



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

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ARTICLE INFO

Article history:

Received 12 January 2011

Received in revised form 13 April 2011

Accepted 14 April 2011

Available online 21 April 2011

Keywords:

Thallium

Amendment

Soil

Uptake

Mustard

ABSTRACT

The influence of illite and birnessite (δ -MnO₂) 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.

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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 -MnO₂

[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 _{H2O} | 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 Tl₂SO₄ (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,H₃O)Al₂(Si,Al)₄O₁₀(OH)₂) (1.5 wt.%) and birnessite (K₄Mn₁₄O₂₇·9H₂O) (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–KMnO₄ 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% P₂O₅; 10% K₂O; 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 (Saville, USA) with 3–6 mL of concentrated HNO₃ (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-

tions with concentrations ranging from 0 to 2000 $\mu\text{mol Tl L}^{-1}$ were prepared using Tl_2SO_4 with 0.01 M NaNO_3 as the background electrolyte. Calculated saturation indices neglected Tl precipitation (e.g., TlOH , TlNO_3) in the experimental solutions. All chemicals used in the sorption experiment were of analytical grade (Fluka, Germany; Lach-Ner, Czech Republic). Thallium solutions were added to the soil samples (2 g L^{-1}) and shaken on an end-over-end shaker for 48 h in order to reach equilibrium. The sorption experiment was conducted in triplicates in centrifugation tubes at a constant temperature of 21 °C. The suspensions were then centrifuged and analyzed for Tl using ICP-MS (see Section 2.5). The concentration of sorbed Tl (Tl_s) was computed as the difference between the initial and the final Tl concentration at equilibrium after the sorption (Tl_{eq}). The values of Tl_s and Tl_{eq} were used for the construction of sorption isotherms (Freundlich and Langmuir) [25]. To avoid well-known limitations associated with the linearization of sorption isotherms, non-linear fitting models based on the least sum of squared errors (SSE) were chosen [26].

2.5. Analyses and quality control

The Tl concentrations in the mineralized plant samples, sequential extraction solutions and sorption solutions were determined using ICP-MS (X Series 2, Thermo Scientific, UK) under standard analytical conditions: measured isotopes ^{203}Tl , ^{205}Tl , ^{209}Bi (internal standard); RF power 1350 W; reflected power <1 W; gas flow rates coolant 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. The concentrations of K, Ca, Fe, Al and Mn were determined using ICP-OES (iCAP 6500, Thermo Scientific, Germany) under standard analytical conditions.

The calibrations of ICP-MS and ICP-OES measurements were performed against the multielement standard solutions Merck VI and Merck IV, respectively (CertiPUR, Merck, Germany). The quality of the analytical measurement was controlled using the standard reference materials INCT-TL-1 (tea leaves) (Institute of Nuclear Chemistry and Technology, Poland) and NIST 2711 (Montana II soil) (National Institute of Standards and Technology, USA). The accuracy of the measurements was <5% RSD.

2.6. Statistical treatment

Thallium concentrations in different plant parts were tested using Analysis of Variance (ANOVA) statistical test at a probability level of 5%. The tested factors in Figs. 1 and 2 with appropriate levels in brackets were as follows: soil treatment (control, soil + illite and soil + birnessite) and plant parts (roots, stems and leaves). For each soil type, the ANOVA test was performed separately. The soil type was not a tested factor. The tested factors in Fig. 3 with appropriate levels in brackets were as follows: soil treatment (control, soil + illite and soil + birnessite) and sequential extraction fractions (exchangeable/acid-extractable, reducible, oxidizable and residual). Again, the soil type was not a tested factor. The Duncan test on the basis of homogenous groups ($P < 0.05$) was chosen for all the post hoc comparisons (presented in Figs. 1–3). If the purpose is to decide which group of treatments is likely to have an effect, then it is better to use a more liberal test such as the Duncan test; however, this test can suffer from the Type I error. All the statistical tests presented in this study were performed using the software Statistica 6.0 [27]. Detailed information on the obtained ANOVA parameters (F criterion, degrees of freedom and probability level) is presented in Table 2.

