

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



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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

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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.

2.2. Soil treatment and vegetation experiment

A mass of 50 g of the model soils, i.e., homogeneously spiked with Tl phases (1 wt.%), was put into 100-ml PP pot. Triplicate treatments were run for all amended soils including the control treatment (no Tl phase). It should be noted that 2 months pre-incubation of the contaminated soils had been performed prior to vegetation experiments, to attain the approximate geochemical equilibrium (mainly in soil pH and solids distribution). The soils were subjected to a wet-dry cycle for 2 months. Approximately 15 ml of deionized H₂O (~60% of WHC) was applied to the soils in 7-day intervals, followed by careful homogenization at the end of the cycle. Subsequently, an appropriate nutrient supply using Kristalon Superior fertilizer (Hydro, Netherlands; 20% N; 10% P₂O₅; 10% K₂O; 2% MgO, in solubilized form) was applied.

White mustard (*Sinapis alba* L.) was chosen as the tested plant species because of its high biomass yields and ability to extract significant amounts of Tl (Vaněk et al., 2010b; Krasnodebska-Ostręga et al., 2012). The experiment was conducted in a greenhouse at a constant temperature of 21 °C, and with a deionized H₂O regime ~60% of WHC. Approximately 20 seeds of mustard were sown in each pot. Normally developed plants were singled out after 14 days and the 10 best-developed plants remained in each pot. Plants were harvested after 28 days; roots, stems and leaves were sampled separately, and then dried at 70 °C. Finally, acid digestion of the biomass in 60-ml PTFE beakers (Savillex, USA) using 1–2 ml of concentrated HNO₃ at 190 °C overnight was performed. The residual solutions were analyzed for Tl and metal concentrations (Fe, Mn, Al, Ca, and K) (see Analyses and quality control).

2.3. Chemical fractionation of Tl in soil

In order to better understand the role of Tl phases in plant uptake, the chemical fractionation of Tl and major (structural) metals in the model (pre-incubated) soils was tested. The fractionation was determined using the optimized BCR sequential extraction procedure (SEP) of Rauret et al. (2000). The fractions determined were as follows: (i) exchangeable/acid-extractable (0.11 M CH₃COOH-extractable); (ii) reducible (0.5 M NH₂OH·HCl-extractable); (iii) oxidizable (8.8 M H₂O₂/1 M CH₃COONH₄-extractable); and (iv) residual (microwave digestion of the residue in a mixture of concentrated acids HNO₃/HCl/HF). The SEP was run in triplicates and the sum of the individual extraction steps was in a good agreement with the total element concentrations (recovery differences were less than 10%). Chemicals of analytical grade (Lach-Ner, Czech Republic) and deionized H₂O were used for the individual extraction steps.

2.4. Analyses and quality control

The concentrations of thallium and metals (Fe, Mn, Al, Ca, and K) in all phases, SEP digests, water leachates, and biomass solutions were determined using a combination of ICP-MS and ICP-OES (X Series 2, ThermoScientific, UK; iCAP 6500, ThermoScientific, Germany) under standard analytical conditions. The ICP-MS conditions for Tl determination were as follows: measured isotopes ²⁰³Tl, ²⁰⁵Tl, ²⁰⁹Bi (internal standard); RF power 1350 W; reflected power < 1 W; gas coolant flow rate 14 L min⁻¹, nebulizer 0.78 L min⁻¹, auxiliary 1.3 L min⁻¹; acquisition mode peak jump; points per peak 3; dwell time 10 ms; replicates 3; number of sweeps 100, detector mode dual. Quality control of Tl and metal analyses was ensured using the standard reference materials NIST 2711 (Montana II soil) (National Institute of Standards and Technology, USA) and INCT-TL-1 (tea leaves) (Institute of Nuclear Chemistry and Technology, Poland). The accuracy of the measurements was generally <5% RSD.

