



Environmental factors determining the trace-level sorption of silver and thallium to soils

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Received 22 March 2004; accepted 15 October 2004

Available online 18 January 2005

Abstract

Silver (Ag) and thallium (Tl) are nonessential elements that can be highly toxic to a number of biota even when present in the environment at trace levels. In spite of that, the literature on the chemistry and fate of Ag and Tl in soils is extremely scanty. In that context, the key objective of this research was to compare the sorption characteristics of trace amounts of Ag and Tl on a range of soils and minerals. A second objective was to determine the extent to which the composition and surface chemistry of the sorbents, as well as other environmental factors (simulated acid rain application and the presence of competing ions like K^+ and NH_4^+) influence the sorption and lability of Ag and Tl. To this end, short-term and long-term sorption isotherms were generated under batch conditions for trace levels of Ag and Tl onto three illite-rich mineral soils from central New York (silt loam and fine sandy loam), a peaty-muck soil drained for agricultural use, and soil minerals (ferrihydrite and birnessite). Silver sorbed more strongly than thallium to all the soils. The peaty-muck soil sorbed Ag more strongly than the mineral soils, confirming that silver sorption to soils is dominated by soil organic matter either through exchange or complexation. The organic matter-rich soil's retention of Tl, however, was similar to that of the sandy soil. Amounts of Ag and Tl sorbed to the mineral soils increased after a 1-year incubation period. Whereas Ag sorption to the peaty-muck soil also increased with time, Tl sorption was unaffected. Short batch studies indicated that high amounts of Tl sorb to birnessite (30% by mass). However, subsequent X-ray diffraction (XRD) analysis of the solid did not detect the presence of any Tl^{3+} as Tl_2O_3 on the MnO_4 . In contrast, $Tl(I)$ was relatively poorly sorbed on noncrystalline ferrihydrite at pH 5.1 (1.5% by mass). Thus, Mn oxides may play a role in Tl retention by soils; whereas, contrary to previous reports, iron oxides do not effectively sorb Tl. Acid rain and addition of potassium (K^+) and ammonium (NH_4^+) as competing ions had no long-term effect on Ag or Tl sorption. Thallium remaining in the all the batch sorption solutions, as determined by flame atomic absorption spectroscopy (FAAS) and differential pulse anodic stripping voltametry (DPASV), was completely labile, which may have important environmental consequences.

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Keywords: Silver; Thallium; Sorption; Acid rain; Selectivity; Soil

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1. Introduction

Silver (Ag) and thallium (Tl) are nonessential trace metals. The monovalent silver ion is more toxic to fish than copper or mercury, and it is an extremely effective bactericide (Smith and Carson, 1977a). Thallium is more toxic to mammals than cadmium, lead, and even mercury (Nriagu, 1998). Yet, there is relatively little literature available regarding the fate of these potentially hazardous elements in terrestrial environments. Both Ag and Tl are included in the US EPA list of priority toxic pollutants.

In general, the Ag content of surface soils ranges from <0.01 to 5 mg kg^{-1} , with most reported values being $<1 \text{ mg kg}^{-1}$ (Mitchell, 1955; Vanselow, 1966; Boyle, 1968; Bradford et al., 1996; Sterckeman et al., 2002; Murray et al., 2004). However, Ag concentrations in soils impacted by industry (e.g., mean, $2.3 \pm 2.2 \text{ mg kg}^{-1}$) or by smelter activity (e.g., up to 2.4 mg kg^{-1}) may be 3–20 times the background (Sterckeman et al., 2002; Murray et al., 2004).

Worldwide, the Tl content of soils seems to depend largely on the geological origin of the parent material (Sager, 1998). In general, Tl concentrations in surface soils range from 0.1 to 2 mg kg^{-1} , with most reported concentrations being $<1 \text{ mg kg}^{-1}$ (Eschnauer et al., 1984; Sholl, 1980; Qi et al., 1992; Bradford et al., 1996; Tremel et al., 1997b). There are exceptions, however, such as the clayey soils developed on the Sinemurian limestone in France with natural Tl contents as high as 55 mg kg^{-1} (Tremel et al., 1997b). Examples of soils contaminated with Tl include soils near cement plants in Germany with concentrations as high as 15 mg kg^{-1} , soils near old mines in Germany with concentrations up to 73 mg kg^{-1} , and mine tailings-impacted soils in China with Tl concentrations up to 61 mg kg^{-1} (Sholl, 1980; Zhou and Liu, 1985).

At first glance, Ag and Tl appear to be remarkably similar. Both metals exist primarily in a +1 oxidation state, are of similar size, and form relatively insoluble compounds with halides (Cl^- , Br^- , and I^-), sulfate (SO_4^{2-}), and sulfides as well as soluble multihalide complexes (e.g., AgCl_4^{3-}). However, in arid moisture regimes, such as in the northeastern United States, typical concentrations of halides or SO_4^{2-} in the soil

solution may be too low to precipitate trace levels of Ag or Tl.

Information about Tl sorption by soils or soil minerals is limited and generally attributed to simple exchange mechanisms on organic matter or oxides with some speculation that micaceous clay minerals may selectively sorb Tl (Brooks, 1932; Crafts, 1934, 1936; Schoer and Nagel, 1980; Jovic, 1993; Tremel et al., 1997b; Tremel and Mench, 1997b; Martin and Kaplan, 1998; Il'in and Konarbaeva, 2000).

Sorption of silver to soils (Jones et al., 1986) has been modeled using Freundlich isotherms. This silver soil adsorption model, however, is based on relatively high concentrations of silver (100 – $1000 \text{ mg Ag (kg soil)}^{-1}$). Little is known about the sorption behavior of Ag at the low levels expected in soils. Soil organic matter (SOM) is known to bind Ag strongly (Jones and Peterson, 1986; Smith and Carson, 1977a) and thus may play an important part in controlling its cycling, mobility, and sorption in soils (Presant and Tupper, 1965; Jones et al., 1990). Both humic and fulvic acids have been shown to have strong retentive capacities of up to 30 mg kg^{-1} for silver (Chen et al., 1978; Jones and Peterson, 1986); thus, biologically available Ag is estimated to be $<5\%$ of the total silver concentration (Jones et al., 1984). In contaminated soils, however, this may be enough to adversely affect soil microbial populations.

