



Bioaccumulation of thallium in a neutral soil as affected by solid-phase association



Zuzana Grösslová^a, Aleš Vaněk^{a,*}, Martin Mihaljevič^b, Vojtěch Ettler^b, Maria Hojdová^c, Tereza Zádorová^a, Lenka Pavlů^a, Vít Penížek^a, Barbora Vaněčková^a, Michael Komárek^d, Vladislav Chrástný^d, Christopher Ash^a

^a Department of Soil Science and Soil Protection, Faculty of Agrobiolgy, Food and Natural Resources, Czech University of Life Sciences Prague, Kamýcká 129, 165 21, Praha 6, Czech Republic

^b Institute of Geochemistry, Mineralogy and Mineral Resources, Faculty of Science, Charles University in Prague, Albertov 6, 128 43, Praha 2, Czech Republic

^c Institute of Geology, Czech Academy of Sciences, Rozvojová 269, 165 00, Praha 6, Czech Republic

^d Department of Environmental Geosciences, Faculty of Environmental Sciences, Czech University of Life Sciences Prague, Kamýcká 129, 165 21, Praha 6, Czech Republic

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ABSTRACT

The work focused on the biogeochemical behavior of synthetic Tl-modified phases, namely birnessite, ferrihydrite, and calcite, in a neutral soil Leptosol. The data presented here clearly demonstrate a strong relationship between the mineralogical position of Tl in the soil and its uptake by the studied plant (*Sinapis alba* L.). All tested Tl phases behaved as potential Tl sources in the rhizosphere, with a maximum for ferrihydrite and minimum for birnessite. Therefore, it can be concluded that Mn(III,IV) oxides, if present in the soil system, may reduce biological uptake of Tl to a substantial degree, including the case of Tl-accumulating species (i.e., *Brassicaceae*). It was proven that even Tl-enriched calcite present in the carbonate-rich soil is an important precursor for further contaminant mobilization, despite its relative resistance to degradation. Our data indicate that the fate of secondary Tl phases in the rhizosphere might be significantly influenced by the pH of the soil matrix, i.e., soils with lower pHs reduce their stability, making them more susceptible to further degradation by root exudates. Bulk soil mineralogy and the content and quality of soil organic matter are thus suggested to be critical parameters controlling the bioaccumulation potential for Tl.

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1. Introduction

The toxicity of Tl (as well as other trace metals/metalloids) depends on its bonding to the individual soil or sediment components; i.e., on chemical speciation, solid-phase association, the complex chemistry of the ecosystem, etc. Thallium retention is generally attributed to simple exchange reactions on oxides, silicates or possibly organic matter (Tremel et al., 1997; Jović, 1999). However, the most efficient scavengers of Tl, consistent also with our findings, include Mn(III,IV) oxides (mainly birnessite, δ -MnO₂) and illite clays (Bidoglio et al., 1993; Jacobson et al., 2005; Gao et al., 2007; Vaněk et al., 2011; Voegelin et al., 2015). This affinity can be explained by a complex process of specific Tl adsorption and/or Tl–K replacement within the mineral structures, resulting from the same valence and similar ionic radius of Tl(I) and K(I) (Nriagu, 1998). The phytoavailability of Tl depends on the plant species, the form of its binding and its content in the soil. However, previous investigations clearly demonstrate that the family *Brassicaceae* has a potential to (hyper)accumulate Tl (Xiao et al., 2004; Scheckel et al., 2007; Madejón et al., 2007; Krasnodębska-Ostrega et al., 2012; Jia et al., 2013; Vaněk et al., 2013). In any case, the plant uptake of Tl is a biogeochemical process that has not yet been fully

explained, with particular consideration to the fact that Tl is relatively “insoluble” in soils and it is associated with a number of various primary/secondary minerals of different stability.

The goal of this study is to describe the behavior of synthetic Tl-modified phases in a neutral Leptosol soil, i.e., soil with low (or limited) H⁺-promoted dissolution potential, to better understand Tl dynamics and/or fate in such polluted (agro)systems. For this purpose, both the alteration/dissolution of birnessite, ferrihydrite, and calcite enriched in Tl, and Tl phase-dependent bioaccumulation in a model vegetation experiment were tested.