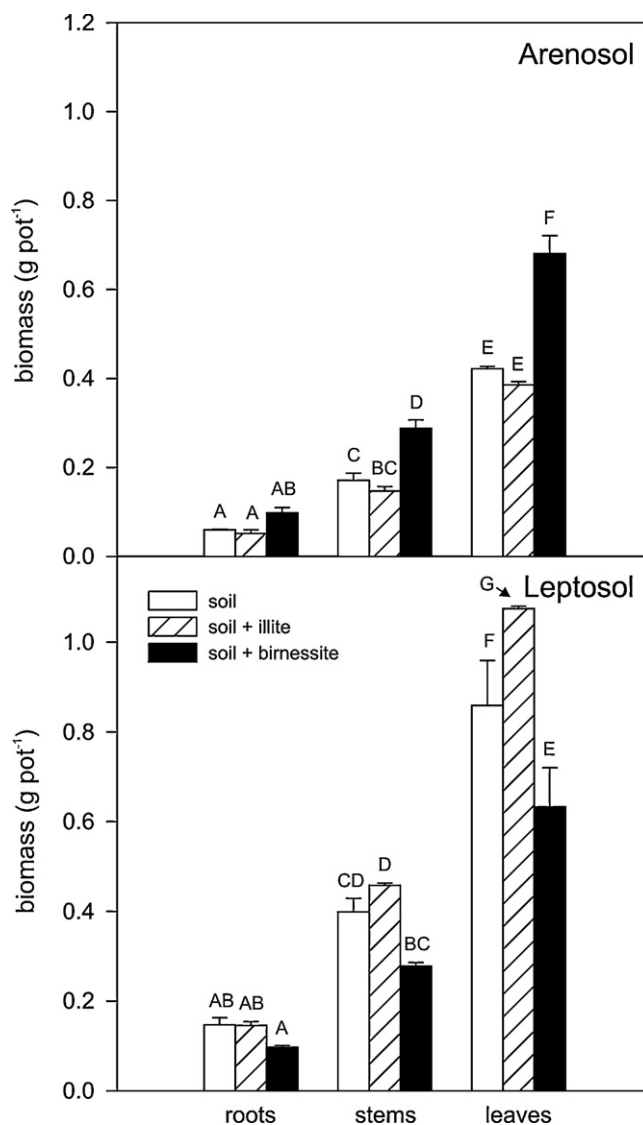


Fig. 1. Dry biomass yields of white mustard grown on the Tl-contaminated soils amended with illite (1.5 wt.%) and birnessite (0.5 wt.%). Data shown are means \pm SD ($N=4$).

3. Results and discussion

3.1. Plant biomass

The application of mineral amendments affected shoot biomass of mustard plants in both soils (Fig. 1). When birnessite was applied to the Arenosol, an increase of stem and leaf yields was observed as compared to the control treatment (non-amended soil). This finding is probably related to the reduced availability of Tl (see Section 3.2) and thus its weak inhibitory effect on plant growth. A similar behavior was found for the Leptosol where the presence of illite increased leaf yields (Fig. 1), possibly indicating a positive role of the amendment in nutrient availability from the soil sorption complex. The reduction of leaf biomass in the birnessite-amended Leptosol is questionable (Fig. 1). The phytotoxicity of Mn cannot be excluded as increased Mn amounts were detected in mustard roots ($\sim 300\text{ mg kg}^{-1}$). On the other hand, even higher Mn concentrations (up to 450 mg kg^{-1}) were found in roots of plants grown on the birnessite-amended Arenosol with a proven positive effect of the Mn oxide on shoot biomass. Therefore, a more probable explanation is that birnessite in the Leptosol

