Effect of natural organic matter on thallium and silver speciation

Loïc A. Martin1,2,3, Caroline Simonucci2, Sétareh Rad4, Marc F. Benedetti1,∗

1 Université de Paris, Institut de physique du globe de Paris, CNRS, F-75005 Paris, France
2 IRSN, PSE-ENV/SIRSE/LER-Nord, BP 17, 92262 Fontenay-aux-Roses Cedex, France
3 Catchment and Eco-Hydrology Research Group, Luxembourg Institute of Science and Technology, L-4422 Belvaux, Luxembourg
4 BRGM, Unité de Géomicrobiologie et Monitoring Environnemental, 45060 Orléans Cedex 2, France

A R T I C L E   I N F O
Article history:
Received 16 January 2020
Revised 1 April 2020
Accepted 1 April 2020
Available online 16 April 2020

Keywords:
Thallium
Organic matter
Speciation
NICA-Donnan model
Soil
Water

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

© 2020 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. Published by Elsevier B.V.

Introduction

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

Processes driving Tl chemical speciation and mobility are well documented but some questions remain open (Twining et al., 2003; Karlsson et al., 2006; Coup and Swedlund, 2015; Voegelin et al., 2015; Campanella et al., 2017; Campanella et al., 2018). Its interaction with natural organic matter (NOM) is one of them (Jacobson et al., 2005a; Liu et al., 2011). It is known that NOM plays an important part in the fate of metal ions and can control ion mobility, concentration in soils and natural waters (Benedetti et al., 1996a). NOM is a complex mixture of compounds but the most studied and the most reactive fractions are the humic substances (HS) consisting of humic (HA) and fulvic (FA) acids (Benedetti et al., 1996a; Koopal et al., 2005). Kaplan and Mattigod (1998) defined two stability constants for Tl(I) binding onto FA with log\( K_{Tl-FAl} \) = 4.83 and log\( K_{Tl-FAl2} \) = 3.32 (no units specified) to predict the impact of NOM on thallium speciation. According to these calculations up to 67% of Tl(I) is bound to organic compounds in bog water despite its very low pH that should not favor Tl(I) binding to NOM (Kaplan and Mattigod, 1998). Thus, NOM could play a non-negligible part in Tl(I) speciation. However, Jacobson et al. (2005a) reported poor Tl(I) complexation within a peat soil. Liu et al. (2011) also studied Tl(I) binding using two purified humic acids and their results also suggested weak Tl(I) interactions with these NOM proxies. However, these studies used very high Tl(I) concentrations, which are mostly relevant for highly polluted sites (i.e., issued from mining activities (Campanella et al., 2017). Investigations made at lower concentration of Tl(I) will allow a better understanding of NOM role on Tl(I) speciation in the critical zone. It is also assumed that Tl(I) chalcophile behavior accounts for Tl(I) complexation to NOM through interactions with the S-rich functional groups of the NOM, such as thiols (Jacobson et al., 2005a, 2005b). However, Tl(I) affinity to sulfur-containing organic compounds, such as cysteine for instance, is still under investigation while no data were found regarding thiol (García Bugarin et al., 1989; Gharib and Shamel, 2005; Rodriguez Mercado et al., 2013).

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

In this study, the main objective is to evaluate the importance and strength of Tl complexation by a NOM proxy. In order to do that, complexation of Tl(I) with a purified humic acid (HA) is investigated at multiple pH and concentrations. Experiments are conducted with Donnan Membrane Technique (Temminhoff et al., 2000) to determine the amount of ion bound to the NOM proxy. These observations are used to calibrate the NICA-Donnan model to predict Tl(I) behavior during complexation. In addition, Tl(I) results are compared to Ag(I) literature data (Sikora and Stevenson, 1988) and the potential role of S-rich functional groups is discussed. Ag(I) specific parameters for NICA-Donnan model are not yet available, thus data of Ag(I) sorption to various HA is described with NICA-Donnan model for the first time in this study (Sikora and Stevenson, 1988; Chen et al., 2012; Kleja et al., 2016). Finally, the role of NOM Tl(I) cycle is also investigated by revisiting existing data from natural waters (Kaplan and Mattigod, 1998) and simulating Tl(I) speciation in soil solutions under different geochemical contexts.