2. Materials and methods

2.1. Experimental soil and Tl phases

A Rendzic Leptosol, originating from the central part of the Czech Republic, was used in this research. Its selection was based on the following criteria: (i) no important source of Tl pollution is present in the close vicinity of the sampling area, (ii) the soil has relatively low contents of secondary (hydr)oxides and soil organic matter (SOM), which typically influence the dynamics of Tl, and (iii) the soil has relatively low potential for H⁺-promoted reactions. Samples were taken from the arable layer (0–20 cm) of agriculturally used soil; the soil was subsequently air-dried, homogenized and sieved through a 2-mm

* Corresponding author.

E-mail address: vaneka@afz.czu.cz (A. Vaněk).

stainless-steel sieve prior to further use or analyses. Complex data on the physico-chemical properties and mineralogical composition of the Leptosol are summarized in Table 1, and were determined as described below.

Soil pH was measured using a 1:5 (v/v) ratio of soil and water or 1 M KCl solution using a Handylab pH 11 multimeter (Schott, Germany). The pH at the point of zero charge (pH_{ZPC}) was determined using the immersion technique of Fiol and Villaescusa (2009). The total organic carbon (TOC), total inorganic carbon (TIC), and total sulfur (TS) were determined by catalytic oxidation (1350 °C) using a combination of ELTRA Metalyt CS 500 and Metalyt CS 530 (Neuss, Germany) elemental analyzers. The cation exchange capacity (CEC) was computed after saturation of the soil with 0.1 M BaCl₂ and subsequent Ba²⁺ release using MgSO₄ (ISO 11260:1994). Acid oxalate extraction (0.2 M ammonium oxalate/oxalic acid at pH 3), indicating the presence of amorphous/poorly crystalline (hydr)oxides, was performed according to Pansu and Gautheyrou (2006); oxalate-extractable concentrations of Fe, Mn and Al were determined using ICP-MS. Particle size distribution was estimated by the hydrometer method (Gee and Bauder, 1986).

In order to simulate mineral associations of Tl occurring in natural soils, the Leptosol samples were individually mixed with the synthetically-prepared phases enriched in Tl. The Tl phases used in the experiment represent secondary soil minerals potentially associated with the contaminant (if present) (Bidoglio et al., 1993; Jacobson et al., 2005; Yang et al., 2005; Gao et al., 2007) and were as follows: crystalline Mn(III,IV) oxide (birnessite), poorly crystalline Fe(III) oxide (ferrihydrite), and Ca carbonate (calcite). However, it should be noted that Tl preferentially enters the structure of birnessite (Bidoglio et al., 1993; Jacobson et al., 2005), as affected by the Tl-K analogy. Thallium phase proportion (1 wt.%) and Tl concentration within the mixed samples were chosen in accordance with their usual quantity in agricultural (organo-mineral) soils, if moderately contaminated by Tl (Tremel

Table 2

Phase composition of the model soils (wt.%) with corresponding thallium concentrations ($\text{mg kg}^{-1} \pm \text{SD}$).

	Soil A		Soil B		Soil C	
	%	Tl	%	Tl	%	Tl
Birnessite	1	5.55 ± 0.13	–	9.64 ± 0	–	–
Ferrihydrite	–	–	1	–	–	–
Calcite	–	–	–	–	1	9.58 ± 0.12
Soil matrix	99	0.60 ± 0.02	99	0.60 ± 0.02	99	0.60 ± 0.02
Σ		6.15		10.24		10.18

et al., 1997; Al-Najar et al., 2003; Yang et al., 2005; Jakubowska et al., 2007). The final composition of the amended soils is listed in Table 2.