3. Results and discussion

3.1. Stability of Tl phases

It is evident from Fig. 1 that partial degradation of Tl phases linked with Tl release took place during the incubation of individual model soils. The highest Tl concentration in the water leachate was identified in soil A (enriched in birnessite), followed by soils C and B (enriched in calcite and ferrihydrite), reaching ~1, 0.5, and 0.4% of total Tl contents, respectively (Fig. 1, Table 2). Taking into account the calculated Tl/Mn, Tl/Fe, and Tl/Ca ratios, compared to the initial values, similar ratios were determined only in soil B, contrary to soils A and C. An approximate two time increase was typical for soil A; the mobilization of Tl from the Mn oxide was thus incongruent, i.e., Tl and Mn were not released in the same proportion as found in the bulk “mineral”, probably because the oxide surface is enriched in Tl to some extent. For example, the tendency of Tl to precipitate as Tl₂O₃ (log K_{sp} = -13; MINTEQA2 database) on the birnessite surface was previously documented (Bidoglio et al., 1993; Voegelin et al., 2015). We assume that a part of such associated Tl can be attacked by mild extractants more easily, including soil H₂O, and after its mobilization, rapid Tl penetration into the soil matrix occurs (see below). An opposite behavior was identified in soil C with calcite, showing a ~3 time decrease in Tl/Ca, potentially because Tl is tightly incorporated in the carbonate structure, although non-specifically, and/or present as more stable (unidentified) Tl(III) carbonate (Yang et al., 2005).

It should be noted that no significant pH change was observed throughout the incubation. Only in the case of soil C, a slight pH increase was noted (<0.2 pH unit), which suggests a positive pH buffering effect of the carbonate, as expected. The identified redox potential (Eh) indicated oxic conditions (~300–400 mV) for all model soils during the experiment (data not shown). The alteration mechanisms proposed for the oxides and the carbonate include H⁺-promoted reactions (although limited), reductive dissolution associated with the oxidation of SOM, and surface complexation of the main cations (mainly Fe and Ca) by simple organic or fulvic acids, forming the Leptosol matrix. It is clear that a part of Tl was redistributed among Tl-free phases, mainly illite (proved by XRD, Table 1), specific soil silicates and oxides, or eventually SOM (Jacobson et al., 2005). Recent investigations dealing with Tl fractionation in contaminated soils document that a large portion of Tl is typically entrapped in soil silicates, i.e., after its mobilization from primary minerals such as sulfides (Karbowska et al., 2014). On the other hand, we suppose that this process affected the dynamics and/or biological uptake of Tl only minimally (see Plant uptake of Tl). Moreover, its readsorption onto the altered Tl phases is also likely, especially in soil

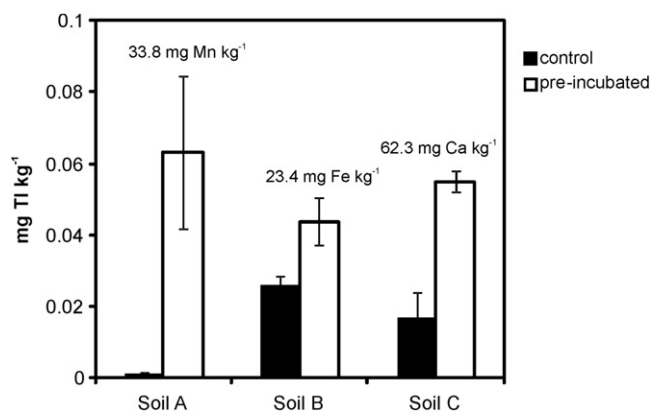


Fig. 1. Thallium and corresponding main metal concentrations in H₂O leachate from the model soils after wet incubation (~60% of WHC) for 2 months; non-incubated soils were used as controls. The Tl data shown are means ± SD (n = 3).

A, resulting from the strong affinity of birnessite for this trace element (Jacobson et al., 2005; Gao et al., 2007).

