,1}$, $\tilde{K}_{i,2}$, $n_{i,1}$ and $n_{i,2}$) were adjust together by fitting Tl experimental data from
230 concentration isotherms only. Parameters specific to the used purified humic acid and proton
231 binding were from Botero et al. (2017) and summarized in Appendix A (Table S5).
232 Experimental errors were calculated according to the propagation of uncertainties theory
233 (details in Appendix A, Eq. 1) while Root Mean Square Error (*RMSE*, Appendix A, S-Eq. 2) was
234 used to estimate the gap between experimental and modelled data. In multiple studies
235 assumptions were made of similar behaviour between K and Tl(I) (Jacobson et al., 2005; Peter
236 and Viraraghavann 2005; Voegelin et al., 2015). While no specific parameters existed for K and
237 no isotherm for K were made, two modelling hypothesis were tested: (i) equal ion specific
238 parameters for both Tl(I) and K (i.e. $\tilde{K}_{i,1}$, $\tilde{K}_{i,2}$, $n_{i,1}$ and $n_{i,2}$) are chosen; (ii) two different sets of
239 parameters specific to each element are considered. K parameters will be discussed in paragraph
240 2.1. and values for K parameters for which the fit was the closest to the experimental data were
241 kept to model Ag and Tl final data (reader has to refer to Appendix A, Fig. S4 for more details).

242

243 **1.6 Ag NICA-Donnan parameter derivation.**

244 No experimental data were newly acquired for Ag in this study, previously published data from
245 Sikora and Stevenson (1988) were used and only Ag(I) NICA-Donnan parameters were
246 optimized. Sikora and Stevenson (1988) used three purified humic acids in their experiments,
247 HA1 from a A horizon taken from sandy silt loam, HA3 from Rifle peat, Ohio and HA8 from a
248 A horizon sample from the Hapster silt loam (Sikora and Stevenson, 1988). Binding isotherms
249 constructed at pH 6.5 with 0.1 mol/L KNO₃ and 0.5 g/L of humic acid (Sikora and Stevenson,
250 1988). Ag specific parameters were adjust to fit experimental data. $Q_{\max 1, H}$ for HA1, HA3 and
251 HA8 were directly taken from Sikora and Stevenson (1988) while the remaining specific
252 parameters for protons ($Q_{\max 2, H}$, p_1 , p_2 , $\log \tilde{K}_{H,1}$, $\log \tilde{K}_{H,2}$) were optimized during modeling and
253 kept within the range of parameters defined for humic acids in Milne et al., (2001). Details are
254 summarized in Appendix A (Table S6).

255

256 **2 Results and discussion**

257 **2.1 Tl(I) and Ag(I) complexation with humic acids.**

258 Specific parameters fitted for K, Ag and Tl are given in **Table 1**. The hypothesis where K(I)
259 parameters are different from Tl(I) parameters gave the best description of the complexation of
260 Tl(I) by the HA.

261 Thallium complexation to HA increases with increasing concentrations (**Fig. 1a**). However, the
262 amount of complexed Tl(I) is low and always below 50% of the total thallium in solution. Ion
263 specific NICA-Donnan parameters were adjusted to fit Tl(I) concentration isotherm values (**Fig.**
264 **1a**). Then, the robustness of the model parameters was tested by comparing measured free Tl(I)
265 to predicted free Tl(I) obtained from sorption edge and fixed pH isotherm experiments (**Fig. 1b**)
266 not used during the calibration procedure. **Fig. 1b** also shows that the predictions were
267 satisfactory for the pH sorption edge data (i.e. within a 5% confidence area) notwithstanding
268 the parameter's optimization made with data corresponding to one pH value (7.35 ± 0.05).
269 Similar conclusions are reached when comparing measured bound-Tl(I) to simulated bound-
270 Tl(I) (**Fig. 1c**). The slope of the concentration isotherm (**Fig. 1a**), close to one (i.e. 0.86),
271 suggests that Langmuirian behaviour dominates the process and that monodentate binding
272 controls Tl(I) sorption onto HA (Koopal et al., 1994). This is confirmed by model parameters
273 since non-ideality parameters partly related to the type of binding (mono vs polydentate) ($n_{i,1}$
274 and $n_{i,2}$, Benedetti et al., 1995; Benedetti et al., 1996a) optimized for Tl(I) are close to 1 (**Table**
275 **1**). Additional data for Tl(I) are presented in Appendix A (Table S7).

276 **Fig. 2** displays Ag(I) modelling results whereas optimized Ag(I) specific parameters are given
277 in **Table 1**. For Ag(I), non-ideality parameters were substantially different from 1, suggesting
278 more **chemical ion specific binding heterogeneity as defined in NICA-Donnan papers (see**
279 **above for references)** during the complexation of Ag(I) when compared to Tl(I). Indeed at pH
280 below 5, the small amount of bound-Tl(I) is controlled by low affinity type of sites. At pH > 5
281 and independently of thallium concentrations, high affinity sites dominate the binding,
282 accounting for more than 65 % of total bound-Tl(I). These results derive from the high values
283 found for the median affinity constant associated to the high affinity sites (**Table 1**). At low pH,
284 15% of total bound-Tl(I) is located in the Donnan gel via Coulombic interactions. In Sikora's
285 study (Sikora and Stevenson, 1988) with pH = 6.5, Ag(I) is almost exclusively bound to high
286 affinity sites and only a small amount is bound to low affinity sites or are in the Donnan gel (i.e.
287 less than 5% of total bound silver). Ag(I) binding to humic acid is strongly controlled by high
288 affinity sites conversely to Tl(I) and the amount of Ag(I) bound is also much higher (**Fig. 3**).

289 Ag has a higher affinity for organic matter than Tl(I) and its mobility is strongly influenced by
290 this type of ligand (Sikora and Stevenson, 1988; Jacobson et al., 2005a). **Fig. 3** also suggests
291 that Ag(I) could compete with divalent cations for binding to NOM reactive sites. The pH-
292 dependency of Ag complexation is smaller than the one of divalent ions. At neutral pH, Ag may
293 compete with cobalt for instance (**Fig. 3**) and at acidic pH, Ag(I) has more affinity for NOM
294 proxies than Co^{2+} , Mn^{2+} and Cd^{2+} (**Fig. 3**).