Studies with silver in aquatic environments have shown that, as expected, given its soft, polarizable nature, Ag is strongly complexed to the reduced sulfur groups on organic matter (Benoit and Rozan, 1997; Adams and Kramer, 1998; Bell and Kramer, 1999). Since Tl is also a large, soft cation, it is predicted to display similar chalcophilic behavior in soil. Indeed, studies by Tremel et al. (1997a) and Tremel and Mench (1997a,b) show that Tl is accumulated by sulfur group-rich brassicas. In addition, studies with Tl in forest soils have found that very little moves down past the surface organic-rich layers of the soil (Heinrichs and Mayer, 1977).

The finding by Heinrichs and Mayer (1977), however, is partly based on the concentration of seepage water collected below the humus layer and tree root zone and thus does not necessarily distinguish between Tl sorption onto soil and Tl uptake by plants. This is an important point because the ionic radius of Tl^+ (1.49 \AA) is similar to that of

the hard cation, potassium (K^+ ; 1.33 Å), so that nondiscriminatory uptake of Tl^+ over K^+ has been suggested as a mechanism for its toxicity to biota (Smith and Carson, 1977b; Mulkey and Oehme, 1993; Tremel and Mench, 1997a). By the same reasoning, it has been proposed that Tl^+ and the similarly sized Ag^+ (1.31 Å) may, like the lithophilic K^+ , be incorporated into the interlayers of illitic or vermiculitic clays (Canney, 1952; Smith and Carson, 1977a,b; Tremel et al., 1997b). The importance of cation selectivity by illitic clays in determining Tl and Ag sorptive behavior is suggested by three types of studies—one designed to illustrate the existence of binding sites in clay minerals with different affinities for certain trace elements, a second indicating that K depletion in the rhizosphere enhances the sorption of certain elements by clay minerals, and a third reporting that the presence of ammonium (NH_4^+) may lead to the mobilization of other cations (Clausen and Karlog, 1977; Kuchenbuch and Jungk, 1984; Guivarch et al., 1999; Sanchez et al., 1999).

Thus, we have two priority pollutant trace metals, of similar size and charge, with affinities for lithophilic, chalcophilic, and organic materials. The clay-sized fraction of New York soils tends to be dominated by illite—the clay mineral purported to selectively retain potassium-like cations. However, New York soils are also subject to a udic moisture regime and acid rain, which promote the leaching of metal and salts. In addition, fertilization can temporarily result in elevated levels of K^+ and, occasionally, NH_4^+ , which could potentially compete with Ag and/or Tl for exchange sites on soil mineral and organic matter surfaces. The question is then: How will these two metals behave in complex soil environments under conditions such as those of the northeastern United States? In these studies, we investigate the dual lithophilic/chalcophilic tendencies of Ag and Tl by characterizing the sorptive behavior of environmentally significant trace levels of these metals to soil. Therefore, we use three central New York mineral soils with textures ranging from sandy loam (7% clay) to silt loam (21% and 26% clay), as well as an organic matter-rich peaty-muck soil (27% total organic carbon) and two oxides (ferrihydrite and manganese oxide) to examine the effects of soil texture, mineral content, and organic

matter content on Ag and Tl sorption. We also study the effect K^+ and NH_4^+ on Ag and Tl sorption. The studies are conducted using acid rain and both short-term (24 h) and long-term (6 months to 1 year) to give a more complete picture of their long-term retention in soils.

2. Materials and methods

2.1. Soils, soil properties, and soil characterization

Four uncontaminated soils from New York State, with different textures and organic matter contents, were used in this study (Table 1). In general, only the surface 0–12 cm of soil were collected, air-dried, and passed through a 2-mm stainless steel screen. The muck soil, however, was maintained in its field moist condition for both processing and experimentation. In addition, a subsurface horizon (20–40 cm) of the Hudson soil was collected in order to have a soil sample with a higher clay content. The three mineral soils, an Arkport fine sandy loam, a Genesee silt loam, and a Hudson silt loam, were collected in Tompkins County, NY. The organic matter-rich soil (peaty-muck) was collected in Orange County, NY, from a drained, former wetland area that is now under cultivation.

Soil pH was measured in 1:1 (mass of soil/mass of solution) suspensions of soil in 10 mM $CaCl_2$ for the mineral soils, and in a 1:2 (mass/mass) suspension of soil in 10 mM $CaCl_2$ for the organic matter-rich soil. CEC was determined by $BaCl_2$ saturation followed by $MgSO_4$ replacement according to the procedure by Rhodes (1982). The extracts were analyzed for Mg by flame atomic absorption spectroscopy (FAAS; Perkin-Elmer 2380 Atomic Absorption Spectrophotometer). Total organic carbon and total carbon were measured using an OI Analytical Total Carbon Analyzer Solids Module. Texture analysis was performed by the pipette method at the Soil Testing and Plant Analysis Laboratory, Cornell University. The clay fraction was treated with sodium acetate at pH 5 at 100 °C for 30 min three times to remove soluble salts according to a procedure used by the Soil Testing and Plant Analysis Laboratory at Rutgers University. Organic matter was removed from the clay fraction with sodium hypochlorite at pH 9.5

Table 1

Selected soil characteristics. The exchangeable cations were extracted with BaCl₂. Inorganic noncrystalline oxides were determined as the difference between the amount of metal extracted with acid ammonium oxalate and that extracted with sodium pyrophosphate. Organically complexed metals were determined by extraction with sodium pyrophosphate. A qualitative indication of the relative amounts of each clay mineral present in the soils is given by the number of stars, with * being the least amount, ***** the most, and below detection (~1%)

	Arkport surface <i>fsl</i>	Genesee surface <i>sil</i>	Hudson surface <i>sil</i>	Hudson sub- surface <i>sil</i>	Orange county <i>peaty- muck</i>
pH	5.3	6.6		7.1	5.1
% TOC	3.1	5.2		0.6	27.4
% Total C	3.2	5.8		1.0	35.1
CEC (mmol kg ⁻¹)	25	161		71	791
<i>Exchangeable cations [mmol kg⁻¹]</i>					
Na	0.098	0.162	0.084	0.114	0.199
K	1.66	2.05	7.62	3.14	1.01
Ca	33.1	107	81.6	59.7	424
Mg	1.35	4.69	2.67	1.41	9.87
Fe	<0.005	<0.005	<0.005	<0.005	<0.024
Al	0.428	0.143	0.285	<0.670	<0.292
Mn	0.275	0.089	0.027	0.007	0.060
<i>Inorganic noncrystalline oxides [mmol kg⁻¹]</i>					
Fe	10.0	21.1	14.8		18.1
Al	4.1	13.4	8.1		10.3
Mn	0.9	3.1	1.0		1.3
<i>Organically complexed metals [mmol kg⁻¹]</i>					
Fe	2.0	4.4	4.4	3.2	
Al	1.7	3.9	3.3	2.3	
Mn	0.3	1.0	0.5	0.2	
<i>Texture</i>					
% Sand	77	9	9	6	
% Silt	16	70	68	68	
% Clay	7	21	23	26	
<i>Clay mineralogy</i>					
Illite	*****	*****	*****	*****	
Chlorite	*	**	**	**	
Smectite	—	—	—	—	
Quartz	*	*	**	*	

(Moore and Reynolds, 1989). The mineral composition of the soluble salt-organic matter-free clay fraction, was determined by X-ray diffraction (XRD) of powdered samples, and oriented samples following K and glycerin saturation (Whittig and Allardice, 1986).

