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Effect of illite and birnessite on thallium retention and bioavailability in contaminated soils

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ABSTRACT

The influence of illite and birnessite (δ-MnO$_2$) amendments on the retention and bioavailability of Tl in contaminated soils was investigated. The efficiency of both phases was evaluated using Tl uptake by white mustard (*Sinapis alba* L.), sequential extraction and sorption experiments. The obtained data demonstrate that the application of birnessite can effectively transform Tl from the labile (easily mobilizable) fraction to its reducible form, thus lowering Tl bioavailability in soil and subsequent accumulation by plants. The Mn oxide added to the soils reduced substantially Tl uptake; Tl levels in the plants decreased by up to 50%, compared to the non-amended soil. The effect of illite on the immobilization and uptake of Tl was less pronounced, and in the carbonate-rich Leptosol has not been proved at all, suggesting the importance of bulk soil mineralogy and nature of the soil sorption complex on the behavior of this amendment. Therefore, the general applicability of illite for Tl stabilization in soils seems to be limited and strongly dependent on soil composition. In contrast, the use of birnessite like soil additive might be an efficient and environment-friendly solution for soil systems contaminated with Tl.

1. Introduction

Thallium (Tl) is a toxic metal [1,2] included in the US EPA list of priority toxic pollutants. Because of its acute and chronic toxicity for most living organisms, which is higher compared to, e.g., Hg, Cd and Pb [2,3], Tl can be thought as one of the most dangerous elements in terrestrial environments. The predominant anthropogenic sources of Tl include emissions and solid wastes from coal combustion, ferrous and non-ferrous mining/smelting activities or eventually cement production [3–5]. Since Tl compounds are volatile at high temperatures, they are not efficiently retained in electrostatic precipitators or other emission-control facilities. Therefore, a large portion of Tl may be released into the atmosphere and enter the surrounding ecosystems. Average Tl levels in soils from such impacted areas commonly exceed 1 mg kg^{-1} [3,4].

The sorption of Tl in soils is generally attributed to simple exchange reactions on oxides, silicates or possibly organic matter [6–8]. According to Jacobson et al. [9], soil phases responsible for Tl retention include primarily Mn oxides (mainly birnessite, δ-MnO$_2$ [10]) and illite clays. Such Tl behavior is consistent with our previous findings [11,12] and can be explained by specific Tl adsorption and/or Tl–K replacement within the mineral structures, resulting from the same valency and similar ionic radius of Tl$^+$ to K$^+$ [4].

The phytoavailability of Tl depends on plant species, its form of binding and content in soil [5]. Previous investigations found that Brassicaceae plants have a potential to accumulate elevated amounts of Tl [13,14]. High accumulation rates were reported for several species, including *Iberis intermedia* Guers. (candytuft), *Biscutella laevigata* L., *Brassica oleracea acephala* L. (kale) and *Brassica napus* L. (rape) [14–18]. Thallium uptake is a result of several processes, which have not yet been fully explained, in particular considering that Tl is relatively stable/insoluble in soils. In addition, sulfur-containing compounds (e.g., amino acids and peptides), considered the main Tl-binding compounds in plant tissues, were found to be of less importance in Tl complexation and transfer in Brassicaceae (i.e., Tl was present as a free ionic and/or as a labile complex) [19].

Studies on remediation of Tl-contaminated soils generally recommend the phytoextraction technique using various species of the Brassicaceae due to their capability to (hyper)accumulate Tl [14–16]. On the other hand, the time needed for effective soil clean up usually reaches several decades. Therefore, such type

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Table 1
Basic physico-chemical characteristics of the investigated soils.

	Arenosol	Leptosol
Particle size distribution (%)		
Clay	1.3	0.4
Silt	6.4	30.6
Sand	92.3	69.0
pH_{H20}	6.7	7.4
pH_{KCl}	6.4	7.0
pH_{ZPC}	6.5	7.7
CEC (cmol kg^{-1})	10.1	28.3
TOC (%)	1.16	3.36
TIC (g kg^{-1})	b.d.l.	3.10
S_{tot} (g kg^{-1})	0.22	0.58
Oxalate extractable (g kg^{-1})		
Fe	1.91	2.23
Al	1.14	1.55
Mn	0.10	0.30
Initial metal concentrations (mg kg^{-1})		
Tl	0.43 ± 0	0.61 ± 0.02
Fe	7450 ± 312	20500 ± 60
Mn	146 ± 12	378 ± 8
Ca	1720 ± 27	14500 ± 60

b.d.l.: below detection limit.

of soil remediation, if applied, would be agro-technologically and financially demanding. To our best knowledge, there is no study describing Tl stabilization/immobilization (i.e., using mineral phases) in contaminated soils, representing an alternative remediation technique of Tl-contaminated soils. For this reason, we focused on biogeochemical behavior of Tl in soils amended with phases having a well-known affinity for this metal. The paper aims to (i) describe the effect of illite and synthetically-prepared Mn(III,IV) oxide (birnessite) added to contaminated soils on Tl retention and its subsequent uptake by white mustard (*Sinapis alba* L.), representing a Tl-accumulating species [20], and (ii) assess the stabilization/immobilization efficiency of individual amendments with respect to different soil composition.

