

THE DESORPTION OF SILVER AND THALLIUM FROM SOILS IN THE PRESENCE OF A CHELATING RESIN WITH THIOL FUNCTIONAL GROUPS

ASTRID R. JACOBSON^{1,*}, SONDR A KLITZKE², MURRAY B. McBRIDE¹,
PHILIPPE BAVEYE¹ and TAMMO S. STEENHUIS³

¹*Department of Crop and Soil Sciences, Cornell University, Bradfield Hall, Ithaca,
NY 14853, U.S.A.*; ²*Department of Soil Science, University of Trier, 54286 Trier, Germany*;

³*Department of Biological and Environmental Engineering, Cornell University, Riley-Robb,
Ithaca, NY 14853, U.S.A.*

(*author for correspondence, e-mail: arj5@cornell.edu, Tel: (607) 255-3156, Fax: (607) 255-8615)

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Abstract. Silver (Ag) and thallium (Tl) are non-essential elements that are toxic to many biota at trace levels, but are rarely studied in soil environments. Ag sorbs strongly to soils, especially those rich in organic matter whereas Tl sorption is influenced by clay content. However, the mobility and bioavailability of Tl and Ag are ultimately affected less by the soil sorptive capacity than by the ease with which these elements desorb from soils. In that context, the strength of Ag and Tl sorption to illite-rich mineral soils with differing textures and an organic peaty-muck soil, from New York State, was investigated by studying their desorption using, as a sink for the metals, a resin (Duolite G-73) containing a thiol functional group. Desorption was monitored over time (1 h, 4 weeks) from soils previously equilibrated with Tl⁺ or Ag⁺ for 24 h (steady-state) or for up to 1 year. Within 24 h, 60% of the sorbed Tl was recovered by the resin. Within 2 weeks, 80–100% of the Tl desorbed from all four soils equilibrated for both 24 h and 1 year periods. Ag was not effectively recovered from the resin. However, qualitative review indicates that more Ag was desorbed after the 24 h sorption period than after the 1 year period. More Ag desorbed from the sandy soil than from the peaty-muck soil or the mineral soils with higher clay contents. However, within two weeks silver was mobilized from the peaty-muck soil. The observed release of Ag and Tl from soils, coupled with their toxicity at trace levels to a broad range of soil organisms, suggests that they may pose an environmental concern when present in soils at elevated concentrations.

Keywords: desorption, Duolite G-73, silver, soil, thallium

1. Introduction

Silver (Ag) and thallium (Tl) are non-essential trace elements that are rarely studied in soil environments. Geochemical concentrations of Ag and Tl are largely dependent on the parent material and concentrations generally range from <0.01 to >5 mg kg⁻¹ (Goldschmidt, 1954; Nriagu, 1998). Thallium is used in limited quantities, mostly by high tech industries, in the production of semiconductors, high refractivity optical glass, and photosensitive devices (Smith and Carson, 1977a; US EPA, 1992; Nriagu, 1998). However, the close association of thallium to sulfur ores and its isomorphic substitution for potassium leads to its environmental release



from nonferrous mining, metal works, coal combustion, and cement plants (Schoer, 1984). Much more silver is consumed industrially than thallium. Its photoreactive and conductive properties make it indispensable to photographic manufacturing (50% of all industrial demand) and the manufacture of electrical contacts and conductors (15% of demand) (Purcell and Peters, 1998). Due to the value of the metal and environmental concern, there is an increasing trend to reclaim silver from waste. However, an estimated 2×10^6 kg Ag yr⁻¹ is lost in the US of which 68% ends up on land as solid waste (Scow *et al.*, 1981; Purcell and Peters, 1998). In addition, the atmospheric deposition of Ag resulting from the burning of coal or from smelting contributes trace amounts of Ag to soils. The distinction between naturally occurring Tl and that released through anthropogenic activity is important because the latter tends to be more exchangeable and bioavailable than the former, which is generally incorporated in the structure of the solid phase (Kaplan and Mattigod, 1998). As with Tl, it is the anthropogenic loading of Ag in soils that is of concern.