Acid ammonium oxalate (noncrystalline inorganic and organically complexed) forms and sodium pyrophosphate (organically complexed) forms of Al and Fe were determined according to the method described by Ross and Wang (1993). The exchangeable cations (Al, Ca, Fe, K, Mg, Mn, and Na) were determined by the BaCl₂ method (Hendershot et al., 1993). The extracts were analyzed for the cations by atomic FAAS (Laboratory Instrument aa/ae Spectrophotometer 551 or Perkin Elmer 372 Atomic Absorption Spectrophotometer). Finally, the electrical conductivity of the soils was determined on saturated pastes with a YSI model 31 conductivity bridge and a model 3418 conductivity cell ($K=0.1 \text{ cm}^{-1}$) (McRae, 1988).

2.2. Batch studies

Short-term Ag and Tl sorption isotherms were obtained by equilibrating 2.5 g of soil with 25 ml of Ag or Tl solution in 50 ml of polycarbonate, Oakridge centrifuge tubes for 24 h on a translational shaker at low speed (3.3 oscillations s⁻¹). Calcium nitrate was chosen as the background electrolyte to avoid using K or NH₄, which might compete with Ag or Tl for sorption within the clay interlayers, or Na, which might enhance soil dispersion. In addition, Ca is, by far, the dominant extractable cation in these soils (Table 1); thus, Ca addition from the electrolyte was only 2% (peaty muck) to 31% (Arkport) of the extractable Ca (by mass) and its impact on the soil/solution chemistry probably minimal. The Ag and Tl solutions, at 0, 20, 40, 60, 80, and 1000 μM concentrations, were prepared from reagent-grade nitrate salts, either in 1 mM Ca(NO₃)₂ or in a synthetic acid rainwater (Richards, 1998), to result in potential loadings of Ag or Tl on soil of 0, 200, 400, 800, or 100 μmol g⁻¹. The long-term sorption isotherms were generated using 1.5 g of soil and 15 ml of Ag or Tl solution at 0, 40, 60, 80, 100, and 120 μM concentrations, in 20-ml polyethylene scintillation vials, for 180, 261, or 403 days. The samples were placed on a translational shaker overnight for 1 week, then one night a week for the first 2 months, one night a month until the end, and for 24 h prior to centrifugation. All the samples and standards were equilibrated and/or stored at room temperature

(21 ± 2 °C) and kept in the dark to prevent possible photoinduced reactions of the Ag or Tl from occurring. Since the muck soil was used in its field moist state (58% moisture), the amount of muck used was increased by 4.6 g to yield 2.7 g of dry muck. Similarly, the Ag and Tl solution concentrations were increased so that the final solution concentration would be the same as for the mineral soils after dilution with the moisture in the muck. The final muck (dry mass)/solution ratio was 1:10 as it was for the mineral soils.

Following the equilibration period, the samples were centrifuged at $30,900 \times g$ for 10 min and then filtered through 0.2- μm cellulosic microsep filters. Analysis of standard solutions of Ag and Tl treated in the same manner as the samples, including filtration, and spanning the sample concentrations revealed no detectable loss or sorption of these elements to the labware or filters. Similarly, blank solutions run through the experimental procedure were below detection limits for Ag and Tl. The filtrates were analyzed for pH, and either total Ag or total and labile Tl. Total Tl was measured by FAAS (Perkin Elmer 2380 or 372 Atomic Absorption Spectrophotometer), whereas labile Tl was analyzed by differential pulse anodic stripping voltametry (DPASV; Princeton Applied Research model 303A Hanging Mercury Drop Electrode, and model 264B Polarographic Analyzer, Princeton, NJ, USA). The detection limits for Tl were 0.2 μM by FAAS and 5 nM by DPASV. Total silver was analyzed by FAAS or by axial view inductively coupled argon plasma optical emission spectroscopy (ICP-OES; SPECTRO Analytical Instruments, SPECTRO CIROS^{CCD}) fitted with a short depth-of-field lens transfer optic (Rutzke, 1999, 2000). The detection limits for Ag were 0.2 μM by FAAS and 10 nM with the modified ICP-OES.

2.3. Sorption of thallium onto oxides

2.3.1. K_{sat} -birnessite

The sorption of Tl(I) onto K_{sat} -birnessite was investigated under conditions chosen to approximate those of the batch studies. The laboratory-synthesized birnessite was prepared by the HCl-KMnO₄ method of McKenzie (1970). The resulting oxide had a zero point-of-charge of 3.6 and surface area

of 25.7 m² g by BET (McBride, 1989). The oxide was poorly crystalline with individual particles that were submicrometer in size and spheroidal (McBride, 1989). For the sorption study, 20 mg of the birnessite was wetted overnight with 20 ml of a solution containing 8.375 mM Ca(NO₃)₂ and 12.5 mM MES (2-(*N*-morpholino) ethane sulfonic acid) buffer adjusted to pH 6.1 with KOH. The samples were then spiked with 5 ml of solutions containing Tl at 0, 0.8, 1.6, 3.2, 4.0, 8.0, 80.0, 800, and 8000 μM . The final solutions were 6.7 mM Ca(NO₃)₂ and 10 mM MES, and the final potential loadings Tl on birnessite were 0, 0.2, 0.4, 0.8, 1.0, 2.0, 20.0, 200, 2000, 6900, and 13,800 $\mu\text{mol g}^{-1}$. The samples were equilibrated for 6 days on a translational shaker at low speed, then centrifuged, filtered, and analyzed for total Tl and Mn in solution by FAAS as described for the batch studies. Samples of birnessite solid with the highest Tl loadings were freeze-dried and analyzed by XRD for evidence of Tl⁺ oxidation to Tl³⁺.