3.2. Plant uptake of Tl

Thallium concentrations in different plant parts are given in Fig. 2. The lowest Tl levels were observed in mustard grown on soil A (3 mg Tl kg⁻¹, maximum), although determined for elevated Tl concentration in the H₂O leachate (Fig. 1). This finding is in accordance with our previous observations (Vaněk et al., 2011, 2013) and reflects the ability of the Mn oxide to efficiently immobilize Tl, which is then difficult for the plant to deplete. Similarly, data from the leaching experiments with synthetically prepared K_{sat}-birnessite imply intensive Tl penetration into the oxide, i.e., in non-exchangeable K-exchanged layers (Vaněk et al., 2010c). An opposite behavior was revealed in the latter ones, showing substantial bioaccumulation of Tl, with a maximum for soil B (Fig. 2), reaching 39 mg Tl kg⁻¹ in stem, followed by leaf (21 mg Tl kg⁻¹), and root (13 mg Tl kg⁻¹). Similar (relative) distributions of Tl among the individual organs, i.e., in the order of stem > leaf > root, were identified in all tested soils (Fig. 2), proving an efficient Tl translocation. The capability of mustard species to accumulate Tl preferentially in the above-ground parts is well known (Krasnodębska-Ostreęga et al., 2008, 2012; Jia et al., 2013) and is consistent with the obtained translocation factors ≤3.1 (a ratio of Tl concentrations between stem or leaf and root). Based on the mustard shoot/soil ratio of Tl, ranging between 0.4 and 3.8, different patterns of the soil–plant transfer are evident. The rate of Tl uptake decreased in the following order: B > C >> A (Fig. 2), demonstrating that both ferrihydrite and calcite (if containing Tl) are able to lose the trace element to a substantial degree, if present in the rhizosphere. Elevated Fe and Ca concentrations in plant roots from soils B and C (~15,000 mg Fe kg⁻¹ and 16,000 mg Ca kg⁻¹, Fig. 3) confirm root-induced dissolution of the synthetic Fe oxide and the carbonate, accompanied by Tl/metals mobilization and plant uptake. Furthermore, the calculated root/soil ratios of Fe and Ca equaled 0.6 and 0.9 for soils B and C, respectively, contrary to soil A with “only” 0.3 for Mn, support this statement.

Apart from passive Tl diffusion, proton and organic ligand excretions (e.g., carboxylic and amino acids, carbohydrates) by roots seem to be important processes influencing Tl uptake from the model soils (Neumann and Römheld, 1999; Dong et al., 2007). However, the question of the degree to which the H⁺-promoted reactions (surface protonation) controlled the mobilization of Tl remains unresolved. Our previous research with the synthetically-prepared soils enriched in Tl phases documents no significant pH change during vegetation, compared to unplanted treatments, indicating efficient pH buffering by the soil matrix (Vaněk et al., 2013). In this experiment with a circum neutral

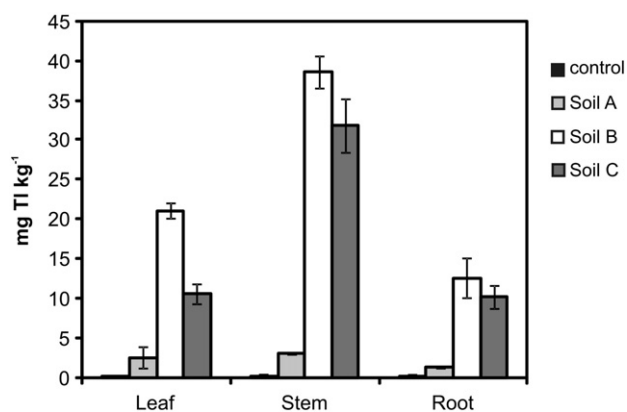


Fig. 2. Thallium concentrations (mg kg⁻¹) in different parts of white mustard grown on the model soils; control treatment represents a non-amended soil. The data shown are means ± SD (n = 3).

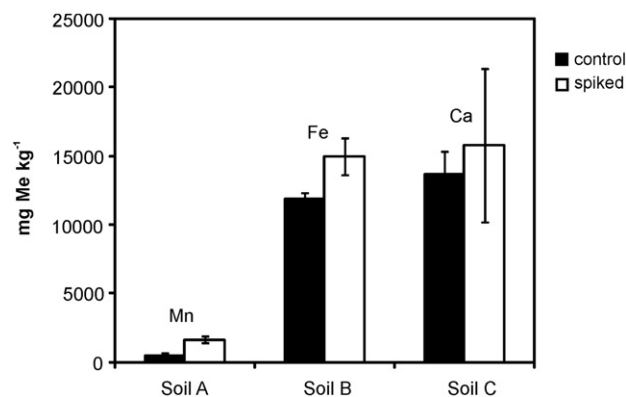


Fig. 3. Main metal concentrations (Mn, Fe, and Ca) (mg kg⁻¹) in plant roots of white mustard; control treatment represents a non-amended soil. The data shown are means ± SD (n = 3).

Leptosol, only a short-term acidic attack may thus be expected. Similarly to the incubation cycle, the Tl redistribution effect is probable during vegetation period; nevertheless, our results indicate that Tl uptake was controlled mainly with the initial solid-phase Tl association, compared to the portion of Tl potentially readsorbed on the surface of individual (Tl-free) solids. This statement favors the fact that the experiment was relatively short-term and the trace element redistribution (kinetically and thermodynamically driven) is strongly time-dependent.