Metal loading or sorption, however, is not a permanent condition because changes in soil environments (e.g., temperature, pH, redox, the composition of the soil solution, microorganism and mesofaunal populations and their activity) may affect the partitioning of metals between the solid and solution and may lead to metal release and thus, mobilization. Desorption, however, is not studied to the same degree as sorption. For some metals such as Ag this is because they are believed to be so strongly sorbed to soil surfaces, or to readily form such insoluble salts and/or compounds, that desorption is assumed to be negligible. Other metals, such as Tl, that are primarily held onto soil surfaces by weak electrostatic interactions are assumed to be easily desorbed and highly mobile. Tl is moderately toxic to microbes (e.g., 0.82–8.2 mg L⁻¹ Tl⁺ in a soil suspension completely inhibits nitrate formation by *Nitrobacter agilis*; Smith and Carson, 1977a, and references therein) but is highly toxic to humans (average reported lethal dose of soluble salts is 10–14 mg kg⁻¹; Repetto *et al.*, 1998, and references therein). Comparatively, Ag is more toxic to microbes (e.g., water contaminated with up to 1900 microbiological units of microorganisms is usually completely sterile within 20 minute with 100–200 µg L⁻¹ Ag⁺; Smith and Carson, 1977b, and references therein) and to aquatic organisms (e.g., 100 µg L⁻¹ Ag⁺ will kill large sticklebacks within 1 day and 4 µg L⁻¹ Ag⁺ will kill them within 7 days, Smith and Carson, 1977b, and references therein). Therefore, information about the rate and extent to which Ag and Tl desorb from soil may be as important in determining their bioavailability, as knowing how much is sorbed.

Since Tl and Ag desorption from soil is environmentally relevant, the method used to investigate the phenomenon in the laboratory must be considered. Guivarch *et al.* (1999), believe that unless desorption is compared to adsorption performed under the same conditions of solution composition and ionic strength, it is wrong to assume fixation, which they equate with non-exchangeability. Traditionally, desorption studies have been conducted by repeatedly replacing the soil solution with fresh, “blank” solution and then summing up the total amount of element released.

However, simple desorption of cations under the same conditions that they were sorbed, determines the amount of that cation that is soluble in the short-term, whereas the use of a stronger sink, e.g., in the form of a resin, provides quantitative information related to longer term solubility. It represents a situation in which the cation in question is continuously being removed from solution by mechanisms such as leaching, plant or microbial uptake, or even sorption onto other surfaces, thus preventing the establishment of a single equilibration between the cations in solution and those sorbed to a particular surface. This method, known as “infinite pool desorption,” involves the use of a resin such as Amberlite or Dowex (Valcke and Cremers, 1994; Vidal *et al.*, 1995; Madruga and Cremers, 1997; Strawn *et al.*, 1998; Maes *et al.*, 1998, 1999a, 1999b). Other merits of this technique are that, it does not modify natural equilibria by dilution with large amounts of distilled water or other solutions; it avoids the problems of entrapment due to soil compaction, and the release of cations from physically lysed microbes inherent to centrifugation methods; it also avoids chemically induced artifacts from strong acid, salt or organic solvents used as extractants; and it avoids confusion between selectivity and desorption (Oscarson *et al.*, 1994).

Since concentrations of Ag and Tl sorbed to soils will be very low in comparison to other exchangeable cations such as Ca^{2+} , a resin with a functional group that is highly selective for Tl and Ag would be preferred. Such a resin should be able to act as sink for Tl and Ag without being completely saturated by cations in the bulk solution, such as Ca^{2+} , Mg^{2+} or K^{+} . Studies with sulfhydryl group containing resins have found them to be highly selective for soft acid cations such as Tl and Ag (Cobianco *et al.*, 2000; Saha *et al.*, 2000; Iglesias *et al.*, 2001). Therefore, we used a sulfhydryl containing polymeric resin as a sink to assess the extent to which sorbed Tl and Ag will desorb from soils, and the rate at which the desorption occurs.