2.3.2. Ferrihydrite

To investigate Tl(I) sorption onto iron oxides, solutions of TlNO₃ in Ca(NO₃)₂ and 5.33 mM MES adjusted to pH 6.5 with Ca(OH)₂ were prepared. These solutions (15 ml) were added to a 5-ml suspension (38.8 mg ml⁻¹; pH 3.73) of laboratory-synthesized ferrihydrite. The ferrihydrite was precipitated by the rapid titration of a Fe(NO₃)₃ solution to pH 6 with alkali in the presence of CO₂. It has a surface area of 170 m² g⁻¹, is predominantly non-crystalline, and is highly reactive as described by Martínez et al. (1999). The resulting 20-ml solution contained 4 mM MES, 2 mM Ca(NO₃)₂, and 0, 0.25, 0.5, 1, 5, 10, or 50 mM Tl. This produced potential loadings of Tl on ferrihydrite of 0, 0.026, 0.052, 0.10, 0.52, 1.03, and 5.15 $\mu\text{mol g}^{-1}$. The samples were equilibrated for 24 h on a translational shaker at low speed, then centrifuged, filtered, and analyzed for total Tl in solution by FAAS as described for the batch studies. Duplicate samples were prepared for every Tl concentration.

2.4. Selectivity

The influence of potassium (K⁺) and ammonium (NH₄⁺) on the sorption of Ag and Tl was

investigated by equilibrating 1.5 g of soil with 15 ml of solution containing 100 μM Ag or Tl and increasing concentrations of K^+ or NH_4^+ from 25 to 2500 μM in a background electrolyte solution of 1 mM $\text{Ca}(\text{NO}_3)_2$. The short-term effects were studied on samples equilibrated for 24 h, while longer-term effects were studied after a 1-year equilibration period. As with the sorption batch studies, 50-ml polycarbonate centrifuge tubes were used for the short-term studies and 20-ml polyethylene scintillation vials were used for the 1-year equilibration samples. The amount of muck soil as well as the solution volume and concentrations of Ag or Tl, and K^+ or NH_4^+ were adjusted as described in the batch studies. Following the equilibration periods, the samples were centrifuged, filtered, and analyzed for pH and total Ag or Tl as described for the batch studies.

3. Results

3.1. Ag and Tl sorption to soils

The Ag and Tl sorption isotherms for the four soils investigated are shown in Fig. 1. Precision for all the duplicate Ag and Tl measurements is such that the standard deviation error bars are smaller than the symbols in the plots shown in this figure. Preliminary time studies indicated that Ag and Tl sorption reach steady state within 24 h. Neither Ag^+ nor Tl^+ hydrolyzes strongly in solution. The pH of the soils was not externally buffered, and while the pH in each soil changed after the addition of Ag or Tl, these slight changes (generally within 0.3 pH units) were not correlated with the amount of element added. Also, there were no notable changes in pH between the short- and long-incubation time samples for each element and soil.

More Ag than Tl sorbed to all the soils. After 24 h, Ag sorption increased in the order:

muck > Hudson surface > Genesee > Hudson subsurface
> Arkport

As with Ag of the mineral soils, the Arkport sorbed the least amount of Tl. In complete contrast to Ag, however, the peaty-muck sorbed just as little Tl in

24 h as the Arkport. Thus, after 24 h, Tl sorption increased in the order:

Genesee \approx Hudson subsurface > Hudson surface
> Arkport \approx muck

The only element/soil sorption that was not affected by extending the sorption time was Tl sorption to the peaty muck. Although the effect of increasing the sorption period of Tl to 261 days was not pronounced for the three mineral soils, Tl sorption to the Arkport soil increased with time and Tl sorption to the Genesee soil increased to a greater degree than sorption to the Hudson subsurface, resulting in a more distinct sorption isotherm order than after 24 h. Thus, the order of Tl sorption to the soils after 261 days is clearly:

Genesee > Hudson subsurface > Hudson surface
> Arkport > muck

Duplicate samples of Tl sorbed to Hudson subsurface and Genesee soils for 403 days did not change from the 261-day isotherms. Despite the high level of Ag sorption observed after 24 h, Ag sorption increased when the sorption period was increased to 1 year. Whereas some scatter was evident in the Ag isotherm for the sandy Arkport soil, the isotherms for the other soils became virtually indistinguishable with time so that in terms of Ag sorption:

muck \approx Hudson surface \approx Genesee
 \approx Hudson subsurface \gg Arkport

The nearly perfect alignment of the open circles/triangles and closed circle/triangles in Fig. 1 suggests that changing the matrix from $\text{Ca}(\text{NO}_3)_2$ to synthetic acid rain had no effect on the sorption behavior of Ag or Tl in these well-buffered soils, even with time, except for the 1-year Ag sorption to Arkport isotherm, which became more scattered.

3.2. Effects of K^+ and NH_4^+ on Tl and Ag sorption

Competitive effects of K^+ and NH_4^+ on the sorption of Tl^+ and Ag^+ to the Arkport, Hudson subsurface, Genesee, and muck soils can be seen in Figs. 2 and 3. While the pH of the soil solution changed from that of the untreated soil, it was only affected by the highest amount of competing cation added to the soils and only for the 24-h reaction time. The presence of up to 25 times as much K^+