295 296 **2.2 The S-rich functional groups.**

297 Two recent studies evaluated the thiol group concentration in natural organic matter (NOM;
298 Rao et al., 2014) calculated a concentration of 0.7 $\mu\text{mol/g}$ for Suwanee River NOM and 3.6
299 $\mu\text{mol/g}$ for a soil HA. Joe-Wong et al., (2012) estimated thiol group concentration at 535 $\mu\text{mol/g}$
300 of dissolved organic matter (DOM). Regardless of the huge discrepancy between these three
301 numbers, in our experiments, the amount of bound Tl(I) at pH 7.35 varied from 68.4 pmol/g of
302 HA to 2.57 $\mu\text{mol/g}$ of HA for the lowest and highest total Tl concentration, respectively. In
303 Sikora's data, (Sikora and Stevenson, 1988) bound silver ranges between 87 $\mu\text{mol/g}$ and 920
304 $\mu\text{mol/g}$ of HA. The amounts of bound Tl(I) and Ag(I) are lower than the range of thiol group
305 concentration. Ag(I) has a high affinity for thiolate (Smith et al., 2002; Kleja et al. 2016) and
306 since Ag-S binding was evidenced (Kleja et al., 2016) thiol groups could definitely play a role
307 in its speciation but other uncharacterized S-rich functional groups cannot be excluded. A
308 similar assumption could be relevant for Tl(I) despite limited access to data investigating the
309 role of thiol groups for Tl(I) biogeochemistry (Garcia Bugarin et al., 1989; Jacobson et al.,
310 2005b; Rodrigez-Mercado et al., 2013).

311 However, due to the low abundance of thiol groups and their expected pK_a value around 8
312 (Smith et al., 2002; Rao et al., 2014), they are probably accounted non-specifically within the
313 high affinity sites continuous distribution of the NICA-Donnan model (Benedetti et al., 1995;
314 Benedetti et al., 1996a, 1996b). The $\log \tilde{K}_{i,2}$ values 4.88 and 2.40, obtained for Ag(I) and Tl(I),
315 respectively (**Table 1**), are higher than the values reported in Milne et al.'s study (2003) and
316 should be used now to simulate Ag or Tl interaction with NOM regardless of the assumptions
317 on the role of S-rich functional groups.

318 319 **2.3. Consequences for Tl(I) geochemical cycle in waters and soils.**

320 In this study, Tl(I) aqueous speciation (dissolved phase), in various natural water systems from
321 Kaplan and Mattigod (1998) is revisited. Data on groundwater, river water, eutrophic lake water,
322 bog water and seawater are gathered together with constants used in Tl(I) speciation modeling

323 in Appendix A (Table S8). The following assumptions are made to simulate the Tl(I) speciation
324 in the above natural water systems. For groundwater, river water, eutrophic lake and sweater it
325 is assumed that DOM was mainly FA and that it is HA for the bog water. 80% in mass of the
326 DOM was assumed to be reactive according to Tipping (2002). In order to get HA or FA
327 concentrations in natural waters, DOM was calculated from DOC values considering a ratio
328 DOM to DOC of 2:1 (by mass of C) (Ren et al., 2015). Constants for other complexes than Tl(I)
329 aqueous species are summarized in Appendix A (Table S9). The parameter values for FA were
330 estimated by making the following hypothesis. The heterogeneity parameters $n_{i,1}$ and $n_{i,2}$ in
331 NICA-Donnan are very similar for HA and FA (Milne et al., 2003). The values obtained here
332 for a HA can thus be used for FA in combination with the other generic binding parameters.
333 Conversely, in Milne et al., (2003) empirical relationship linking $n_{i,1}$, $\tilde{K}_{i,1}$ and K_{OH} for FA and
334 HA are similar. Therefore, combining those two observations, we assumed that the derived Tl(I)
335 HA parameters can be used in combination with the generic FA parameters from Milne et al.'s
336 study (2003) to simulate the Tl(I) interaction to the low affinity site of the DOM. A similar
337 reasoning is made for the high affinity sites to derive $\tilde{K}_{i,2}$. The generic parameters used to
338 describe the FA and HA interaction with Tl(I) are given in Appendix A (Table S10). With the
339 following assumptions, we are now able to simulate the different aquatic ecosystems and the
340 results are given in Appendix A (Table S11) and presented in **Fig. 4**. This figure shows that
341 only two dissolved aqueous species of Tl(I) would exist in natural waters, Tl(I) represents
342 between 76 and 98% of total dissolved Tl while Tl bound to NOM analogues represents the
343 remaining thallium, except for the seawater system where TlCl and TlCl₂⁻ account for 46% of
344 the total thallium. However, unlike Kaplan and Mattigod's results (1998) it seems that there is
345 not a major contribution of Tl-NOM species in bog water (i.e. TlHA is < 10%). This is the result
346 of the competition between protons and Tl(I) to the same type of sites. Under the low pH
347 conditions of the peat bog the protons compete very efficiently and prevent Tl(I) binding to the
348 bog NOM. In this study, Tl(I)-NOM complex is **however slightly** more important for all other
349 conditions if compared to Kaplan and Mattigod's results (1998) (Table S11). Discrepancies
350 with Kaplan and Mattigod's study (1998) are probably due to the different type of modelling
351 performed in both studies as well as the available binding data. Indeed, NICA-Donnan or
352 WHAM 7 models were proven to give much more robust prediction of metal ion speciation
353 even outside of the range of metal ion concentrations used for their calibration (Benedetti et al.,
354 1996b; Tipping, 2002). These findings support that our modelling predictions could be more
355 robust than previous ones as far as concentration is concerned. In addition, the range of

356 concentration used in this study, to derive parameters, is always difficult to simulate for models
357 (Benedetti et al., 1996b; Tipping, 2002). Most models always performed well at high
358 concentration but their extrapolations to much lower concentration ranges are always much
359 more problematic (Benedetti et al., 1996b; Tipping, 2002). As expected, no Tl(I)-NOM
360 complexes are found in seawater and half of thallium is free Tl(I) ions and half is chloride
361 complex species (TlCl and TlCl₂, **Table 1**).

362 Thallium speciation in soil solution was modelled. Compositions of soil solutions are taken
363 from Kinniburgh et al., (1983). Various concentrations relevant to pristine or polluted systems
364 are taken into consideration. Many organic molecules are regrouped as NOM in soil solutions.
365 According to Ren et al. (2015), approximately 29% are humic substances, 66% are hydrophilic
366 acids and 5% are non-reactive organic components. During modelling, hydrophilic acids are
367 equally divided in acetic acid, citric acid and oxalic acid, three low molecular weight organic
368 acids (LMWOAs). Humic substances are modelled as FA since Ren et al., (2015) and van
369 Zomeren and Comans, (2007) revealed that they are FA and not HA as previously imagined.
370 Details of used binding parameters, compositions and results are presented in Appendix A
371 (Tables S10 and S12). Results are gathered in **Fig. 5**. Thallium does not strongly complex with
372 such LMWOA as shown in Vanek et al., (2012). Therefore, like for natural water systems, only
373 two species control Tl(I) speciation: Tl(I) ions and Tl-FA. At low Tl(I) concentrations (≤ 1
374 nmol.L⁻¹), up to 35% of the thallium is bound to NOM (**Fig. 5**). Conversely, at higher Tl(I)
375 concentrations (≥ 1 nmol.L⁻¹), less than 10% of Tl(I) is bound to NOM (**Fig. 5**).