In this general context, the key objective of the present research was to systematically investigate the effect of clay and organic matter contents on Ag and Tl retention in three mineral soils from New York State with different textures, and in an organic peaty-muck soil. We studied the effect of aging by monitoring desorption from soils equilibrated with Tl or Ag for either 24 h or 1 year. Ultimately this information characterizing the rate (1 h, 4 weeks) and extent of Tl and Ag desorption, as well as the key soil components affecting their behavior, will be important in determining the bioavailability and mobility of Tl and Ag in soils.

2. Materials and Methods

2.1. SOILS, SOIL PROPERTIES AND SOIL CHARACTERIZATION

Four New York soils with different textures and organic matter contents were used in this study. 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. Another exception is that 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 were collected in Tompkins County, NY: an Arkport fine sandy loam (Lamellic Hapludalf) currently used as a horse pasture, a Genesee silt loam (Mollic Endoaquent) from a grass-covered riparian/agriculture buffer zone, and a Hudson silt loam–silty-clay loam (Glossaquic Hapludalf) from a grass covered portion of an apple orchard. The clay-sized fraction of the soils was dominated by illite. The organic soil was collected in Orange County, NY, and is a peaty-muck that has been drained for agricultural use. The properties of the soils are listed in Table I.

Soil pH was measured in 1:1 soil:10 mM CaCl₂ (by mass) suspensions for the mineral soils and in a 1:2 soil:10 mM CaCl₂ (by mass) suspension for the muck. Additional solution was used for the pH measurement of the muck to ensure the presence of free-standing solution with this highly sorbing material. CEC was determined by BaCl₂ saturation followed by MgSO₄ replacement according to the procedure by Rhodes (1982). The extracts were analyzed for Mg by atomic absorption spectrometry (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 pipet method by 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 the soluble salts according to the procedure used by the Soil Testing and Plant Analysis Laboratory, Rutgers University. Organic matter was removed from the clay fraction with sodium hypochlorite at pH 9.5 (Moore and Reynolds, 1989). The mineral composition of the soluble salt, organic-matter free clay fraction was determined by X-ray diffraction 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 Fe and Al were determined according to the method described by Ross and Wang (1993). The exchangeable cations (Ca, Mg, K, Na, Al, Fe and Mn) 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. Ag AND Tl SORPTION

Short-term Ag and Tl sorption samples were prepared by equilibrating 2.5 g of soil with 25 ml of 100 μM Ag or Tl solution in 50 ml polycarbonate, Oakridge centrifuge tubes for 24 h on a translational shaker at low speed (3.3 oscillations

TABLE I
Selected soil characteristics

	Arkport surface <i>fsl</i>	Genesee surface <i>sil</i>	Hudson subsurface <i>sil-sicl</i>	Orange County <i>peaty-muck</i>
pH	5.3	6.6	7.1	5.1
CEC (mmol kg ⁻¹)	25	161	71	791
Total C (%)	3.2	5.8	1.0	35.1
TOC (%)	3.1	5.2	0.6	27.4
Extractable cations (BaCl ₂ extractable) (mmol kg ⁻¹)				
Na	0.098	0.162	0.114	0.199
K	1.66	2.05	3.14	1.01
Ca	33.1	107	59.7	424
Mg	1.35	4.69	1.41	9.87
Fe	<0.005	<0.005	<0.005	<0.024
Al	0.428	0.143	<0.670	<0.292
Mn	0.275	0.089	0.007	0.060
Inorganic-noncrystalline oxides (acid ammonium oxalate–pyrophosphate extractable) (mmol kg ⁻¹)				
Fe	10.0	21.1	18.1	
Al	4.1	13.4	10.3	
Mn	0.9	3.1	1.3	
Organically complexed metals (pyrophosphate extractable) (mmol kg ⁻¹)				
Fe	2.0	4.4	3.2	
Al	1.7	3.9	2.3	
Mn	0.3	1.0	0.2	
Texture (pipet method)				
Sand (%)	77	9	6	
Silt (%)	16	70	68	
Clay (%)	7	21	26	
Clay mineralogy				
Illite	*****	*****	*****	
Chlorite	*	**	**	
Smectite	—	—	—	
Quartz	*	*	*	