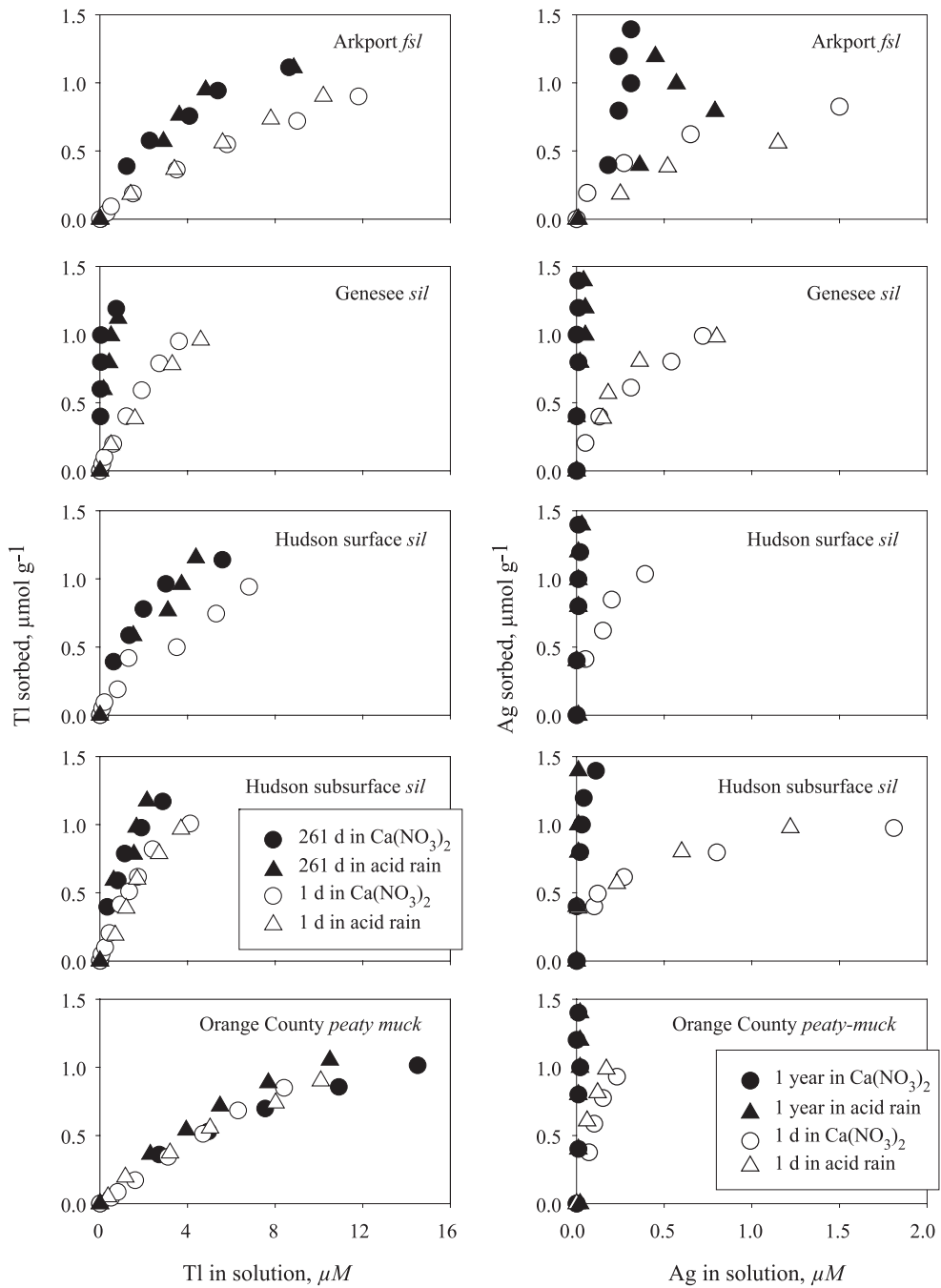


Fig. 1. Sorption isotherms of thallium and silver in New York soils. Circles represent sorption in a 1-mM $\text{Ca}(\text{NO}_3)_2$ matrix. Triangles represent sorption in synthetic acid rain reacted for the same amount of time as those in $\text{Ca}(\text{NO}_3)_2$. Each symbol is the mean of duplicate samples. The 1 S.D. error bars are smaller than the symbols.

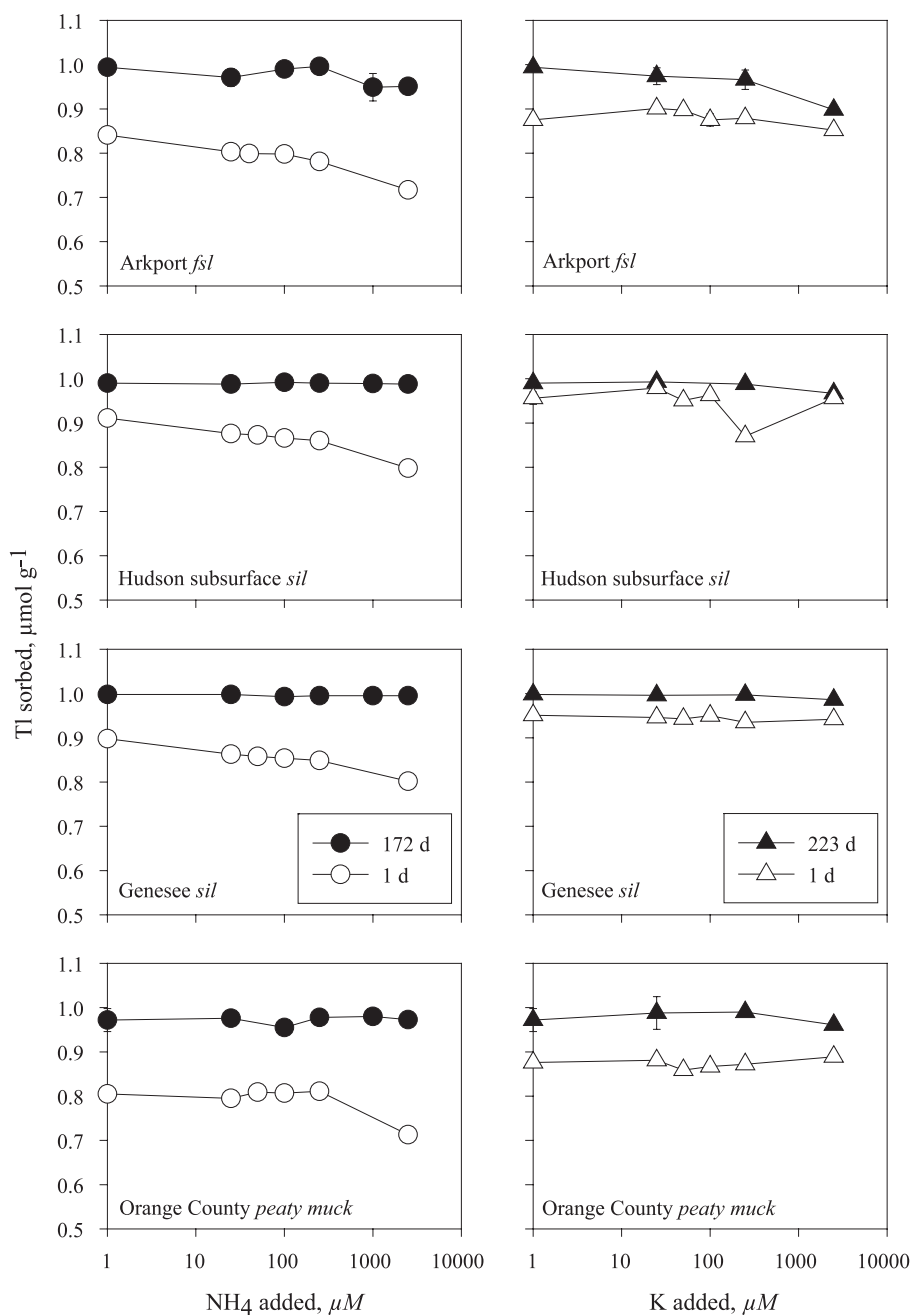


Fig. 2. Effect of increasing concentrations of K^+ or NH_4^+ on Tl sorption. Each symbol is the mean of duplicate samples. The 1 S.D. error bars that are not visible are smaller than the symbols.