3.3. Thallium dynamics in the rhizosphere

Despite the fact that the BCR SEP suffers from two main drawbacks, i.e., non-selective nature of the extracting solutions and redistribution (by readsorption) of trace elements among individual soil components during leaching (Tack and Verloo, 1996), its application for comparison purposes can be a way how to interpret changes in Tl fractionation between the tested soils, if detailed information about the phase composition is available.

All model soils indicated the majority of Tl present in the reducible fraction, with a maximum in soil A (85%) (Fig. 4), suggesting relative stability of Tl phases, as well as strict Tl uptake from the “structural” positions of birnessite. For soils B and C, the portion of labile Tl, i.e., associated with the acid-extractable fraction, such as exchangeable/surface positions or unstable Tl species, was obviously increased and accounted for 10–20% of total Tl (Fig. 4). This is consistent with the highest Tl bioaccumulation rates recorded in these soils (Fig. 2), indicating a clear relationship between the content of labile Tl in soil and its uptake by the plant. Subsequently, more stable Tl

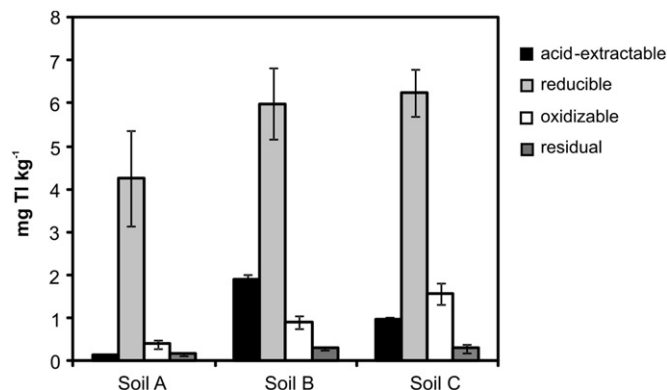


Fig. 4. Chemical distribution of Tl (mg kg⁻¹) in the model soils. The data shown are means ± SD (n = 3).

associations (so-called reducible and oxidizable) were possibly attacked by the plant, as affected by root exudates. Nevertheless, their contribution to the complex process of Tl uptake can hardly be quantified, as there is no evidence on their depletion during vegetation. However, Al-Najar et al. (2003) also highlight that these Tl fractions, including the Tl associated with silicates, are plant available. Furthermore, a shift in the Tl equilibrium toward the more stable (unidentified) Tl species after root exudation and Tl bioaccumulation is likely (Vaněk et al., 2013).

3.4. Agro-environmental implications

The rate of plant uptake of Tl was highly dependent on the solid phase association present in the model soils, showing that soil mineralogy plays a key role in its phytoavailability. From this point of view, it can be generally concluded that Mn(III,IV) oxides present in soils reduce plant uptake of Tl, including uptake by Tl-accumulating species (mainly *Brassicaceae*). In contrast, poorly-crystalline Fe(III) oxides and/or Ca carbonates, if enriched in Tl, represent an important source for further Tl mobilization. This behavior can be significantly enhanced by the pH of the soil matrix; i.e., the stability of Tl phases may be reduced in Cambisols, Arenosols, etc., making them more susceptible to further degradation by root exudates. It must be highlighted that the obtained data document only actual phase-dependent bioaccumulation of Tl, as the experimental scheme is based on synthetically amended soils in which the long-term stability of Tl phases and the rate of Tl redistribution are unknown. On the other hand, the role of carbonate-rich soil matrices in the complex dynamics of Tl will presumably be less pronounced in the long-term, apart from in acidic soils. However, Tl (co)precipitation with the newly formed carbonates, following CaCO_3 dissolution in the rhizosphere (Yang et al., 2005), and/or well-known stabilization behavior of illite clays (Jacobson et al., 2005; Voegelin et al., 2015) must be also taken into account. Therefore, Tl and bulk soil mineralogy, as well as the content and quality of SOM are suggested to be critical parameters controlling Tl bioaccumulation potential.

Because of the high toxicity of Tl, cultivation of Tl-accumulating species should be monitored and alternatively excluded from cultivation for human nutrition in areas with both high anthropogenic or natural Tl inputs. Similarly, the mineralogical aspect should be taken into account prior to general environmental recommendations. It should be noted that there are no threshold limits for Tl in soils and foodstuffs in most countries.