2. Materials and methods

2.1. Soils

Two sandy soils with different characteristics (originating from the region of Central Bohemia, Czech Republic), a Haplic Arenosol and a Rendzic Leptosol [21], were used in this work. The soil samples were taken from the arable layers (0–20 cm) of agriculturally used soils. There were no major sources of Tl pollution in the close vicinities of the sampling areas. Samples used for soil characteristic determination were air-dried, homogenized and sieved through a 2 mm stainless-steel sieve prior to analyses. Soils used for pot experiments were air-dried, homogenized and sieved through a 5 mm stainless-steel sieve. Data on physico-chemical properties of the investigated soils are summarized in Table 1 and were determined using common methods described in Vaněk et al. [20]. Data on bulk soil mineralogy are given elsewhere [22].

2.2. Pot experiments and treatment

White mustard (*Sinapis alba* L.) was chosen as the tested plant species because of its high biomass yields and capability of extracting significant amounts of Tl [20]. The soils were artificially contaminated with Tl by making a single application of Tl_2SO_4 (analytical grade; Fluka, Germany) dissolved in deionized water to achieve 5 mg Tl kg^{-1}. Such Tl level approximately reflects an average/median concentration observed in topsoils from highly Tl-contaminated agroecosystems [3,6,14]. The contamination was followed by a wet–dry cycle for 6 months with consequent 2 vegetation seasons as described in Vaněk et al. [20].

The Tl-contaminated soils were put into 0.75 L plastic pots (0.8 kg of soil per pot) and separately treated with illite ($(K,H_3O)Al_2(Si,Al)_4O_{10}(OH)_2$) (1.5 wt.%) and birnessite ($K_4Mn_{14}O_{27}\cdot 9H_2O$) (0.5 wt.%). Illite used in this study was derived from the clay standard IMt-1 (Cambrian shale, Silver Hill, Montana, USA) supplied by the Clay Minerals Society (The Source Clays Repository, Purdue University, USA). The illite preparation included crushing and clay particle separation (<2 μm) using gravity sedimentation and centrifugation. Birnessite was synthesized according to the HCl–$KMnO_4$ method of McKenzie [23]. The amounts of minerals applied corresponded to their concentrations observed in agricultural soils [11]. The mineral applications to the soils were followed by a wet–dry cycle for 1 month in order to reach approximate geochemical equilibrium (mainly of soil pH and amendment distribution) in both soils. Approximately 150 mL of deionized water (∼60% of water holding capacity) was applied to the soils in seven-day intervals; the soils were homogenized at the end of the incubation.

The vegetation experiment was conducted in a greenhouse at temperatures between 18 and 25 °C. Four replicates were used for each soil and treatment; i.e., 24 pots in the experiment including the control treatments (without mineral amendments). In order to provide a sufficient nutrient supply, the soils were fertilized with 0.2 g pot^{-1} Kristalon Superior Soluble fertilizer (Hydro, Netherlands) (20% N; 10% P_2O_5; 10% K_2O; 2% MgO). Ten seeds of white mustard were sown in each pot. Normally developed plants were singled out after 1 month, i.e., five best-developed plants remained in each pot. The plants were harvested after 8 weeks of growth and roots, stems and leaves were sampled separately.

Biomass samples were carefully washed using deionized water, dried at 70 °C to constant weight and finely ground in a laboratory biomass grinder (MF 10 Basic, IKA, Germany) prior to decomposition. The samples (0.1–0.5 g) were digested in 60 mL PTFE beakers (Savillex, USA) with 3–6 mL of concentrated HNO_3 (suprapure grade, Merck, Germany) at 190 °C for 24 h. The residual solution was subsequently dissolved in deionized water (MILLI-Q Element, Millipore, France) and analyzed (see Section 2.5).

2.3. Chemical fractionation of Tl in the soils

In order to understand the role of individual amendments in Tl uptake from the soils, the chemical fractionation of Tl in the rhizosphere was investigated. For this purpose, soils at a close distance (0–5 mm) to rhizoplanes, with a maximum concentration of root exudates [5], were analyzed. As a control treatment, a non-amended rhizosphere soil subjected to the same fertilization/watering regime was used. The Tl fractionation in the soils was determined using the optimized BCR sequential extraction procedure by Rauret et al. [24]. A detailed description of the procedure is given elsewhere [24]. The residue from the third extraction step was digested in *aqua regia* using a microwave digestion unit (Mars 5, CEM, USA) and represents the residual Tl fraction. The sequential extraction was performed in four replicates and the sum of individual extraction steps was in good agreement with total Tl concentration (recovery differences were less than 10%). Chemicals of analytical grade (Lach-Ner, Czech Republic) and deionized water were used for individual extraction steps. Thallium concentrations in all digests were determined using ICP-MS (see Section 2.5).

2.4. Sorption experiments

A simple batch equilibrium experiment was performed in order to describe Tl sorption behavior in the studied soils. Thallium solu-