or NH_4^+ as Tl^+ or Ag^+ seems to have no effect on the long-term sorption (172–223 days) of Tl or Ag. Similarly, the addition of K^+ has no noticeable

effect on the 24-h sorption of Tl. However, the addition of NH_4^+ at 25 times the concentration of Tl^+ depressed Tl sorption in all the soils. The 24-h

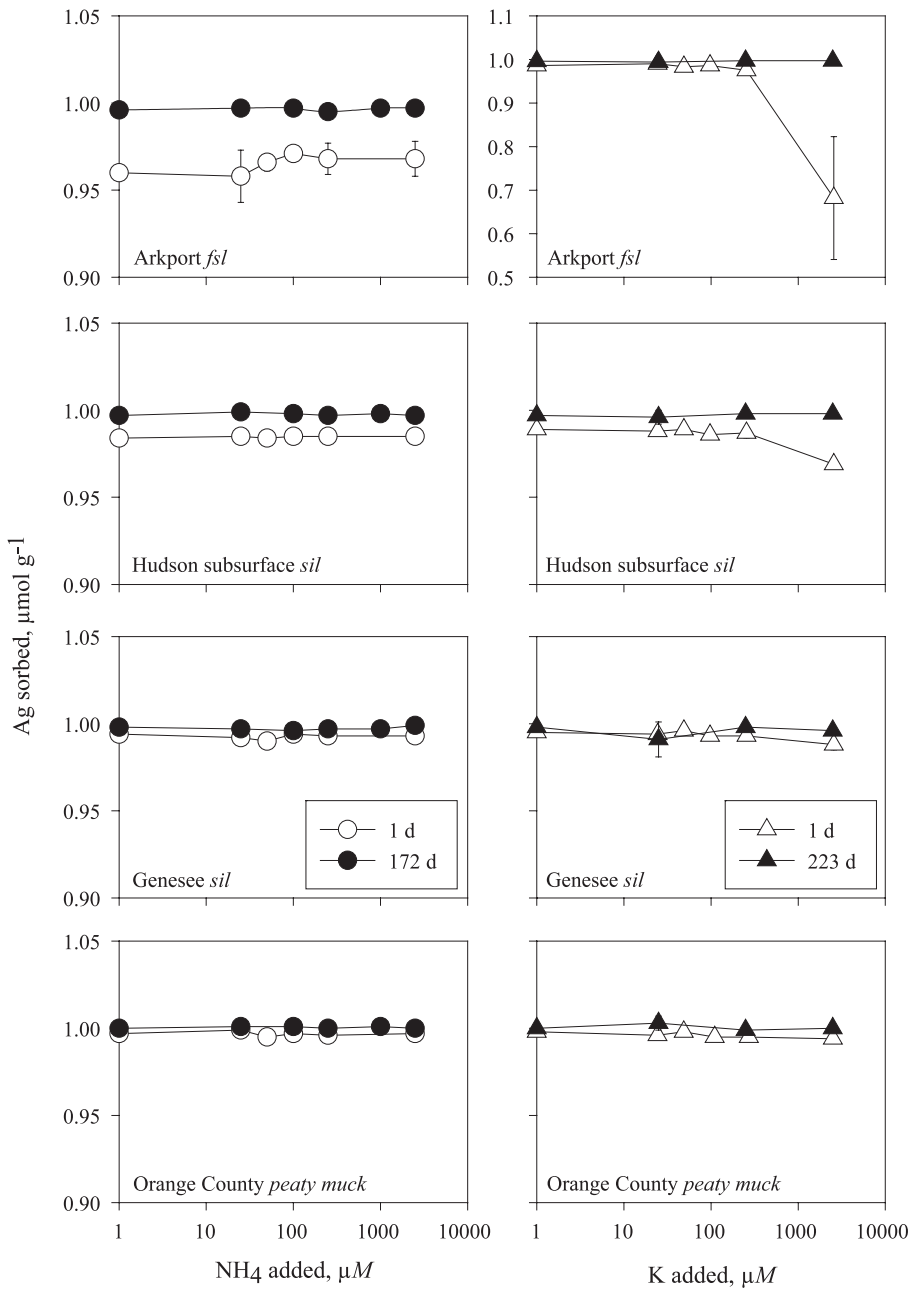


Fig. 3. Effect of increasing concentrations of K^+ or NH_4^+ on Ag sorption. Each symbol is the mean of duplicate samples. The 1 S.D. error bars that are not visible are smaller than the symbols.

sorption of Ag^+ to the four soils seems unaffected by the presence of NH_4^+ . Likewise, K^+ had no effect on the 24-h sorption of Ag^+ to the organic matter-rich Genesee and muck soils, although at the

highest levels added, K^+ slightly depressed Ag sorption to the Hudson subsurface soil and significantly depressed Ag sorption to the sandy Arkport soil.

4. Discussion

4.1. The effect of SOM

The sorption results from these experiments demonstrate that organic matter content could be a dominant factor in Ag sorption but not in Tl sorption by soils. This behavior is consistent with the reportedly strong complexation of Ag by humic and fulvic acids, and by SOM, especially thiol groups, as well as with the allegedly weak complexation of Tl with most organic ligands ($\log K$, 0.5–2), fulvic acids ($\log K$, 3.32–4.83), and humic acids (Sillen and Martell, 1964; Boyle, 1968; Lee, 1971; Smith and Carson, 1977a,b; Jones and Peterson, 1986; Kaplan and Mattigod, 1998). Given the electron configurations of Tl(I) ($[\text{Xe}] 4f^{14} 5d^{10} 6s^2$) and Ag(I) ($[\text{Kr}] 4d^{10}$), it might be expected that Tl(I) would be more reactive than the nobly configured Ag(I). However, the two electrons in Tl(I)'s outer $6s$ orbital are σ -antibonding electrons and thus resist covalent bonding; whereas two electrons in the Ag(I)'s $4d_{z^2}$ orbital are able to move to its empty $5s$ orbital, leaving the $4d_{z^2}$ orbital free to form relatively strong bonds with

vertically aligned orbitals (Durrant and Durrant, 1970; Lee, 1971).