per second). The Ag⁺ and Tl⁺ solutions were prepared from reagent grade nitrate salts in 1 mM Ca(NO₃)₂ as a background electrolyte to result in potential loadings of 100 μmol Ag or Tl g⁻¹ soil. The long-term (1 year) sorption samples were generated using 1.5 g soil and 15 ml of 100 μM Ag or Tl solution in polyethylene scintillation vials. The samples were placed on an end-to-end shaker overnight for 1 week, then 1 night a week for the first two months, 1 night a month until the end, and for the 24 h prior to adding the resin. All the Ag samples and standards were

shaken and stored in the dark to prevent photoreduction of Ag or Tl. Long-term sorption samples were periodically opened at random to assess whether reduction conditions were developing. There was never an indication, at least by smell, that such processes were occurring even after 1 year of incubation. That is not entirely unexpected given the inhibitory effect of these elements, especially Ag^+ , on the microbial activity.

Since the muck soil was used in its field-moist state (58% moisture), the amount of muck used was increased 4.6 g to yield 2.7 g 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) to solution ratio was 1:10 as it was for the mineral soils.

2.3. DESORPTION WITH RESIN

In order to easily separate the resin from the soils, small bags (2×3 cm) were prepared from a sheer 100% polyester fabric (Casa sheer) and nylon thread. Approximately 0.38 g Duolite G-73 resin was weighed into each bag, which was then sewn closed, rinsed with deionized-distilled water (dd- H_2O) and stored in a sealed plastic container to keep the resin moist until it was used. The CEC of the resin is 1.290×10^6 mmol kg^{-1} ; therefore, the exchange capacity of resin was 196,080–326,800 times the amount of Tl or Ag added. A large excess of resin was used to compensate for exchangeable cations on the soil.

To initiate the desorption process, a moist resin bag was added to a Ag or Tl sorption sample vial that was resealed and placed on a translational shaker. Resin bags were also added to vials containing only 15 ml of 100 μM Ag^+ or Tl^+ spiking solution (no soil). These samples were treated like all the others and were used to determine the amount of Ag and Tl that could be recovered from the resin at each sampling time. Samples were removed from the shaker after 1, 2, 4, 8, 16, 24, 28, 72 h and 1, 2 and 4 weeks desorption periods. At the end of the desorption time, the resin bags were removed from the vials, rinsed with dd- H_2O to remove any soil adhering to the outside of the bag as well as any small particles that had worked their way inside the bag. Both the rinsing solutions and sample soil solutions were analyzed periodically for Ag or Tl. The concentrations were always below detection.

To recover metals, the resin bags used to desorb Tl were placed in 50 ml centrifuge tubes, to which 15 ml of 8 M HNO_3 were added, and placed on a translational shaker for a minimum of 4 h. At that time the acid was decanted from the resin and analyzed for Tl. The resin bags used to desorb Ag were placed in 50 ml beakers to which 15 ml of 5 M HNO_3 were added, and placed in a water bath at 60–70 $^\circ\text{C}$ for a minimum of 4 h. At the end of the hot acid extraction, the acid was quantitatively transferred to a 50 ml volumetric flask, made to volume with dd- H_2O , and analyzed for Ag.

Total Tl was measured by FAAS (Perkin-Elmer 2380 or 372 Atomic Absorption Spectrophotometer). The detection limit for Tl was $0.2 \mu\text{M}$ by FAAS. 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 $0.2 \mu\text{M}$ by FAAS and 10 nM with the modified ICP-OES.