Synthetic birnessite ($\text{K}_4\text{Mn}_{14}\text{O}_{27} \cdot 9\text{H}_2\text{O}$) was prepared by the HCl-KMnO₄ method of McKenzie (1971). The two-line ferrihydrite ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$) was prepared by the KOH-Fe(NO₃)₃ method of Schwertmann and Cornell (2000). Prior to the addition of HCl or KOH reaction solutions, dissolved KMnO₄ or Fe(NO₃)₃ was enriched in Tl so that ~1 mg Tl could be available for synthesis of 1 g of the Mn and Fe oxide formed. The Tl concentrations in birnessite and ferrihydrite reached $555 \pm 13 \mu\text{g Tl g}^{-1}$, and 964 ± 0 respectively. Reduced Tl concentration in birnessite, compared to ferrihydrite, results probably from decreased stability of Tl on the mineral surface during the phase precipitation in a boiling solution. The oxides were used in the model soils A and B, respectively. Thallium-modified calcite (CaCO_3) was prepared with 47.2 g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in 500 ml deionized H₂O enriched in Tl, so that the Tl concentration corresponded to ~1 mg g⁻¹ CaCO₃. The carbonate was precipitated after adding 200 ml of 1 M Na₂CO₃ · 10H₂O solution. The suspension was aged at 30 °C for 5 days, then filtered, rinsed with H₂O and dried at 105 °C to constant weight. The Tl concentration in CaCO₃ reached $958 \pm 12 \mu\text{g Tl g}^{-1}$. The carbonate was used in the model soil C.

Chemicals of analytical grade (Fluka, Germany; Lach-Ner, Czech Republic) and deionized H₂O (MILLI-Q Element, Millipore, France) were used for the preparation of all phases. The Tl source was a water solution of dissolved Tl₂SO₄ (p.a.), which was added to the reaction mixtures for synthesis of the oxides and the carbonate. Considering the specific or non-specific incorporation of Tl into the structures of individual solids, typical for natural soil systems (with varying redox potential and/or pH value) (Vaněk et al., 2010a), co-precipitation was chosen as a more suitable method for Tl enrichment of the precipitates, compared to Tl adsorption onto the mineral surfaces. After the synthesis, precipitates were pulverized in an agate mortar (Pulverisette 0, Fritsch, Germany) to preserve their chemical homogeneity. The chemical composition of Tl phases was determined in 0.3–0.5 g of homogenized sample, which was digested in a mixture of HNO₃ ± H₂O₂ using a microwave digestion unit (Mars 5, CEM, USA). The residual solutions were then dissolved in deionized H₂O and analyzed (see Analyses and quality control). X-ray diffraction analysis (X'Pert Pro diffractometer, PANalytical, The Netherlands) was used to assure the bulk mineralogy of individual Tl phases. The analyses were performed under the following conditions: CuKα radiation, 40 kV, 30 mA, step scanning at 0.02°/150 s in the range 3–80° 2θ. Qualitative analysis was performed with XPert HighScore software 1.0d, equipped with the JCPDS PDF-2 database.

To assess the stability of Tl phases in the model soils (i.e., A, B, and C), aliquot parts (20 g) of the amended soils were subjected to H₂O saturation (~60% of water holding capacity, WHC) for 2 months; 100-ml PE bottles (periodically aerated) were used for the incubation. Afterwards, a simple batch leaching experiment at a solid-to-liquid ratio of 1/10 was performed for 2 h (2 g of soil in 20 ml of deionized H₂O, n = 3); non-incubated soils were used as controls. Finally, the pH values and metal concentrations in the water leachates were determined.

Table 1

Physico-chemical properties and bulk mineralogy of the Leptosol.

Particle size distribution (%)	
Clay	0.4
Silt	30.6
Sand	69.0
pH _{H2O}	7.4
pH _{KCl}	7.0
pH _{ZPC}	7.7
CEC (cmol kg ⁻¹) ^a	28.3 ± 2.9
TOC (%) ^a	3.36 ± 0.44
TIC (g kg ⁻¹) ^a	3.10 ± 0.20
TS (g kg ⁻¹) ^a	0.58 ± 0.05
Oxalate-extractable (g kg ⁻¹) ^a	
Fe	2.23 ± 0.35
Al	1.55 ± 0.18
Mn	0.30 ± 0.01
Total concentrations (mg kg ⁻¹) ^a	
Tl	0.61 ± 0.02
Fe	20,500 ± 100
Mn	378 ± 8
Ca	14,500 ± 100
Mineralogical composition ^b	
Quartz (SiO ₂)	***
K/Na feldspars (K/NaAlSi ₃ O ₈)	**
Calcite (CaCO ₃)	**
Illite ((K,H ₃ O)Al ₂ (SiAl) ₄ O ₁₀ (OH) ₂)	*
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	*
Goethite (FeOOH)	*

^a The presented data are means ± SD (n = 3).

^b Data obtained by X-ray diffraction analysis.

*** Majority.

** present.

* minority.

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