Among the different functional groups on SOM, Ag^+ forms especially strong complexes with thiol groups to the extent that it can displace or replace metals more weakly complexed to thiols such as Fe in $>\text{S}-\text{Fe}-\text{S}<$ groups (Manolopoulos, 1997). Although Tl will also bind to sulfide groups, it is not as polarizable as Ag and if specific metal complexing sites on organic matter are occupied by other cations, the slightly “harder” Tl is more likely to loosely associate with exchange sites on the SOM. Given the great quantities of O^- functional groups on OM, it is not surprising that GEOCHEM-PC calculations by Kaplan and Mattigod (1998) suggest that 16% of the total dissolved Tl(I) would complex to fulvic acid in typical river waters (5 mg l^{-1} organic carbon), and that up to 67% of the Tl could complex to fulvic acid in typical bog waters (30 mg l^{-1} organic carbon). Our analyses of the Tl sorption soil solutions by DPASV indicate that all the Tl remaining in solution is labile (Fig. 4). That is, all the Tl is present either as free Tl^+ , or as weak or small organic complexes that are readily converted to free Tl^+ , in all four of the soils tested—

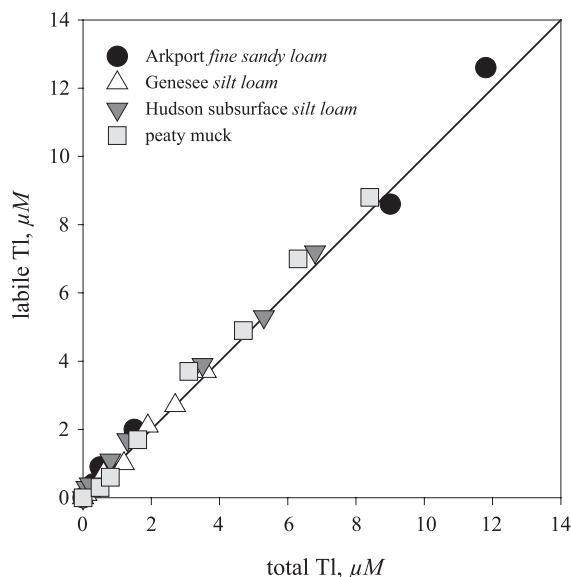


Fig. 4. Plots showing the 1:1 correspondence of labile Tl (measured by DPASV) and total Tl (measured by FAAS) remaining in the soil solution. These values were measured in the 24-h sorption samples in $1 \text{ mM Ca}(\text{NO}_3)_2$, but the relationship did not change with time or matrix. Each symbol is the mean of duplicate samples. The 1 S.D. error bars are smaller than the symbols.

including the highly organic peaty-muck. Considering the high total lability of Tl together with its suspected high bioaffinity based on observations of its indiscriminant uptake with K^+ , a noteworthy implication of these results is that the entire solution concentration of the highly toxic element meets the basic conditions for bioavailability as outlined by Van Leeuwen (1999).

4.2. Influence of CEC

Since Tl is known to resist complex formation, most of its sorption has been attributed to simple exchange. Thus, higher sorption of Tl to the muck than the Arkport fine sandy loam might be expected just on the basis of the large difference in CEC (muck, 791 mmol kg^{-1} ; Arkport, 25 mmol kg^{-1}). However, Tl may not be able to effectively displace the high concentrations of divalent Ca on the exchange sites, especially considering that the background electrolyte also contains Ca (1 mM). The concentrations of exchangeable Na^+ and K^+ on the Arkport (0.098 and $1.66 \text{ mmol kg}^{-1}$, respectively) and on the muck (0.199 and $1.01 \text{ mmol kg}^{-1}$, respectively) are quite similar. Tl exchange would be expected to be more competitive for these monovalent cations and thus could explain the similarity in short-term Tl sorption to these very different soils.

Exchange reactions are also purported to play an important role in Ag^+ sorption to soils (Dyck, 1968; Anderson et al., 1973). This may partly explain why more Ag^+ sorbs to the Hudson subsurface soil than to the Arkport despite a more than three times higher concentration of TOC, which we have indicated should dominate Ag sorption behavior in the Arkport soil. First of all, the Hudson subsurface soil has a higher pH than the Arkport (7.1 vs. 5.3), which results in more negatively charged sites. Compared with the Arkport soil, the Hudson subsurface soil is finer-textured with a higher surface area, and contains more noncrystalline oxides and higher concentrations of the more easily displaced monovalent cations. In this case, the Hudson subsurface CEC is almost three times that of the Arkport, resulting in higher Ag sorption.

4.3. Effect of oxides

The Genesee silt loam sorbed just as much Tl in 24 h as the Hudson subsurface soil, and considerably

more after a 261-day incubation period, despite having a lower clay content and pH. The CEC of the Genesee soil is much higher than that of the Hudson subsurface due largely to its TOC content. While this may partly explain the elevated Tl sorption to the Genesee soil, another possibility is that the slightly higher concentration of noncrystalline Mn oxides present in the Genesee soil relative to the Hudson subsurface soil may be responsible for the observed differences. Manganese oxides display an especially strong affinity for Tl as its enrichment in oceanic manganese nodules and certain US Mn deposits attests (Shaw, 1952; Smith and Carson, 1977b). Although the acidic character of $\delta\text{-MnO}_2(\text{s})$ may initiate this behavior, the actual mechanism for the close association is believed to be the oxidation of Tl^+ to Tl^{3+} , which is then tightly sorbed to the Mn oxide surface or is precipitated on the Mn oxide surface as Tl_2O_3 (Kozawa and Yeager, 1965; Rao-gadde and Laitinen, 1974; Bidoglio et al., 1993; Dahal and Lawrance, 1996). This redox mechanism is especially relevant to the Genesee soil, which has distinctive mottling and redoximorphic features in its lower horizons. The increase in Tl sorption with time that we observed in the Genesee soil may be due to retarded reaction rates attributable to the amorphous nature of the oxides in the soil and the stability of Tl^+ in aqueous solution, or perhaps the experimental conditions. We conducted a small batch experiment with Tl^+ and a K^+ -saturated synthetic birnessite under conditions similar to those of the sorption batch experiments with the soils. While a significantly high concentration of Tl sorbed to the oxide (1.5 mmol g^{-1} or $\sim 30\%$ by mass), XRD analysis of the solid subsequent to the sorption reaction did not detect the presence of any Tl^{3+} as Tl_2O_3 . However, the detection limit for Tl_2O_3 by XRD is approximately 1%, so it is possible that some oxidation had occurred although not to any significant extent. It is also possible that experimental conditions interfered with the redox reaction, the precipitate was too amorphous, another Tl^{3+} species such as $Tl(\text{OH})_3$ formed, or that the reaction time (7 days) was too short.