376 Wick et al., (2018) gathered data on Tl binding to a number of phases from clay minerals, to
377 manganese oxides. When compared to these results, our data suggest that similar amounts of
378 Tl(I) are complexed by humic substance as ferrihydrite, illite and smectite (Wick et al., 2018;
379 Martin et al., 2018). In addition, our results are close to the ones from Liu et al., (2011). Despite
380 similar affinity for organic matter and illitic clays, observations in soils showed a limited role
381 of organic matter on thallium uptake (Vanek et al., 2009; Vanek et al., 2013; Voegelin et al.,
382 2015). Thus, thallium seems to be highly mobile and labile when it is observed in organic rich
383 soil horizons (Vanek et al., 2009; Vanek et al., 2013) in agreement with results showed in **Fig.**
384 **5**. Furthermore, natural organic matter could also lead to release thallium in soil by enhancing
385 silicate alteration/weathering as suggested in some studies (Vanek et al., 2009; Ren et al., 2015).
386 Tl(I) in critical zone conditions will behave more like a lithophile element close to alkali metals
387 (K⁺, Rb⁺ and Cs⁺). This conclusion is supported by observations made that illitic clay systems
388 control the mobility of Tl(I) like for K⁺ and Cs⁺ (Jacobson et al., 2005; Voegelin et al., 2015;
389 Wick et al., 2018; Martin et al., 2018). These results also point out that in rivers, Tl(I) is

390 predominantly a highly bioavailable free ion (Tl^+). Indeed, various studies highlighted that $Tl(I)$
391 poorly reacts with particulate phases and remains mainly in the dissolved fraction as a free ion
392 (**Fig. 4**) (Law and Turner, 2011; Boning et al., 2017; Casiot et al., 2017). However, several
393 questions regarding thallium remain open, especially the role of $Tl(III)$ and its
394 abundance/stability in the environment (Lin and Nriagu, 1999; Twining et al., 2003; Karlsson
395 et al., 2006; Watanabe and Takahashi, 2015). Only one paper reported the binding of $Tl(III)$ to
396 HA (Watanabe and Takahashi, 2015), the $Tl(III)$ species would be stabilized by HA but only at
397 low pH and high redox potential values. The reactivity of $Tl(III)$ with NOM needs more studies
398 to fully picture the Tl environmental biogeochemistry. The combination of HPLC-ICP-MS
399 system designed based on previous studies (Campanella et al., 2017; Casiot et al., 2017) and
400 the presently used DMT approach would greatly help to make progress. Finally, in order to
401 complete the database, $Tl(I/III)$ interactions with other analogues of NOM should be studied.

402

403 **3 Conclusion**

404 Thallium complexation was compared to silver complexation using literature data and using the
405 same NICA-Donnan formalism. We report here, for the first time, parameters for these two
406 cations. Results display low thallium complexation to the NOM proxy while silver competes
407 with divalent cations for the NOM binding sites. Calculated speciation for dissolved thallium
408 highlights the dominance of free thallium (Tl^+) in solution whereas Tl -NOM complexes
409 contribute roughly 15% to total $Tl(I)$ species in river and lake type waters. Similar results are
410 obtained for soil solutions, Tl -bound to NOM < 30% of total, from UK soils with different land
411 use and geochemistry. However, several questions regarding thallium remain open, especially
412 the role of $Tl(III)$ and its abundance/stability in the environment.

413

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418

419 **Appendix A. Supplementary data**

420 Supplementary data associated with this article can be found in the online version at xxxxxx.

421

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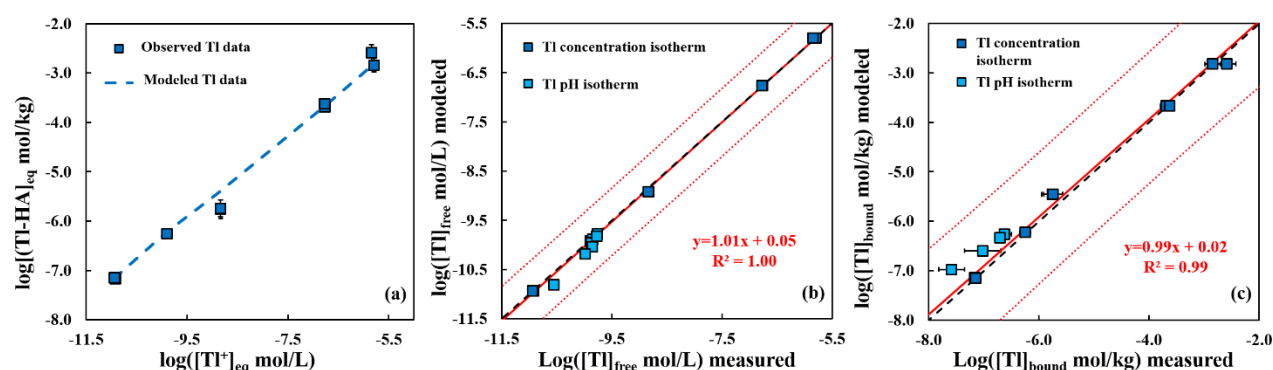
617 **List of tables**

618 **Table 1** Ion specific parameters (ISP) for the NICA-Donnan model selected after adjustment
619 with experimental data. *RMSE* were calculated only with data used for ISP adjustments. For
620 Tl(I) it means only data from the concentration isotherm. Subscript 1 and 2 correspond
621 respectively to low affinity and high affinity sites of the humic substances as defined in NICA-
622 Donnan model theory (Benedetti et al., 1995; Benedetti et al., 1996a)

Element	$\log\tilde{K}_{i,1}$	$n_{i,1}$	$\log\tilde{K}_{i,2}$	$n_{i,2}$	<i>RMSE</i> for free ion	<i>RMSE</i> for bound ion
Tl(I)	0.20	0.88	2.40	0.84	0.04 (n = 9)	0.16 (n = 9)
Ag(I)	-0.10	0.59	4.88	0.71	-	0.02 (n = 62)
K(I)	0.2	0.88	1.14	0.84	-	-