3. Results and Discussion

The Duolite G-73 resin was chosen for these experiments because it contains a sulfhydryl group (–SH). Both Ag and Tl form strong bonds with sulfides, as indicated by the solubility constants of their sulfide minerals: $\log K_{\beta\text{-Ag}_2\text{S}}^0 = -48.97$ (Lindsay, 1979) and $\log K_{\text{Tl}_2\text{S}}^0 = -21.2$ (Lin and Nriagu, 1998). Therefore, once the metals bind to the –SH functional group on the resin, they should not be readily released back into solution. This way the concentrations of Ag and Tl in the soil solutions were maintained at low levels driving desorption of these elements from the soil. Of course, this would only be true for Ag or Tl that was less strongly held by the soil (i.e., complexed, chemisorbed or electrostatically held to functional groups on the soil minerals or organic matter, or trapped within clay mineral interlayers) than by the resin. Another indication of the strong affinity of the resin functional groups for Ag and Tl was the difficulty experienced in recovering the metals from the resin by hot acid extraction at the end of the experiment. At least in the case of Ag, this method, which partially decomposed the resin, was not completely successful. Another problem that could have occurred with this method is colloidal entrapment or adhesion to the resins. This would have had a “false positive” effect in that the metals would have been removed from the batch systems without necessarily being desorbed from clay surfaces or de-complexed from soil organic matter. Although at the end of the experiments the resin samples were rinsed with dd-H₂O until they reverted to their original khaki color, it is possible that some clay colloids, organic matter or even a similarly colored mineral such as goethite, remained on the surface. The generally high agreement between replicate samples and smoothness of the desorption curves suggests that this was not a significant problem.

In general, Tl was readily released from the soils and reached the maximum recoverable level within 1 day (Figure 1), suggesting that exchange reactions dominate thallium retention by soils. By virtue of its similar size and charge, Tl may exchange with K in the interlayers of micaceous clays (Maes *et al.*, 1999b). Since Tl⁺ is more electronegative than K⁺ and has a higher hydration energy, it should be selectively retained and fixed by the clay as water is removed and the layers collapse around the cations. As seen in Table I, the clay mineralogy of the three mineral soils used in this study is very similar in composition. The clay fractions contain small amounts of quartz and chlorite, but the predominant clay mineral,

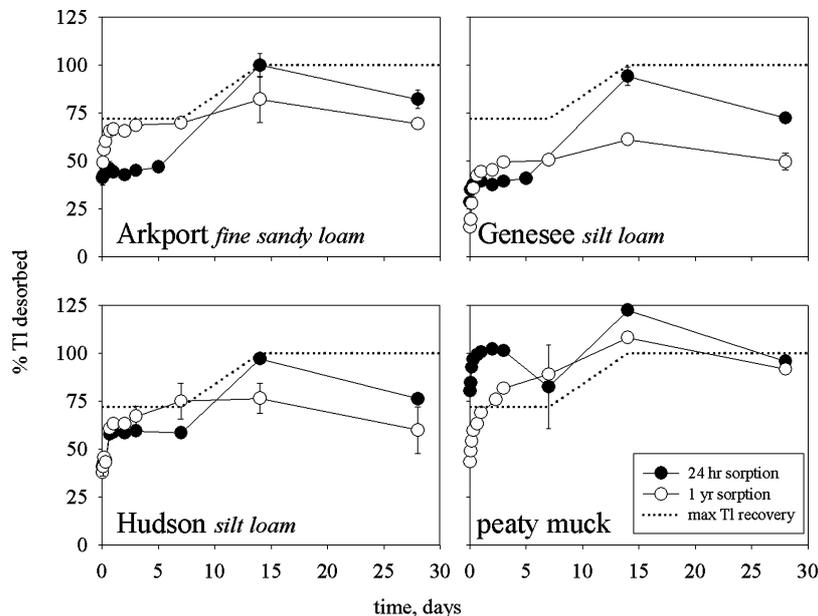


Figure 1. Tl desorption in the soils over time. The symbols represent the mean of two samples. The amount of element desorbed is based on the amount of the element released from the resin relative to the amount of Tl known to sorb to the soil based on sorption experiments. The amount of Tl remaining in solution after the sorption period was subtracted from the amount extracted from the resin to determine the net amount of Tl that was desorbed from the soil. Error bars (1 standard deviation) that are not visible, are smaller than the symbols. The dotted line represents the maximum Tl recovery from the resin at the time of the extractions.