1. Materials and methods

1.1. Experimental approach

Donnan Membrane Technique (DMT) was first described by Temminghoff et al. (2000). Additional developments were performed to fully constrain the kinetics aspect of the technique (Weng et al., 2005) and to adapt the geometry of the cells (Kalis et al., 2006, 2007). In this study, the DMT device, used for the experiments, is similar to the one used in Kalis et al. (2006, 2007) and its design shown in Appendix A Fig. S1. Prior to experiments with humic acids, the time to reach Donnan equilibrium for Tl(I) was evaluated. Experiments with only free Tl(I) ions in a 50 mmol/L KNO\(_3\) background electrolyte were performed and showed that equilibrium was reached after 24 hr (Appendix A Fig. S3).

1.2. Reagents and chemicals

In order to have Tl(I) at the beginning of all experiments, the source of thallium is a Tl(NO\(_3\)) salt (99.9%, Sigma Aldrich). Tl(I) should be the only stable thallium species under our experimental conditions (Vink, 1993; Xiong, 2005; Campanella et al., 2017; Casiot et al., 2017). Tl(I) oxidation to Tl(III) happens in highly acidic conditions or on mineral surfaces which stabilize Tl(III), either on vacant sites or as oxides like Tl\(_2\)O\(_3\) (Watanabe and Takahashi, 2015; Campanella et al., 2017; Prytulack et al., 2017). Consequently, free Tl(III) should not be present in our solutions because of the chosen conditions i.e., pH > 4 and moderate Eh. Background electrolyte solutions were prepared with KNO\(_3\) (VWR Chemical) and Ca(NO\(_3\))\(_2\) (VWR Chemical) dissolved in ultrapure water (milli Q, Millipore). pH was adjusted with distilled 0.1 mol/L HNO\(_3\) and 0.5 mol/L NaOH (VWR Chemical). A peat purified humic acid from the Mogi river region of Ribeirão Preto, São Paulo State, Brazil was used in all experiments. Detailed of purification procedures and chemical compositions are described in Botero et al. (2017). Thallium calibration standards were diluted from a thallium ICP standard solution (TraceCERT\textsuperscript{®}, Sigma Aldrich). Chemical blanks were analyzed with HR-ICP-MS Element 2 (Thermo Scientific) and no thallium was detected.

1.3. Tl isotherms

Experiments were performed at room temperature (23 ± 1 °C) open to atmosphere with a unique concentration of soluble HA. Previous studies reported low Tl(I) complexation to humic acid (Jacobson et al., 2005a, 2005b; Liu et al., 2011). Then, 150 mg/L was used during experiments (pH and concentration isotherms) to maximize Tl(I) complexation to humic acid and to derive NICA-Donnan parameters for Tl(I). The effects of Tl(I) concentration and pH were tested. For sorption edge experiments pH ranged from 3.98 to 7.89 ± 0.05 and the total Tl(I) initial concentration was 200 pmol/L. In the case of concentration isotherms, the pH was fixed at 7.35 ± 0.05 and initial concentrations ranged from 20 pmol/L to 2.0 μmol/L. The use of this range of concentrations was reported for Tl in the literature for freshwater (pristine and
polluted). 20 pmol/L correspond to Tl concentration in most of the world big rivers (Kaplan and Mattigod, 1998; Nielsen et al., 2005) and 2.0 µmol/L is close to the highest Tl values measured in polluted rivers in mining areas (Casiot et al., 2011; Campanella et al., 2017). The background electrolyte in the donor and acceptor sides was KNO₃ 50 mmol/L. DMT were run in duplicates for each experimental data point.

Prior to isotherm experiments, all cells, bottles and beakers used for the donor solution were washed with Suprapur HNO₃ (Merck) 2% and ultrapure water (milliQ). The cation exchange membrane (551,652 U, VWR Chemicals) was prepared by successive washing as in previous studies (Temminghoff et al., 2000; Wenzel et al., 2006; Chen et al., 2017). At each pH or concentration steps, two new DMT cells were added in the donor solution whereas the two at equilibrium with the solution conditions were removed from the later and both acceptor and donor solutions were sampled. The donor solution corresponded to the sample with Tl(I) ions, HA and the background electrolyte while the acceptor solution was the one inside the DMT device and contained the electrolyte and also the free Tl(I) ions after the Donnan equilibrium was reached in 24 h (Appendix A Fig. S3). Preliminary modeling suggested that only free Tl(I) ions were stable in the acceptor solution (Appendix A Table S1). Every dissolved species in solution were sum up in Appendix A Table S2. For more details on the experimental design readers are invited to refer to supporting information (Appendix A Figs. S1 and S2). Finally, collected samples were acidified to pH 3 with distilled HNO₃ 2%, diluted when necessary and stored for further analysis.