623

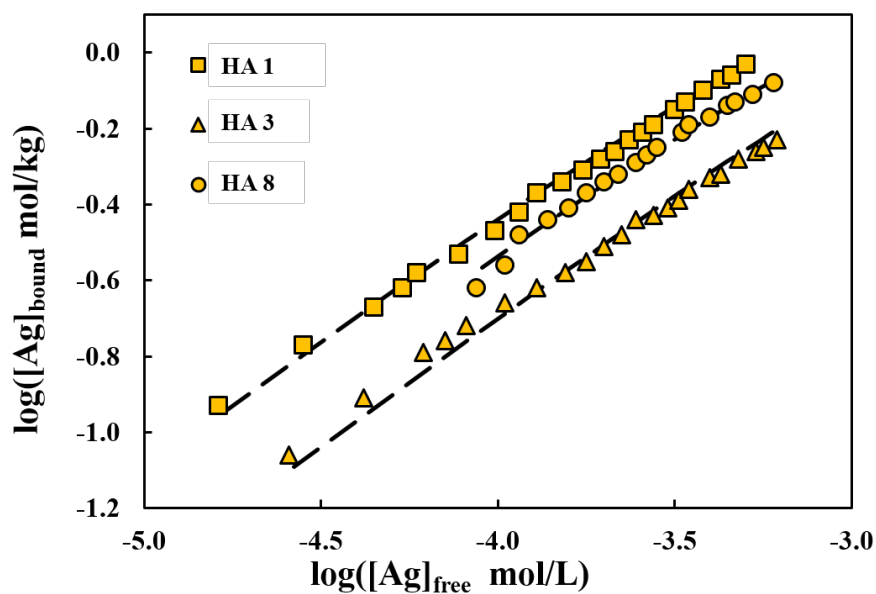
624 **List of figures**



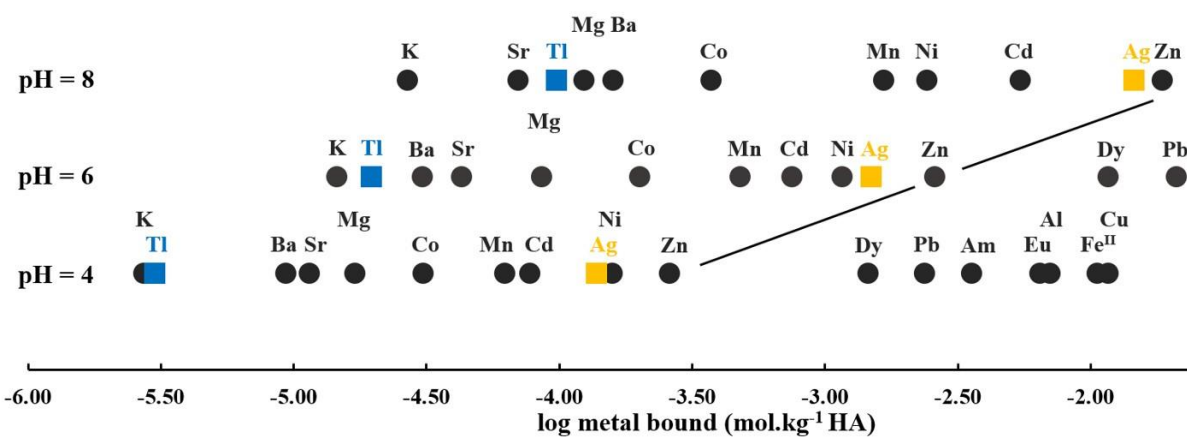
625

626 **Fig. 1** (a) Evolution of bound thallium as function of free thallium. pH for measured data was
627 7.35 ± 0.05 with $[HA] = 150$ mg/L. For free Tl: *RMSE* = 0.04 (n = 9) and for bound Tl(I): *RMSE*
628 = 0.16 (n = 9). (b) Calculated free thallium after the optimization of NICA-Donnan parameters
629 with the data set given in (a) vs. measured free Tl(I). (c) Measured vs. calculated for
630 complexed/bound thallium. For b and c, red lines are regression lines whereas dashed red lines
631 correspond to the confidence area (5%) of the regressions. The dashed black lines are one to
632 one lines. Error bars are $\pm 2\sigma$.

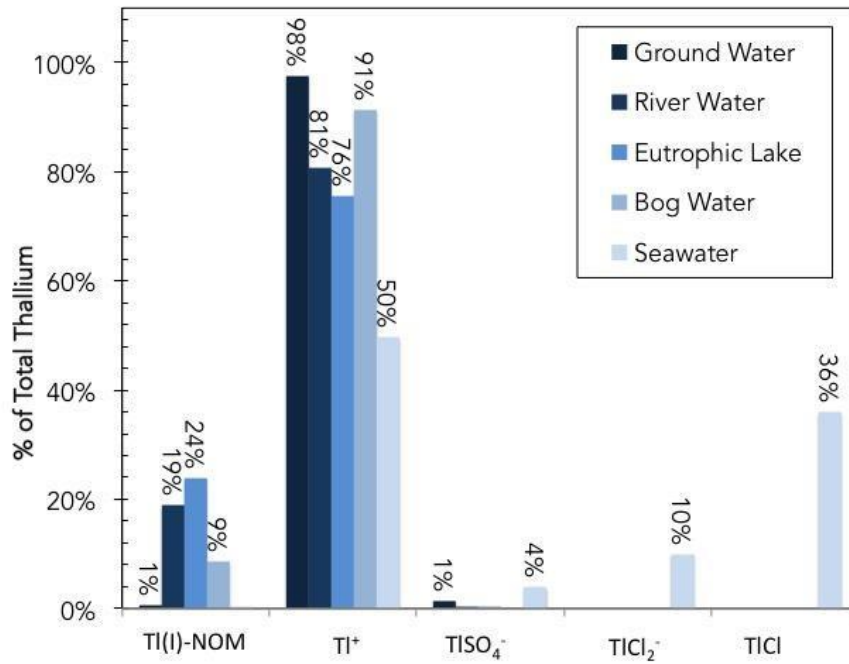
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634
 635 **Fig. 2** Bound silver versus free silver for three humic acids (HA1, 3 and 8). Experimental points
 636 are from Sikora and Stevenson (1988). Background electrolyte was KNO_3 0.1 mol/L, pH was
 637 6.5 and $[\text{HA}] = 500$ mg/L. Dashed black lines corresponding to NICA-Donnan simulation
 638 obtained after adjustment of NICA-Donnan model parameters values
 639