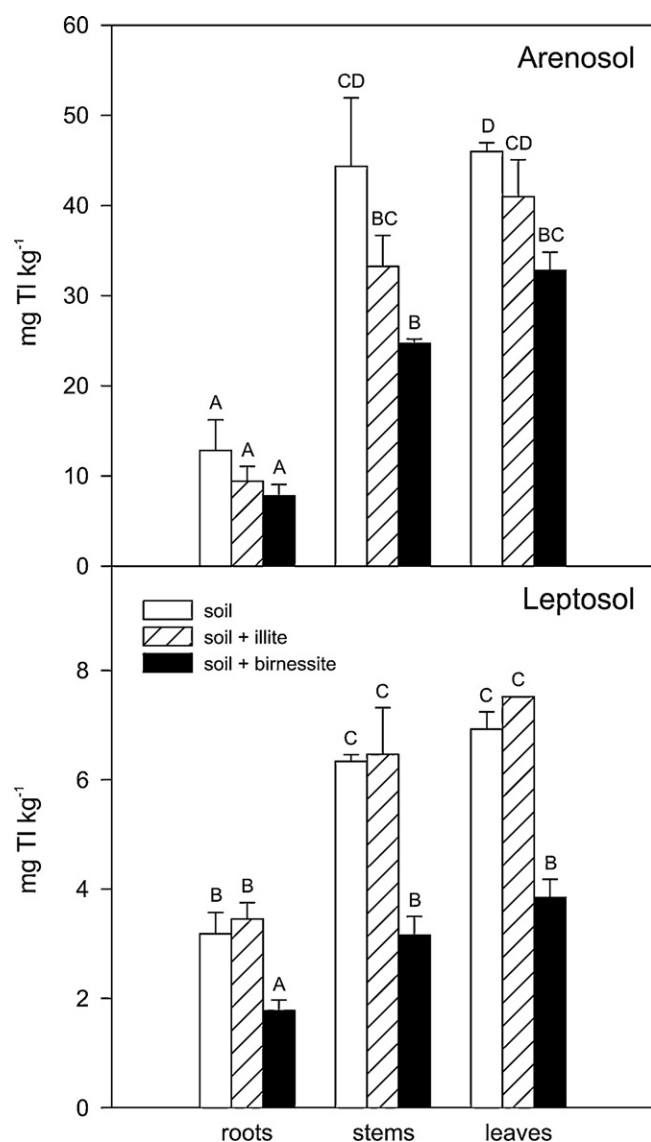


Fig. 2. Thallium concentrations (mg kg^{-1}) in different parts of white mustard grown on the Tl-contaminated soils amended with illite and birnessite. Data shown are means \pm SD ($N=4$). Same letters represent statistically identical values according to the Duncan test ($P<0.05$); each soil was treated separately.

matrix somehow limits the availability of specific nutrients (mainly K).

3.2. Plant uptake of Tl

Thallium concentrations in different parts of mustard plants are summarized in Fig. 2. Higher Tl levels were observed in shoots than in roots of mustard grown on both soils, proving a substantial translocation of Tl within the plant. The maximum Tl concentration (46 mg kg^{-1}) was detected in leaves of mustard grown on the non-amended Arenosol, followed by stems (44 mg kg^{-1}) and roots (13 mg kg^{-1}) (Fig. 2). Approximately 7-fold lower concentrations of Tl (7 mg kg^{-1} , in maximum) were found in stems and leaves from the Leptosol (i.e., non-amended). These findings suggest that the rate of Tl uptake by mustard and other Brassicaceae species is strongly dependent on soil type (especially bulk mineralogy) and its form in soil (adsorbed, bound to oxides, silicates, etc.). This is also consistent with a relatively large portion of labile Tl determined in the rhizosphere of the Arenosol (see Section 3.3).