1.4. Measurements of cations in solution

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

1.5. Modeling

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

\[
Q_i = \frac{n_{i,1}Q_{\text{max,1,H}}}{\text{NH}_1} \left( \frac{\sum \left( \frac{K_{i,1}C_i}{n_{i,1}} \right)^{n_i} P_i}{\sum_n \left( \frac{K_{i,1}C_i}{n_{i,1}} \right)^{n_i}} + \frac{n_{i,2}Q_{\text{max,2,H}}}{\text{NH}_2} \left( \frac{\sum \left( \frac{K_{i,2}C_i}{n_{i,2}} \right)^{n_i} P_i}{\sum_n \left( \frac{K_{i,2}C_i}{n_{i,2}} \right)^{n_i}} \right) \right)
\]

where the amount of bound ion i, Q_i (mol/kg) at solution concentration C_i (mol/L) is given by the sum of two identical binding expressions, the first one for low affinity type of site (subscript 1) and the second one for high affinity type of site (subscript 2) distributions. Four parameters describe intrinsic heterogeneity of HS (Q_{\text{max,1,H}}, Q_{\text{max,2,H}}, P_1 and P_2) and four ion specific parameters (K_{i,1}, K_{i,2}, n_{i,1} and n_{i,2}) portray ion binding. P_1 and P_2 define the width of the affinity distributions and condense the intrinsic heterogeneity of HS. Q_{\text{max,1,H}} (mol/kg) and Q_{\text{max,2,H}} (mol/kg) are the maximum proton binding capacity of HS. K_{i,1} and K_{i,2}, are the median values of the affinity distributions for ion i, and n_{i,1} and n_{i,2} express the non-idealities of the ion-binding for each distribution. For further NICA-Donnan theory, the reader has to refer to the following studies (Benedetti et al., 1995, 1996a and b; Kinniburgh et al., 1996; Milne et al., 2001; Koopal et al., 2005; Milne et al., 2003).

Input data were total concentrations of K and Tl, or Ag in solution, pH and ionic strength. Tl and K (K_i, 1, K_i, 2, n_{i,1} and n_{i,2}) were adjusted together by fitting Tl experimental data from concentration isotherms only. Parameters specific to the used purified humic acid and proton binding were from Botero et al. (2017) and summarized in Appendix A Table S5. Experimental errors were calculated according to the propagation of uncertainties theory (details in Appendix A, Eq. (S1)) while Root Mean Square Error (RMSE, Appendix A Eq. (S2)) was used to estimate the gap between experimental and modelled data. In multiple studies assumptions were made of similar behavior between K and Tl(I) (Jacobson et al., 2005a, 2005b; Peter and Vitaravaghavan, 2005; Voegelin et al., 2015). While no specific parameters existed for K and no isotherm for K were made, two modeling hypothesis were tested: (i) equal ion specific parameters for both Tl(I) and K (i.e., K_{i,1}, K_{i,2}, n_{i,1} and n_{i,2}) are chosen; (ii) two different sets of parameters specific to each element are considered. K parameters will be discussed in Section 3.1 and values for K parameters for which the fit was the closest to the experimental data were kept to model Ag and Tl final data (reader has to refer to Appendix A, Fig. S4 for more details).

1.6. Ag NICA-Donnan parameter derivation

No experimental data were newly acquired for Ag in this study, previously published data from Sikora and Stevenson (1988) were used and only Ag(I) NICA-Donnan parameters were optimized. Sikora and Stevenson (1988) used three purified humic acids in their experiments, HA1 from a A horizon taken from sandy silt loam, HA3 from Rifle peat, Ohio and HA8 from a A horizon sample from the Hapster silt loam (Sikora and Stevenson, 1988). Binding isotherms constructed at pH 6.5 with 0.1 mol/L KNO₃ and 0.5 g/L of humic acid (Sikora and Stevenson, 1988). Ag specific parameters were adjusted to fit experimental data. Q_{\text{max,1}} for HA1, HA3 and HA8 were directly taken from Sikora and Stevenson (1988) while the remaining specific parameters for protons (Q_{\text{max,2,H}}, P_1, P_2, logK_{1,1}, logK_{1,2}) were optimized during modeling and kept within the range of parameters defined for humic acids in Milne et al. (2001). Details are summarized in Appendix A Table S6.
Table 1 – Ion specific parameters (ISP) for the NICA-Donnan model selected after adjustment with experimental data.