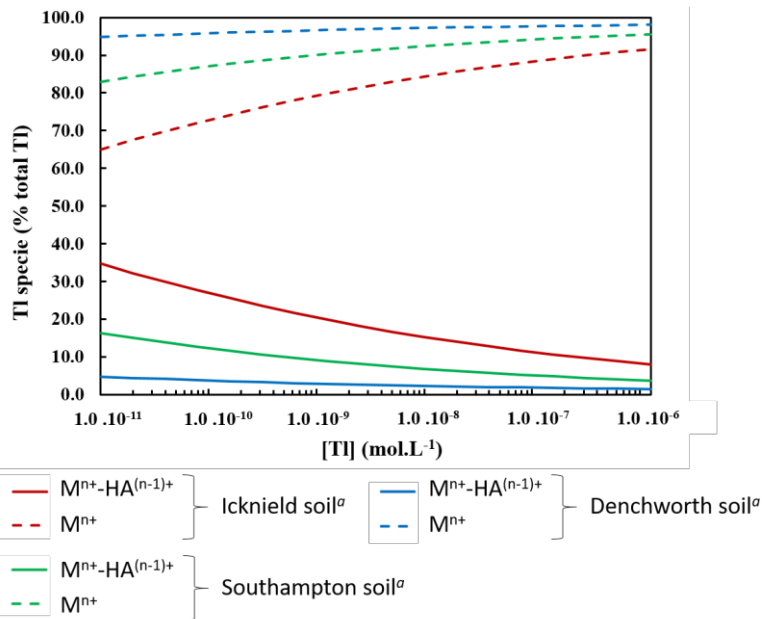


640
 641 **Fig. 3** Log [metal bound] calculated with NICA-Donnan generic parameters for humic acids
 642 from Milne et al., (2003) for metal ions represented by black dots. Tl and Ag parameters come
 643 from the present study. The total metal concentration is equal to 10 nmol/L of a given metal and
 644 a background concentration of 1 mmol/L of Ca^{2+} is used for each calculations.
 645



646
647
648

Fig. 4 Modeled Tl speciation in various natural water systems from Kaplan and Mattigod (1998)



649

Fig. 5 Modeled Tl speciation in three soil solutions at relevant environmental concentrations. More details are summarized in Appendix A (Tables S10 to S12 from Kinniburgh and Miles, 1983).

650
651
652

1 **Appendix A. Supplementary data**

2

3 **Effect of natural organic matter on thallium and silver speciation**

4

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6

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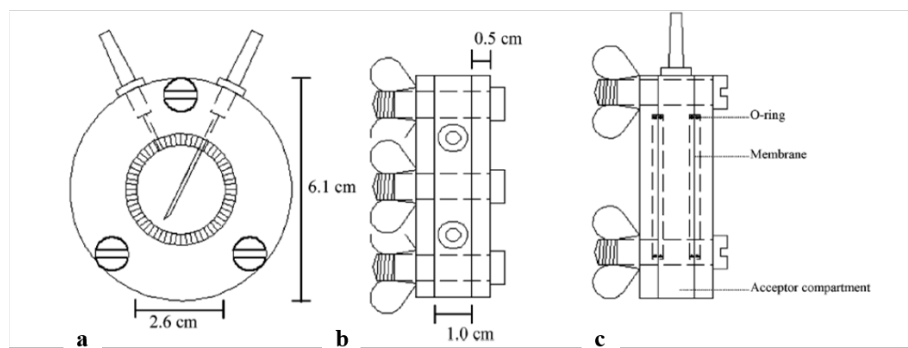
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15 *Corresponding authors. *Email address:* benedetti@ipgp.fr

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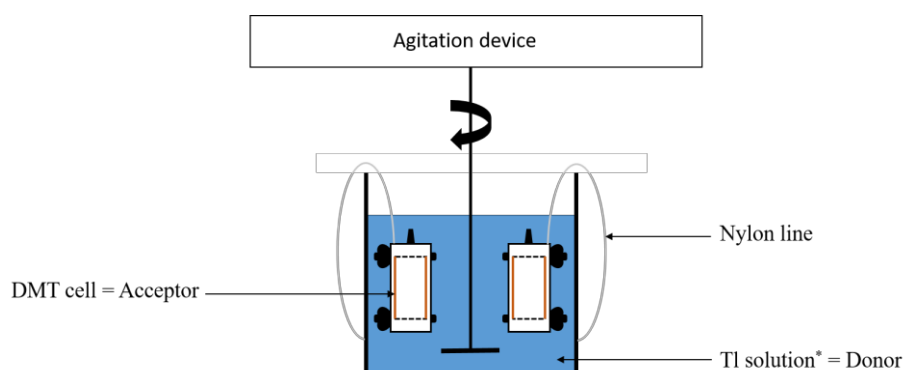
18 **1 Experimental setup with Field-Donnan Membrane Technique (Kalis et al., 2007)**



19

20 **Fig. S1** Field-DMT from Kalis et al. 2007 (a) Front view; (b) top view; (c) DMT cell.

21

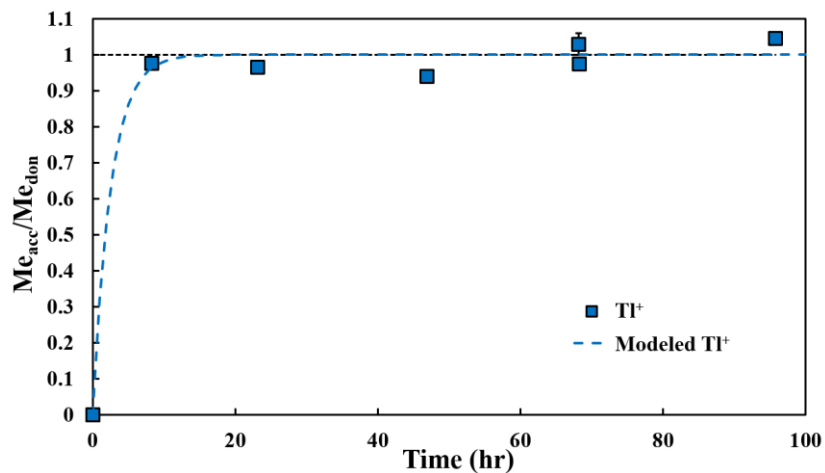


22

23 **Fig. S2** Experimental set-up used for Tl(I) experiments. *Tl solution” = Donor solution is a
24 mixture that contains Tl(I)⁺, K⁺, NO₃⁻ and humic acid.