and reactive clay species, is illite (>50%). Thus, the amount of illite in each soil is proportional to the clay content of the soil. The Hudson soil contains more than three times as much clay as the Arkport soil and could then be expected to retain more Tl. However, the desorption curves for Tl sorbed to the soils for 1 year are nearly identical for the two soils. A lower percentage of Tl is removed from the Arkport soil than the Hudson after 24 h sorption in the short-term. However, by 2 weeks, essentially all the Tl sorbed to both soils was desorbed. These results suggest that regardless of the amount of illite in the soil, a large percentage of Tl is retained to the clay by exchange. For both soils, however, the fraction of Tl that is desorbed from soils to which Tl was sorbed over 1 year reached a plateau after 3 days, whereas that desorbed from soils after a 24 h sorption period continued to increase to 100%. This behavior suggests that with time, illite may indeed fix a small fraction of Tl.

The Genesee soil contains almost as much clay as the Hudson. Thallium desorption from the Genesee silt loam samples, to which Tl was only sorbed for 24 h, is almost identical to Tl desorption from the 24 h sorption Arkport samples. However, the desorption curve for Tl sorbed to the Genesee soil over a year plateaus at a

much lower percentage (45%) than those of the Hudson or Arkport soils (75%). The Genesee silt loam has a higher OC content and thus much higher CEC than the other two mineral soils; however, as can be seen in the desorption curve for the muck soil, sorption by SOM does not provide a mechanism for the long-term retention of Tl. A more probable explanation for the greater Tl retention observed in the Genesee soil, following long-term sorption, is its slightly higher noncrystalline Mn oxide content. Enrichment of Tl in oceanic manganese nodules and certain US manganese deposits suggests a strong affinity of Mn oxides for Tl (Shaw, 1952; Smith and Carson, 1977a). A selectivity study of Tl sorption to a Mn oxide surface relative to other cations suggests that Tl is initially attracted to the oxide surface in its 1+ oxidation state (Dahal *et al.*, 1998); however, the mechanism for the close association is believed to be the oxidation of Tl^+ to Tl^{3+} by the Mn oxide. The thallic ion 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; Raogadde and Laitinen, 1974; Bidoglio *et al.*, 1993; Dahal and Lawrance, 1996). While association with Mn oxides may provide a means for Tl retention in soils, this mechanism is likely to be effective only to the extent that the oxides are stable. Mottling and other redoximorphic features evident in the lower horizons of the Genesee soil suggest that reducing conditions periodically exist in the soil. Under such conditions, the Mn could be reduced; so that, it would not be an effective sorbant for Tl^+ . The Tl^{3+} might also be reduced to Tl^+ under such conditions, and thus remobilized in the soil solution.

More Tl was recovered from the 24 h samples peaty-muck samples than from the control solutions, suggesting that some Tl containing colloidal organic matter could have adhered to the resin surface and removed the metal that way rather than by true desorption. However, since this problem was not observed with peat-muck Ag samples, which received the same treatment, it is unlikely that OM adhesion/entrapment explains the whole problem.

The artifacts, if present, did not overly affect the significance of the experimental results. Tl was readily desorbed from the muck soil. Tl sorbed in 24 h was desorbed in the same amount of time (24 h). Tl sorbed to the muck over a year was almost as quickly removed and within a week, completely desorbed. This behavior suggests that Tl is retained by the muck almost exclusively by weak electrostatic attraction. The "soft" nature of the thallic ion suggests that it should have a strong affinity for thiol groups on the SOM. However, the desorption plots indicate that either an insignificant amount of Tl is retained in such a manner, or that Tl is not able to displace or exchange with other cations, such as Fe, that may be complexed to the -SH groups. In any case, unlike with other metals, OM may not offer strong protection against Tl mobility in soils. These results seem to run counter to findings of field studies such as those by Heinrich and Mayer (1977) and Martin and Kaplan (1998), which were interpreted to mean that Tl is retained or even accumulated in organic-rich surface horizons. In Martin and Kaplan's (1998) study, Tl_2SO_4 was added to a low CEC, clay and OM soil in South Carolina. While some Tl