<table>
<thead>
<tr>
<th>Element</th>
<th>log$K_{1}$</th>
<th>$n_{1}$</th>
<th>log$K_{2}$</th>
<th>$n_{2}$</th>
<th>RMSE for free ion</th>
<th>RMSE for bound ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl(I)</td>
<td>0.20</td>
<td>0.88</td>
<td>2.40</td>
<td>0.84</td>
<td>0.04 (n = 9)</td>
<td>0.16 (n = 9)</td>
</tr>
<tr>
<td>Ag(I)</td>
<td>-0.10</td>
<td>0.59</td>
<td>4.88</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K(I)</td>
<td>0.2</td>
<td>0.88</td>
<td>1.14</td>
<td>0.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RMSE were calculated only with data used for ISP adjustments. For Tl(I) it means only data from the concentration isotherm. Subscript 1 and 2 correspond respectively to low affinity and high affinity sites of the humic substances as defined in NICA-Donnan model theory (Benedetti et al., 1995, 1996a).

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

2. Results and discussion

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

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

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

Additional data for Tl(I) are presented in Appendix A Table S7.

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

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

2.2. The S-rich functional groups

Two recent studies evaluated the thiol group concentration in natural organic matter (NOM; Rao et al., 2014) calculated a concentration of 0.7 μmol/g for Suwanee River NOM and 3.6 μmol/g for a soil HA. Joe-Wong et al. (2012) estimated thiol group concentration at 535 μmol/g of dissolved organic mat-
Fig. 2 – Bound silver versus free silver for three humic acids (HA1, 3 and 8). Experimental points are from Sikora and Stevenson (1988). Background electrolyte was KNO₃, 0.1 mol/L, pH was 6.5 and [HA] = 500 mg/L. Dashed black lines corresponding to NICA Donnan simulation obtained after adjustment of NICA-Donnan model parameters values.

Fig. 3 – Log metal bound calculated with NICA-Donnan generic parameters for humic acids from Milne et al. (2003) for metal ions represented by black dots. Tl and Ag parameters come from the present study. The total metal concentration is equal to 10 mmol/L of a given metal and a background concentration of 1 mmol/L of Ca²⁺ is used for each calculation.

...ter (DOM). Regardless of the huge discrepancy between these three numbers, in our experiments, the amount of bound Tl(I) at pH 7.35 varied from 68.4 pmol/g of HA to 2.57 µmol/g of HA for the lowest and highest total Tl concentration, respectively. In Sikora's data, (Sikora and Stevenson, 1988) bound silver ranges between 87 µmol/g and 920 µmol/g of HA. The amounts of bound Tl(I) and Ag(I) are lower than the range of thiol group concentration. Ag(I) has a high affinity for thiolate (Smith et al., 2002; Kleja et al., 2016) and since Ag-S binding was evidenced (Kleja et al., 2016) thiol groups could definitely play a role in its speciation but other uncharacterized S-rich functional groups cannot be excluded. A similar assumption could be relevant for Tl(I) despite limited access to data investigating the role of thiol groups for Tl(I) biogeochemistry (Garcia Bugarin et al., 1989; Jacobson et al., 2003b; Rodriguez-Mercado et al., 2013).

However, due to the low abundance of thiol groups and their expected pKₐ value around 8 (Smith et al., 2002; Rao et al., 2014), they are probably accounted non-specifically within the high affinity sites continuous distribution of the NICA-Donnan model (Benedetti et al., 1995, 1996a, 1996b). The logKₐ₂ values 4.88 and 2.40, obtained for Ag(I) and Tl(I), respectively (Table 1), are higher than the values reported by Milne et al. (2003) and should be used now to simulate Ag or Tl interaction with NOM regardless of the assumptions on the role of S-rich functional groups.