25

26 **2 Time to equilibrium for Tl⁺ (Donnan Membrane Technique)**



27

28 **Fig. S3** Time to reach equilibrium for Tl⁺ at pH = 4.0 ± 0.1, between the DMT compartments
29 (i.e. acceptor vs. donor sides) in absence of humic acid. Error bars are ±2σ of the experimental
30 data. Time to reach equilibrium is **24 hrs** for Tl⁺ Dashed lines correspond to the modeled
31 variation of cation concentrations as function of time during experiments. Model equation is
32 given in Temminghoff et al., 2000.

33

34 **3 Composition and calculated speciation of experimental solutions**

35 **Table S1** Calculated Tl speciation in the acceptor side of the DMT. Modeled with CHESS 2.0.
 36 Only species corresponding to more than 1% of total concentration are presented here.
 37 Saturations indices indicate that under-saturation towards Tl bearing minerals (TlOH, TlNO₃,)
 38 is expected during the experiments. Additional constants came from Casiot et al. (2011).

Element	Total concentration (mol/L)	Species	Abundance in % of total						
			pH = 3	pH = 4	pH = 5	pH = 6	pH = 7	pH = 8	pH = 9
Tl	2. 10 ⁻¹⁰	Tl ⁺	100	100	100	100	100	100	99.99
	2. 10 ⁻⁶	Tl ⁺	100	100	100	100	100	100	99.99

39
 40 **Table S2** Compositions of donor and acceptor solutions at t=0. TlNO₃ is not present because it
 41 only exists as a solid specie.

Tl isotherms	
Donor	Tl ⁺ , K ⁺ , NO ₃ ⁻ , Humic Acids, Na ⁺ (after basic pH)
Acceptor	K ⁺ , NO ₃ ⁻

42
 43 **4 ²⁰⁵Tl measurements with HR-ICP-MS Element 2 (Thermo Scientific)**

44 **Table S3** Operating conditions and data acquisition parameters for HR-ICP-MS Element 2 used
 45 for ²⁰⁵Tl measurements. Thallium was measured only in low-resolution mode.

<u>HR-ICP-MS</u>	
Rf power (W)	1350
Sample uptake rate (mL.min ⁻¹) 1)	0.2
Argon flow rates (L.min ⁻¹)	
Cool	16
Auxiliary	1.0
Sample	Between 0.9 and 1.0 (depends of sensibility)
Torch	Quartz torch with a separate quartz injector tube
Nebulizer	PFA ST microflow nebulizer

Spray chamber	Quartz Cyclo spray chamber
Sampler cone	Nickel
Skimmer cone	Nickel

<u>Data acquisition</u>	<u>Low Resolution</u>
No. of passes	3
Mass window (%)	20
Search window (%)	0
Integration window (%)	20
Samples per peak	25
Sample time (s)	1.0 (²⁰⁵ Tl)

46

47 **Table S4** Measured Tl values for TM23.4 and TM24.4 certified materials (Environment
48 Canada).

	TM 23.4		TM24.4	
	<u>Expected</u>	<u>Average Measured</u>	<u>Expected</u>	<u>Average Measured</u>
[Tl] µg/L	3.97	4.08 (n=6)	4.20	4.27 (n = 4)
Error or SD	0.33	0.10	0.34	0.06
Difference to expected value (%)	-	2.67	-	1.55

49

50 **5 NICA-Donnan model parameters**

51 **Table S5** Purified humic acid specific parameters used during NICA-Donnan modeling are
52 from Botero et al., 2017.

A	β	$Q_{\max,1}$ (mol/kg)	$\log \tilde{K}_{H,1}$	$n_{1,H}$	$Q_{\max,2}$ (mol/kg)	$\log \tilde{K}_{H,2}$	$n_{2,H}$	p_1	p_2
0.60	-0.27	3.18	3.65	0.84	3.02	8.07	0.65	0.79	0.44

53

54 **6 Estimation of experimental errors and RMSE calculations**

55 Uncertainties reported in this section are calculated from the propagation of known
56 measurements or lab errors following the same approach as Reinoso-Maset et al (2014). These
57 did not take into account the humic acid variability. Experimental errors were hence calculated

58 for each experimental point following the propagation errors theory. The variance of a G
 59 function of different x_i variable can be calculated from the variances of the variables x_i using
 60 the following expression:

$$61 \quad \sigma_G^2 = \sum_{i=1}^n \left(\frac{\partial G}{\partial x_i} \right)^2 \sigma_i^2 + 2 \sum_i \sum_j \frac{\partial G}{\partial x_i} \frac{\partial G}{\partial x_j} \sigma_{ij} \quad (\text{S Eq. 1})$$

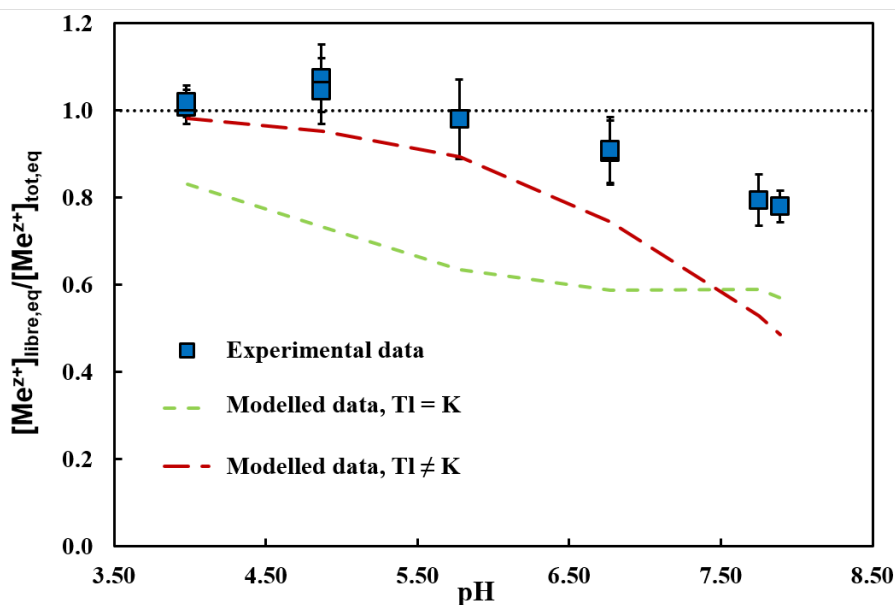
62 where $(\delta G/\delta x_i)$ is the partial derivative of G with respect to x_i , σ^2 is the variance of x_i and
 63 σ_{ij} the covariance of the x_i and x_j variables. If these variables are independents, the covariance
 64 term is then equal to zero.