was detained in the surface horizons, there was evidence that Tl was leaching to subhorizons (increasing Tl concentrations). Heinrich and Mayer (1977) were studying natural forest systems in which Tl was being continuously deposited on the soil in the form of precipitation or as dry deposition on the surface of falling leaves. Thus the accumulation of Tl in the surface horizons may be more a function of the system kinetics (slow release of Tl from decaying leaves, adsorption by roots) than an indication that Tl is retained by SOM, especially since there was evidence of Tl in the lower soil horizons. Clearly, Tl sorption/desorption phenomena are more complex in natural systems than the batch studies would suggest, and will depend on the chemical speciation of Tl in the inputs and characteristics of the receptor media. However, the results indicate that in soils, Tl resulting from anthropogenic activity can be highly mobile and bioavailable.

Despite preliminary tests with the resin indicating that 98% of the Ag could be recovered by heating the resin in 5 M HNO₃ for at least 2 h, in the actual experiments involving Ag, only 26% Ag could be recovered (Figure 2). Therefore, the results for Ag only give qualitative indications concerning its desorption behavior. In general, a higher percentage of Ag was desorbed from the soils after a 24 h sorption time

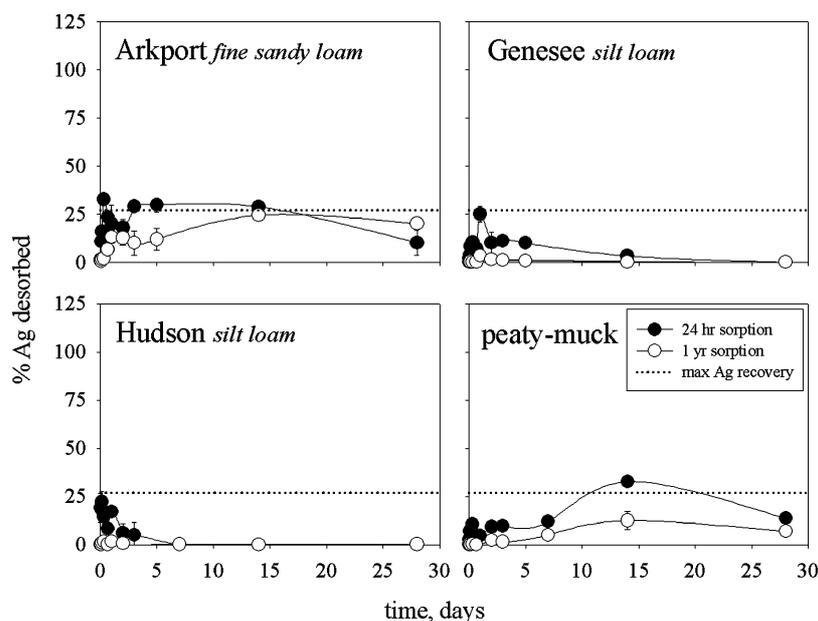


Figure 2. Ag desorption in the soils over time. The symbols represent the mean of two samples. The amount of element desorbed is based on the amount of the element released from the resin relative to the amount of Ag known to sorb to the soil based on sorption experiments. The amount of Ag remaining in solution after the sorption period was subtracted from the amount extracted from the resin to determine the net amount of Ag that was desorbed from the soil. Error bars (1 standard deviation) that are not visible, are smaller than the symbols. The dotted line represents the maximum Ag recovery from the resin at the time of the extractions.