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

In this study, Tl(I) aqueous speciation (dissolved phase), in various natural water systems from Kaplan and Mattigod (1998) is revisited. Data on groundwater, river water, eutrophic lake water, bog water and seawater are gathered together with constants used in Tl(I) speciation modeling in Appendix A Table S8. The following assumptions are made to simulate the Tl(I) speciation in the above natural water systems. For groundwater, river water, eutrophic lake and sweater it is assumed that DOM was mainly FA and that it is HA for the bog water. 80% in mass of the DOM was assumed to be reactive according to Tipping (2002). In order to get HA or FA...
concentrations in natural waters, DOM was calculated from DOC values considering a ratio DOM to DOC of 2:1 (by mass of C) (Ren et al., 2015). Constants for other complexes than Tl(I) aqueous species are summarized in Appendix A Table S9. The parameter values for FA were estimated by making the following hypothesis. The heterogeneity parameters \( n_{1,1} \) and \( n_{1,2} \) in NICA-Donnan are very similar for HA and FA (Milne et al., 2003). The values obtained here for a HA can thus be used for FA in combination with the other generic binding parameters. Conversely, in Milne et al. (2003) empirical relationship linking \( n_{1,1}, K_{f1} \) and \( K_{OM} \) for FA and HA are similar. Therefore, combining those two observations, we assumed that the derived Tl(I) HA parameters can be used in combination with the generic FA parameters from the study of Milne et al. (2003) to simulate the Tl(I) interaction to the low affinity site of the DOM. A similar reasoning is made for the high affinity sites to derive \( K_{f2} \). The generic parameters used to describe the FA and HA interaction with Tl(I) are given in Appendix A Table S10. With the following assumptions, we are now able to simulate the different aquatic ecosystems and the results are given in Appendix A Table S11 and presented in Fig. 4. This figure shows that only two dissolved aqueous species of Tl(I) would exist in natural waters, Tl(I) represents between 76 and 98% of total dissolved Tl while Tl bound to NOM analogues represents the remaining thallium, except for the seawater system where TlCl and TlCl\(_2^-\) account for 46% of the total thallium. However, unlike the results from Kaplan and Mattigod (1998) it seems that there is not a major contribution of Tl-NOM species in bog water (i.e., TlHA is < 10%). This is the result of the competition between protons and Tl(I) to the same type of sites. Under the low pH conditions of the peat bog the protons compete very efficiently and prevent Tl(I) binding to the bog NOM. In this study, Tl(I)-NOM complex is however slightly more important for all other conditions if compared to the results from Kaplan and Mattigod (1998) (Appendix A Table S11). Discrepancies with the study of Kaplan and Mattigod (1998) are probably due to the different type of modeling performed in both studies as well as the available binding data. Indeed, NICA-Donnan or WHAM 7 models were proven to give much more robust prediction of metal ion speciation even outside of the range of metal ion concentrations used for their calibration (Benedetti et al., 1996b; Tipping, 2002). These findings support that our modeling predictions could be more robust than previous ones as far as concentration is concerned. In addition, the range of concentration used in this study, to derive parameters, is always difficult to simulate for models (Benedetti et al., 1996b; Tipping, 2002). Most models always performed well at high concentration but their extrapolations to much lower concentration ranges are always much more problematic (Benedetti et al., 1996b; Tipping, 2002). As expected, no Tl(I)-NOM complexes are found in seawater and half of thallium is free Tl(I) ions and half is chloride complex species (TlCl and TlCl\(_2^-\), Table 1).

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

Wick et al. (2018) gathered data on Tl binding to a number of phases from clay minerals, to manganese oxides. When compared to these results, our data suggest that similar amounts of Tl(I) are complexed by humic substance as ferricydrite, illite and smectite (Wick et al., 2018; Martin et al., 2018). In addition, our results are close to the ones from Liu et al. (2011). Despite similar affinity for organic matter and illitic clays, observations in soils showed a limited role of organic matter on thallium uptake (Vanek et al., 2009; Vanek et al., 2013; Voegelin et al., 2015). Thus, thallium seems to be highly mobile and labile when it is observed in organic rich soil horizons (Vanek et al., 2009, 2013) in agreement with results.
showed in Fig. 5. Furthermore, natural organic matter could also lead to release thallium in soil by enhancing silicate alteration/weathering as suggested in some studies (Vanek et al., 2009; Ren et al., 2015). Tl(I) in critical zone conditions will behave more like a lithophile element close to alkaline metals (K⁺, Rb⁺ and Cs⁺). This conclusion is supported by observations made that illicite clay systems control the mobility of Tl(I) like for K⁺ and Cs⁺ (Jacobson et al., 2005a, 2005b; Voegelin et al., 2015; Wick et al., 2018; Martin et al., 2018). These results also point out that in rivers, Tl(I) is predominantly a highly bioavailable free ion (Tl⁺). Indeed, various studies highlighted that Tl(I) poorly reacts with particulate phases and remains mainly in the dissolved fraction as a free ion (Fig. 4) (Law and Turner, 2011; Boning et al., 2017). However, several questions regarding thallium remain open, especially the role of Tl(III) and its abundance/stability in the environment. Moreover, the present DMT approach would greatly help to make progress. Finally, in order to complete the database, Tl(III) interactions with other analogues of NOM should be studied.

3. Conclusion

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

Acknowledgments

The authors thank IRSN, CEA, BRGM and IPGP for funding this research Grant n° DEN 3841. Parts of this work were also supported by IPGP multidisciplinary program PARIS and by Region Ile de France SESAME Grant no. 12015908.

Appendix A. Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.04.001.

REFERENCES