65 Root Mean Square Error (*RMSE*, S Eq. 2) was calculated to assess the gap between
 66 experimental and modelled values for each series.

$$67 \quad RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (\log[\text{Me}^{z+}]_{i,\text{measured}} - \log[\text{Me}^{z+}]_{i,\text{modelled}})^2} \quad (\text{S Eq. 2})$$

68

69 7 Experimental data and additional modeled data



70

71 **Fig. S4** Free Tl concentration over total Tl concentration function of pH. When Tl = K is
 72 mentioned (green dashed line), it means that ion-specific parameters, $\tilde{K}_{i,1}$, $\tilde{K}_{i,2}$, $n_{i,1}$ and $n_{i,2}$ for
 73 both Tl and K were the same during modeling. On the opposite, when Tl \neq K is mentioned (red
 74 dashed line), those parameters were different. Experimental error bars are $\pm 2\sigma$.

75

76 8 Silver complexation with humic acids

77 **Table S6** Parameters used during modeling with ECOSAT software for experimental data of
 78 silver complexation to three humic acids from Sikora et al. (1988). In all simulations, pH=6.5,

79 background electrolyte was KNO₃ 0.1 mol/L and HA concentration was 0.5 g/L. Values in bold
 80 and italic are those that were adjusted. $m_i = n_i p_i$ (Benedetti et al., 1995).

	HA1	HA3	HA8
B	0.49	0.49	0.49
$Q_{\max 1, H}$	4.43 (from Sikora <i>et al.</i> , 1988)	3.95 (from Sikora <i>et al.</i> , 1988)	3.95
p ₁	0.62	0.62	0.62
$\log \tilde{K}_{H,1}$	3.00	3.00	3.00
n _{H,1}	0.80	0.80	0.80
$Q_{\max 2, H}$	3.30	3.30	3.30
p ₂	0.41	0.41	0.41
$\log \tilde{K}_{H,2}$	7.00	7.60	7.25
n _{H,2}	0.63	0.63	0.63
$\log \tilde{K}_{K,1}$	0.20	0.20	0.20
n _{K,1}	0.88	0.88	0.88
$\log \tilde{K}_{K,2}$	1.14	1.14	1.14
n _{K,2}	0.84	0.84	0.84
$\log \tilde{K}_{Ag,1}$	-0.10	-0.10	-0.10
n _{Ag,1}	0.59	0.59	0.59
$\log \tilde{K}_{Ag,2}$	4.88	4.88	4.88
n _{Ag,2}	0.71	0.71	0.71
m ₁	0.50	0.50	0.50
m ₂	0.26	0.26	0.26

81

82 **Table S7** Experimental data acquired for Tl(I) and used for calculations. n.s. not significant

[Tl] _{donor, eq} (mol/L)	[Tl] _{acceptor, eq} (mol/L)	[Tl] _{free, don, eq} (mol/L)	[Tl] _{complexed} (mol/kg)	$\log[Tl]_{\text{free}}$ (mol/L)	$\log[Tl]_{\text{complexed}}$ (mol/kg)	T _{avg} (°C)	pH
2.24E-11	1.67E-11	1.210E-11	6.84E-08	-10.92	-7.17	24.4	7.39
2.24E-11	1.68E-11	1.16E-11	7.17E-08	-10.94	-7.14	24.4	7.39
2.11E-10	3.08E-10	1.27E-10	5.59E-07	-9.90	-6.25	23.5	7.40
1.73E-09	2.59E-09	1.47E-09	1.74E-06	-8.83	-5.76	24.2	7.35
1.73E-09	2.57E-09	1.46E-09	1.81E-06	-8.84	-5.74	24.2	7.35

2.03E-07	2.78E-07	1.72E-07	2.05E-04	-6.76	-3.69	23.1	7.31
2.03E-07	2.76E-07	1.67E-07	2.39E-04	-6.78	-3.62	23.1	7.31
1.82E-06	2.79E-06	1.60E-06	1.43E-03	-5.79	-2.84	23.4	7.31
1.82E-06	2.62E-06	1.43E-06	2.57E-03	-5.84	-2.59	23.4	7.31
1.71E-10	1.81E-10	1.73E-10	n.s.	-9.76	n.s.	20.9	3.98
1.71E-10	1.84E-10	1.75E-10	n.s.	-9.76	n.s.	20.9	3.98
1.57E-10	1.57E-10	1.69E-10	n.s.	-9.77	n.s.	21.6	4.87
1.57E-10	1.55E-10	1.65E-10	n.s.	-9.78	n.s.	21.6	4.87
1.45E-10	1.39E-10	1.43E-10	1.88E-08	-9.85	-7.73	22.3	5.78
1.48E-10	1.28E-10	1.33E-10	9.49E-08	-9.88	-7.02	20.9	6.77
1.48E-10	1.29E-10	1.34E-10	8.93E-08	-9.87	-7.05	20.9	6.77
1.74E-10	1.22E-10	1.38E-10	2.38E-07	-9.86	-6.62	22.5	7.75
1.34E-10	1.13E-10	1.04E-10	1.96E-07	-9.98	-6.71	22.0	7.89
3.17E-11	2.89E-11	2.84E-11	2.16E-08	-10.55	-7.67	22.3	7.5
3.17E-11	2.75E-11	2.78E-11	2.60E-08	-10.56	-7.59	22.3	7.5

83

84 **9 Kaplan and Mattigod's original data**

85 **Table S8** Concentrations reported by Kaplan and Mattigod (1998) for Tl(I) speciation
86 calculation in the dissolved phase in selected natural water systems. Authors reported the
87 following references for water composition: Groundwater and lake water (Stumm and Morgan
88 1981); river water (Hem 1985); bog water (Thurman 1985); seawater (Nordstrom *et al.*, 1979);
89 organic carbon (Thurman 1985).

	Groundwater	River water	Eutrophic Lake Water	Bog water	Seawater
[Tl(I)] _{tot} (mol/L)	3.55 · 10 ⁻⁸	9.79 · 10 ⁻¹¹	9.79 · 10 ⁻¹¹	9.79 · 10 ⁻¹¹	6.36 · 10 ⁻¹¹
[Ca] (mg/L)	59	15	40	0.2	422
[Mg] (mg/L)	26	4.1	10	0.19	1,322
[Na] (mg/L)	22	6.3	9	1.5	11,020
[K] (mg/L)	4	2.3	2	0.31	408
[CO ₃] (mg/L)	266	57	122	0.06	145
[SO ₄] (mg/L)	108	11	24	0.53	2,775
[Cl] (mg/L)	11	7.8	9	0.99	19,805
[F] (mg/L)	0.1	1	1	0.1	1.4

[NO ₃] (mg/L)	39	1	3.4	1	0.3
[PO ₄] (mg/L)	0.1	0.0767	0.6	0.0767	0.0614
[H ₄ SiO ₄] (mg/L)	48	20.8	2	20.8	4.4
Org. Carbon (mg/L)	0.7	5.0	10.0	30.0	0.5
pH	7.14	8.01	7.70	3.60	8.22

90

91 **10 Constants and associated references used in this paper**92 **Table S9** Table of constant used in Tl(I) speciation modeling with ECOSAT software.