than after a 1 year sorption time. Since Ag sorption to these soils increased over time, so that the absolute amount of Ag on the long-term reacted soils was greater than that on the 24 h sorption samples, the results suggest that there is at least some Ag bound to the soils by exchange mechanisms and that this fraction may be mobilized. This finding is especially significant in the case of the muck soil because OM has been observed (Jones *et al.*, 1986; Jones and Peterson, 1986; Pirestani *et al.*, 1997) to complex or bind Ag so strongly that for all practical purposes Ag may be considered irreversibly sorbed. Our observation that some Ag may be released from highly organic soils is corroborated by the release of Ag (24 h sorption), at least to the extent recoverable from the resin, within 2 weeks. Complexation reactions, such as Ag to $-SH$, do not occur as rapidly as exchange reactions, suggesting that after the 24 h sorption period, less Ag was complexed than after the 1 year sorption period. Ag could also be desorbed from the Arkport soil. This soil has 77% sand, low pH and CEC, and low clay, organic matter and oxide concentrations. Clearly it has minimal capacity to sorb or retain Ag.

Very little can be discerned about Ag desorption behavior from the Genesee and Hudson soils. The desorption curves for both soils are strange in that the amount of Ag recovered decreases after 4 days. If the amount of Ag had simply reached a plateau, the amount of Ag released could be attributed to poor recovery of Ag from the resin. The decrease, however, indicates that another process is occurring. The only feature these soils have in common, relative to the Arkport and the muck, is an elevated clay content. It could be therefore that with time clay is clogging the resin pores trapping the Ag inside so that it cannot be removed with the acid. For both soils, almost none of the Ag sorbed over 1 year could be removed. The amount of Ag released was low even relative to the maximum recoverable Ag, which suggests that the result may be more than an artifact. Since the Genesee and Hudson soils contain a fair amount of illitic clay, one possibility is that Ag replaced K^+ in the interlayers of illite and became fixed there over time. This hypothesis is supported by a study of Ag sorption to kaolinite (Daniels and Rao, 1983) in which Ag sorption exceeded the exchange capacity of the clay. This excess sorption was attributed to Ag binding at intra-layer sites.

Silver reactions are varied and complex. For example another, albeit slim, possibility for the poor recovery of Ag is that it was reduced to metallic Ag either in the soil or on the resin. Even at low concentrations Ag is an effective microbicide and thus would deter biotically induced redox reactions. However, Chanda *et al.* (1986) suggested that Ag^+ could be reduced to Ag^0 by mercaptyl resins based on their EPR evidence of a similar reaction occurring with Cu, and the higher reduction potential of Ag (0.799 V) relative to Cu (0.158 V). Much more vigorous conditions would be necessary to remove Ag^0 from the soil or resin than were used in this study or than generally occur in the environment. Thus, given the possibility that SOM may be oxidized, it may be that, in the long run, fixation in clays or the reduction of Ag to Ag^0 are more important mechanisms for the retention of Ag in soils than sorption to organic matter.

4. Conclusions

The desorption studies described in the present article indicated that thallium sorption could be reversed within two weeks from both high organic and sandy soils. Whereas increases in the illitic clay contents of the soils did not significantly affect the extent or rate of Tl desorption, a small increase in the manganese oxide content resulted in a lower fraction of desorbed thallium after long-term sorption. Due to poor recovery of silver from the resin, the results of the silver desorption study are more qualitative. Within two weeks, silver was desorbed from the sandy and muck soils. Negligible amounts of silver were released from the soils with higher clay contents. Possible mechanisms of silver for long-term silver retention in soils include reduction by organic matter functional groups such as quinones or phenolics to metallic silver or fixation in the interlayers of clay minerals. These experimental results demonstrate the ease with which Tl may be released from soils, as well as Ag release from sandy soils and even somewhat from organic-matter rich soils. They have practical implications for the remobilization of these metals in soil environments and given the toxicity of these elements at trace levels to a broad range of organisms, suggest that elevated concentrations of Ag and Tl may have significant environmental consequences, as yet not fully recognized.

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