4. Conclusions

We identified a significant effect of solid phase Tl association on the rate of Tl release in the soil and subsequent plant uptake. All tested Tl phases behaved as potential Tl sorbents in soils, as well as its secondary sources in the rhizosphere, with a maximum for ferrihydrite and minimum for birnessite. It was proven that even Tl-enriched calcite present in the carbonate-rich soil poses an important precursor for further contaminant mobilization. Despite the fact that the presented data are based only on a short-term model experiment, the biogeochemistry of Tl may be generalized, providing us basic information about approximate retention capacity of organo-mineral soils and the environmental fate of this trace element, if the complex soil composition is known. However, further research dealing with surface complexation and speciation of Tl onto its efficient scavengers (mainly Mn oxides and illite) is needed for a more detailed insight of Tl behavior at the soil–plant interface.

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References

- Al-Najar, H., Schulz, R., Römheld, V., 2003. Plant availability of thallium in the rhizosphere of hyperaccumulator plants: a key factor for assessment of phytoextraction. *Plant Soil* 249, 97–105.
- Bidoglio, G., Bibson, P.N., O'Gorman, M., Roberts, K.J., 1993. X-ray absorption spectroscopy investigation of surface redox transformations of thallium and chromium on colloidal mineral oxides. *Geochim. Cosmochim. Acta* 57, 2389–2394.
- Dong, J., Mao, W.H., Zhang, G.P., Wu, F.B., Cai, Z., 2007. Root excretion and plant tolerance to cadmium toxicity—a review. *Plant Soil Environ.* 53, 193–200.
- Fiol, N., Villaescusa, I., 2009. Determination of sorbent point of zero charge: usefulness in sorption studies. *Environ. Chem. Lett.* 7, 79–84.
- Gao, Y., Leermakers, M., Elskens, M., Billon, G., Ouddane, B., Fischer, J.C., Baeyens, W., 2007. High resolution profiles of thallium, manganese and iron assessed by DET and DGT techniques in riverine sediment pore waters. *Sci. Total Environ.* 373, 526–533.
- Gee, G.W., Bauder, J.W., 1986. Particle-Size Analysis. In Klute, A. (Ed.), *Methods of Soil Analysis. Part I: Physical and Mineralogical Methods*. American Society of Agronomy-Soil Science Society of America, Madison, WI, pp. 383–411.
- Jacobson, A.R., McBride, M.B., Baveye, P., Steenhuis, T.S., 2005. Environmental factors determining the trace-level sorption of silver and thallium to soils. *Sci. Total Environ.* 345, 191–205.
- Jakubowska, M., Pasieczna, A., Zembrzusi, W., Świt, Z., Lukaszewski, Z., 2007. Thallium in fractions of soil formed on floodplain terraces. *Chemosphere* 66, 611–618.
- Jia, Y., Xiao, T., Zhou, G., Ning, Z., 2013. Thallium at the interface of soil and green cabbage (*Brassica oleracea* L. var. capitata L.): soil–plant transfer and influencing factors. *Sci. Total Environ.* 450–451, 140–147.
- Jović, V., 1999. Thallium. In: Marshall, C.P., Fairbridge, R.W. (Eds.), *Encyclopedia of Geochemistry*. Kluwer Academic Publishers, Dordrecht, Germany, pp. 622–623.
- Karbowska, B., Zembrzusi, W., Jakubowska, M., Wojtkowiak, T., Pasieczna, A., Lukaszewski, Z., 2014. Translocation and mobility of thallium from zinc-lead ores. *J. Geochem. Explor.* 143, 127–135.
- Krasnodębska-Ostręga, B., Asztemborska, M., Strusińska, K., Golimowski, J., 2008. Determination of thallium form in plants extracts by anion exchange chromatography with inductively coupled plasma mass spectrometry detection (IC-ICP-MS). *J. Anal. At. Spectrom.* 23, 1632–1635.
- Krasnodębska-Ostręga, B., Sadowska, M., Ostrowska, S., 2012. Thallium speciation in plant tissue-Tl(III) found in *Sinapis alba* L. grown in soil polluted with tailing sediment containing thallium minerals. *Talanta* 93, 326–329.