In one of the few Tl field studies, Tl_2SO_4 was applied to a highly weathered soil in South Carolina, USA. Martin and Kaplan (1998) reported that thallium displayed low mobility during a 30-month period and suggested that iron and aluminum oxides,

as well as some hydroxy-interlayered vermiculite, were responsible for retaining the Tl in these soils. First of all, it is not clear from the data presented that Tl was highly retained in the soil. Bush beans planted a month after the Tl application failed to germinate presumably due to Tl toxicity. One year later, however, planted beans did grow, suggesting that the Tl concentration had been sufficiently lowered. The surface of soil was limed to pH 6.5; so that, a higher pH-related CEC, and the slightly higher OM content could explain the Tl retention observed at the top of the soil profile. The unlimed subsoil is at pH 5.1. Data indicate that some Tl is moving to the subsoil since the fraction of the total Tl extracted from the soil increased with time in the subsoil. However, such data only indicate how much of an element is retained by the subsoil, not how much has passed through it (Baveye et al., 1999). Secondly, given the low adsorption constants for Tl(I) on iron oxide, it is unlikely that it could be responsible for retaining Tl—especially at pH 5.1. The results of a simple batch study we conducted, of Tl(I) sorption on noncrystalline ferrihydrite at pH 5.1, indicate that Tl is extremely poorly sorbed by the oxide. At a potential Tl on ferrihydrite loading of $5.15 \text{ mmol kg}^{-1}$, only $0.07 \text{ mmol kg}^{-1}$, or 1.5% of the potential load, was retained. Although Tl sorption to iron oxides should increase slightly at pH values closer to the zero point-of-charge of the mineral (pH 7.8), it is clear that at the pH of the South Carolina soil, and certainly at pH 3, synthetic iron oxides do not significantly sorb Tl(I). The oxides occurring naturally in soil, however, are more complex than the model oxides synthesized in the laboratory due to the presence of other ions and organic matter during their formation and crystallization. Furthermore, in pseudoenvironments, oxides may be coated with clay or organic matter films, effectively changing the sorptive surface. Thus, it may be clay films that are responsible for the observed Tl retention in the South Carolina soils. In the present study, however, Tl retention by the Genesee and Hudson soils that is attributable to oxides must be due to Mn rather than Fe oxides.

One of the reasons given for silver immobility in soils with $\text{pH} > 4$ is that Ag sorbs readily to oxides, particularly iron and manganese oxides, largely by exchange processes (Dyck, 1968; Anderson et al., 1973; Smith and Carson, 1977a). However, Anderson

et al. (1973) found that the amount of silver sorbed to the manganese oxide is more related to the amount of occluded K and/or Na on the mineral rather than its surface area, and that Ag exchange for structural K, Na, and/or Mn in the mineral structure was another important factor governing its sorption. Thus, structural exchange in poorly crystalline oxides may partially explain the increase in Ag sorption to the soils over time—especially to those such as the Arkport and Hudson subsurface that have low OC contents.

4.4. Effect of NH_4 and K on Ag and Tl sorption

Since K^+ and NH_4^+ compete for many of the same sites as Ag^+ and Tl^+ , on soil minerals, and since they may be present at elevated concentrations in soils due to fertilizer additions or accumulation in cool, moist environments, we investigated their effects on Ag and Tl sorption. A classic selectivity study, in which the ratios of Ag^+ or Tl^+ to K^+ or NH_4^+ are varied, was not a viable option because it would have been impossible to completely remove all the K^+ from the soils. Therefore, we simply added increasing increments of K^+ and NH_4^+ to the soils starting at $25 \text{ } \mu\text{M K}^+$ ($\sim 1 \text{ mg l}^{-1}$ is commonly found in the soil solution of these soils) and going up two orders of magnitude to $2500 \text{ } \mu\text{M}$. Ammonium was added to a second set of soil samples, at the same concentration as K^+ , for comparison.

The total maximum amount of cations added to the soils ($54 \text{ } \mu\text{mol}$) is much less than the cation exchange capacities of the Genesee ($240 \text{ } \mu\text{mol}$) and muck ($1190 \text{ } \mu\text{mol}$) soils; therefore, it is not surprising that K and NH_4^+ had no effect, in general, on Ag or Tl sorption to these soils (Figs. 2 and 3). The amount of cation added exceeds the cation exchange capacities of the Arkport ($38 \text{ } \mu\text{mol}$) and is just over half that of the Hudson subsurface ($107 \text{ } \mu\text{mol}$) which explains the drop in Ag sorption with K^+ on these low organic matter soils (exacerbated by a drop in pH in these two samples) but then begs the question of why the same effect is not seen with Tl and the two cations or with Ag and NH_4^+ . A possible explanation for the Ag results was alluded to above: Ag binds strongly to thiol groups. It also forms linear complexes with amine and NH_4^+ groups (Cowan et al., 1985). Thus, there could be some $-\text{N}-\text{Ag}-\text{N}-$ or $-\text{S}-\text{Ag}-\text{N}-$

ternary complexes forming on the soils that diminish the competitive effect of NH_4^+ . The lack of effect of K^+ on Tl sorption to the Arkport and Hudson subsurface soils might be indicative of specific sorption of Tl at the illitic clay interlayer. This suggests that Tl is sorbed preferentially to K at these sites, which is reasonable given its lower hydration energy. The illitic clay wedge sites are purported to have a higher affinity for NH_4^+ than K^+ (Sanchez et al., 1999) and, at least in the short term, appear to also be slightly preferred to Tl as the slight drop in Tl sorption at the high NH_4^+ concentration implies. The drop in Tl sorption in the high CEC muck soil that does not contain detectable amounts of illite remains unexplained. With time, however, all the metals added to the soils were sorbed, which serves to illustrate the high sorptive capacity of these soils for trace levels of Ag and Tl.

5. Conclusions

The research described in this article confirms that silver sorption to soil is dominated by SOM either through exchange or complexation. Over time, however, illitic clays and oxides also appear to be important in retaining silver. Irrespective of soil type or time, silver is more strongly sorbed than thallium. Another difference in the sorption behavior of the two elements is that Tl sorption is dominated by illitic clay content and only weakly affected by SOM. In the long term, Mn oxides may also play a role in Tl retention by soils; whereas, contrary to previous reports, iron oxides do not effectively sorb Tl. Given the high CEC and buffering capacity of the soils used in this research, neither the addition of K^+ and NH_4^+ , nor the presence of acid rain, had a long-term effect on Tl or Ag sorption. The partitioning of Tl between soil solids and solution has important environmental implications because Tl in solution is completely labile and potentially highly bioavailable.

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