Reaction	logK (298.15K)	Reference
Tl ⁺ + OH ⁻ ↔ TlOH	0.63	This study
Tl ⁺ + SO ₄ ²⁻ ↔ TlSO ₄ ⁻	1.37	a
Tl ⁺ + Cl ⁻ ↔ TlCl(aq)	0.51	a
Tl ⁺ + 2Cl ⁻ ↔ TlCl ₂ ⁻	0.28	a
Tl ⁺ + CO ₃ ²⁻ ↔ TlCO ₃ ⁻	2.16	a
Tl ⁺ + 2CO ₃ ²⁻ ↔ Tl(CO ₃) ₂ ³⁻	0.11	a
Tl ⁺ + HCO ₃ ⁻ ↔ TlHCO ₃	0.90	a
Tl ⁺ + HPO ₄ ²⁻ ↔ TlHPO ₄ ⁻	1.27	b
Tl ⁺ + PO ₄ ³⁻ ↔ TlPO ₄ ²⁻	3.54	c
Tl ⁺ + F ⁻ ↔ TlF	0.10	c
Tl ⁺ + Cit ³⁻ ↔ TlCit ²⁻	2.00	c
Tl ⁺ + Ox ²⁻ ↔ TlOx ⁻	1.39	b
Tl ⁺ + Ac ⁻ ↔ TlAc ⁰	-0.11	c
Tl ⁺ + 2SO ₄ ²⁻ + 3Fe ³⁺ + 6OH ⁻ ↔ TlFe ₃ (SO ₄) ₂ (OH) ₆ (s)	3.36	b
Tl ⁺ + 2SO ₄ ²⁻ + 3Al ³⁺ + 24H ⁺ ↔ TlAl(SO ₄) ₂ ·12H ₂ (s)	7.46	c
Tl ⁺ + OH ⁻ ↔ TlOH(s)	1.08	c
Tl ⁺ + Cl ⁻ ↔ TlCl(s)	-3.65	b
2Tl ⁺ + CO ₃ ²⁻ ↔ Tl ₂ CO ₃ (s)	3.84	d
2Tl ⁺ + SO ₄ ²⁻ ↔ Tl ₂ SO ₄ (s)	3.79	a
Tl ⁺ + NO ₃ ⁻ ↔ TlNO ₃ (s)	1.06	b

93 * Calculated from Gibbs free energy of formation

94 a: Lin and Nriagu, (1999); b: Vink, (1983); c: Xiong, (2009) and d: Casiot et al., (2011)

95

96 **Table S10** Table of generic NICA-Donnan constants used in Tl speciation modeling with
 97 ECOSAT software for the description of NOM in various aquatic systems or soil solutions.
 98 Parameters for other elements are taken form Milne et al. (2003)

	$Q_{\max,1}$ (mol/kg)	$\log \tilde{K}_{H,1}$	$n_{1,H}$	$Q_{\max,2}$ (mol/kg)	$\log \tilde{K}_{H,2}$	$n_{2,H}$	p_1	p_2
FA	5.88	2.34	0.88	1.86	8.6	0.84	0.59	0.70
HA	3.15	2.93	0.81	3.15	8.0	0.68	0.62	0.41

99

100 **Table S11** Calculated distribution of Tl(I) species for the dissolved phase in selected natural
 101 water systems according to Kaplan and Mattigod (1998). Species not reported here are
 102 negligible.

	Groundwater	River water	Eutrophic Lake Water	Bog water	Seawater
Tl ⁺	90.4	82.7	76.8	32.4	51.9
TlHCO ₃ [°]	4.4	1.2	2.0	-	0.5
TlCO ₃ ⁻	-	-	-	-	0.1
TlSO ₄ ⁻	3.6	0.4	0.8	-	11.2
TlCl [°]	0.1	0.1	0.1	-	30.7
TlCl ₂ ⁻	-	-	-	-	5.4
Tl-Fulvate [°]	1.4	15.6	20.3	67.6	0.2

103

104 **11 Modeling with soil solutions**

105 **Table S12:** Calculated dissolved Tl(I) speciation in soil solution with ECOSAT. Compositions
 106 of solutions and soils characteristics are in Kinniburgh et al. (1983). DOM (Dissolved organic
 107 matter) is composed of 29.3% of humic substances, 66.2% of hydrophilic acids and 4.5% is
 108 considered non-reactive according to average from Ren et al. (2015) and Groenenberg et al.
 109 (2010). Humic substances are simplified as only fulvic acids and hydrophilic acids are
 110 simplified (one third for each) as combination of citric acid (Cit), oxalic acid (Ox) and acetic
 111 acid (Ac). Tl minerals taken in consideration are lanmuchangite, dorallecharite, TlCl(s),
 112 TlNO₃(s) and Tl₂SO₄(s). No precipitation occurred. Only species with above 1 % are reported.
 113 Tl-Cit²⁻, Tl-Ox⁻, Tl-Ac, TlCl(aq), TlOH and TlSO₄⁻ are negligible. Constants (minerals and
 114 dissolved complexes) used in calculation are summarized in Table S9.

Soil	pH	HA (mg/L)	[Tl]total (nmol/L)	Tl-FA (% Tl total)	Tl ⁺ (% Tl total)
<u>Icknield</u>	7.8	27.0	1.00 .10 ⁻²	34.7	65.0
			0.16	25.5	74.2
			1.26	19.9	79.8
			10.00	15.3	84.4
			158.49	10.6	89.0
			1258.90	8.0	91.6
<u>Denchworth</u>	7.0	32.8	1.00 .10 ⁻²	16.3	83.0
			0.16	11.6	87.7
			1.26	8.9	90.4
			10.00	6.8	92.4
			158.49	4.8	94.5
			1258.90	3.7	95.6
<u>Southampton</u>	4.3	50.4	1.00 .10 ⁻²	4.8	94.8
			0.16	3.5	96.0
			1.26	2.8	96.7
			10.00	2.3	97.2
			158.49	1.8	97.8
			1258.90	1.5	98.1

115

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