- Madejón, P., Murillo, J.M., Maranon, T., Lepp, N.W., 2007. Factors affecting accumulation of thallium and other trace elements in two wild *Brassicaceae* spontaneously growing on soils contaminated by tailings dam waste. *Chemosphere* 67, 20–28.
- McKenzie, R.M., 1971. The synthesis of birnessite, cryptomelane, and some other oxides and hydroxides of manganese. *Mineral. Mag.* 38, 493–502.
- Neumann, G., Römheld, V., 1999. Root excretion of carboxylic acids and protons in phosphorus-deficient plants. *Plant Soil* 211, 121–130.
- Nriagu, J.O., 1998. *Thallium in the Environment*. John Wiley & Sons, New York, NY, USA.
- Pansu, M., Gautheryou, J., 2006. *Handbook of soil analysis. Mineralogical, Organic and Inorganic Methods*. Springer-Verlag, Berlin, Heidelberg.
- Rauret, G., López-Sánchez, J.F., Sahuquillo, A., Barahona, E., Lachica, M., Ure, A.M., Davidson, C.M., Gomez, A., Lück, D., Bacon, M., Yli-Halla, M., Muntau, H., Quevauviller, P., 2000. Application of a modified BCR sequential extraction (three-step) procedure for the determination of extractable trace metal contents in a sewage sludge amended soil reference material (CRM 483), complemented by a three-year stability study of acetic acid and EDTA extractable metal content. *J. Environ. Monit.* 2, 228–233.
- Scheckel, K.G., Hamon, R., Jassogne, L., Rivers, M., Lombi, E., 2007. Synchrotron, X-ray absorption-edge computed microtomography imaging of thallium compartmentalization in *Iberis intermedia*. *Plant Soil* 290, 51–60.
- Schwertmann, U., Cornell, R.M., 2000. *Iron Oxides in the Laboratory*. John Wiley & Sons, Germany.
- Tack, F.M.G., Verloo, M.G., 1996. Estimated solid phase distribution of metals released in the acid extractable and reducible steps of a sequential extraction. *Int. J. Environ. Anal. Chem.* 64, 171–177.
- Tremel, A., Masson, P., Sterckeman, T., Baize, D., Mench, M., 1997a. Thallium in French agrosystems: I. Thallium contents in arable soils. *Environ. Pollut.* 95, 293–302.
- Vaněk, A., Chrástný, V., Komárek, M., Galušková, I., Drahot, P., Grygar, T., Tejnecký, V., Drábek, O., 2010a. Thallium dynamics in contrasting light sandy soil–soil vulnerability assessment to anthropogenic contamination. *J. Hazard. Mater.* 173, 717–723.
- Vaněk, A., Chrástný, V., Bečka, D., Mihaljevič, M., Šebek, O., Panušková, G., Schusterová, Z., 2010b. Thallium uptake by white mustard (*Sinapis alba* L.) grown on moderately contaminated soils—agro-environmental implications. *J. Hazard. Mater.* 182, 303–308.
- Vaněk, A., Grygar, T., Chrástný, V., Tejnecký, V., Drahot, P., Komárek, M., 2010c. Assessment of the BCR sequential extraction procedure for thallium fractionation using synthetic mineral mixtures. *J. Hazard. Mater.* 176, 913–918.
- Vaněk, A., Komárek, M., Vokurková, P., Mihaljevič, M., Šebek, O., Panušková, G., Chrástný, V., Drábek, O., 2011. Effect of illite and birnessite on thallium retention and bioavailability in contaminated soils. *J. Hazard. Mater.* 191, 190–196.
- Vaněk, A., Mihaljevič, M., Galušková, I., Chrástný, V., Komárek, M., Penížek, V., Zádorová, T., Drábek, O., 2013. Phase-dependent phytoavailability of thallium—a synthetic soil experiment. *J. Hazard. Mater.* 250–251, 265–271.
- Voegelin, A., Pfenninger, N., Petrikis, J., Majzlan, J., Plötze, M., Senn, A.C., Mangold, S., Steiner, R., Göttlicher, J., 2015. Thallium speciation and extractability in a thallium- and arsenic-rich soil developed from mineralized carbonate rock. *Environ. Sci. Technol.* 49, 5390–5398.
- Xiao, T., Guha, J., Boyle, D., Liu, C.Q., Chen, J., 2004. Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China. *Sci. Total Environ.* 318, 223–244.
- Yang, C., Chen, Y., Peng, P., Li, C., Chang, X., Xie, C., 2005. Distribution of natural and anthropogenic thallium in the soils in an industrial pyrite slag disposing area. *Sci. Total Environ.* 341, 159–172.