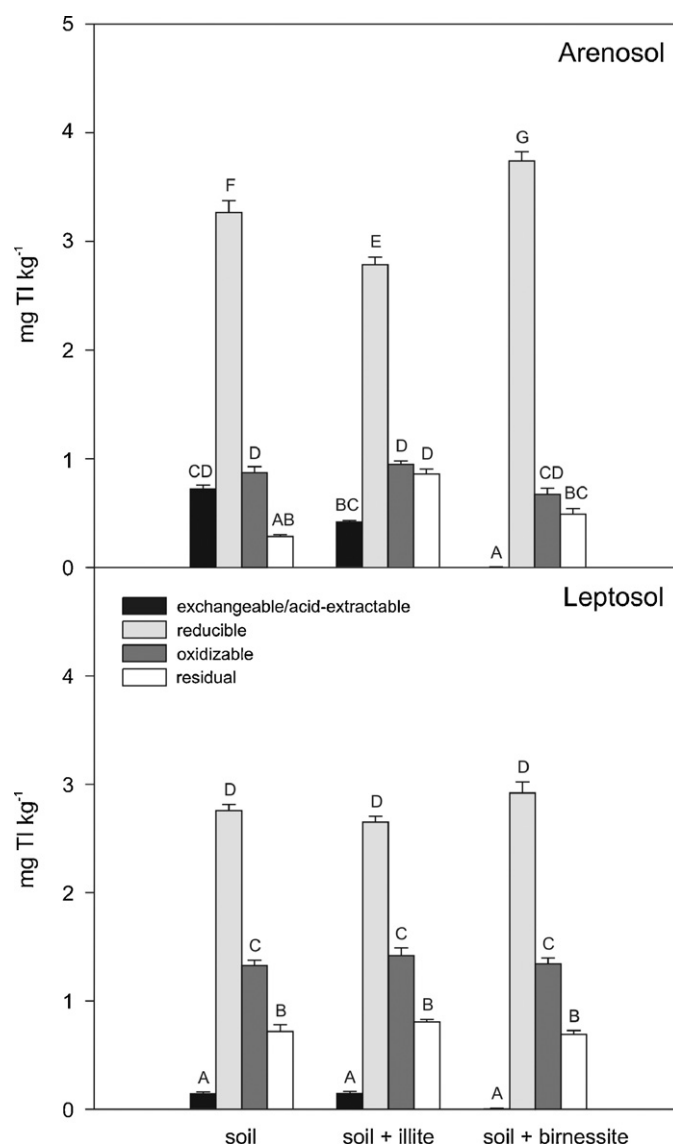


Fig. 3. Chemical distribution of Tl in the rhizosphere soils (i.e., amended and non-amended). Data shown are means \pm SD ($N=4$). Same letters represent statistically identical values according to the Duncan test ($P<0.05$); each soil was treated separately.

The addition of both birnessite and illite to the Arenosol reduced Tl concentrations in plant tissues (Fig. 2). Nevertheless, it must be highlighted that only birnessite affected significantly Tl uptake/immobilization; Tl levels in stems and leaves decreased by 44% and 29%, respectively, compared to the non-amended soil. This fact may be attributed to the strong affinity of this Mn(III,IV) oxide for Tl, as documented by Jacobson et al. [9]. It is believed that the association of Mn oxides with Tl results from the acidic character of these phases (pH_{ZPC} of MnO_2 2.8–4.5 [28]) and the oxidation of Tl^+ to Tl^{3+} , which is then tightly adsorbed or precipitated as Tl_2O_3 ($\log K_{\text{sp}} = -13$; MINTEQA2 database) on the oxide surface [10]. Furthermore, we propose a rapid incorporation of Tl into the birnessite structure (in K-exchanged layers) [12]. The influence of illite in the Arenosol was less pronounced; Tl levels in stems and leaves decreased by 25% and 11% (Fig. 2), respectively. A decrease in Tl uptake from the illite-amended Arenosol, although statistically insignificant, is in accordance with the ability of illite to efficiently sorb Tl. Specific adsorption of Tl, resulting from the structural Tl–K exchange [4], within the interlayers of illite has been already proven [6,29,30].

Table 2

The results of statistical evaluation using the ANOVA test (d.f.—degrees of freedom, F — F criterion and p —probability achieved in the test).

| | d.f. | F | p |
|---|------|------|-------|
| Dry biomass yields | | | |
| Soil type (A) | 1 | 383 | 0.000 |
| Plant part (B) | 2 | 72.8 | 0.000 |
| Soil treatment (C) | 2 | 13.7 | 0.000 |
| <u>A × B</u> | 2 | 47.1 | 0.000 |
| <u>A × C</u> | 2 | 6.22 | 0.009 |
| <u>B × C</u> | 4 | 1.44 | 0.261 |
| <u>A × B × C</u> | 4 | 0.85 | 0.512 |
| Thallium in plant parts | | | |
| Soil type (A) | 1 | 383 | 0.000 |
| Plant part (B) | 2 | 72.8 | 0.000 |
| Soil treatment (C) | 2 | 13.7 | 0.000 |
| <u>A × B</u> | 2 | 47.1 | 0.000 |
| <u>A × C</u> | 2 | 6.22 | 0.009 |
| <u>B × C</u> | 4 | 1.44 | 0.261 |
| <u>A × B × C</u> | 4 | 0.85 | 0.512 |
| Sequential extraction analysis | | | |
| Soil type (A) | 1 | 0.02 | 0.893 |
| Soil treatment (B) | 2 | 0.14 | 0.873 |
| SE fraction (C) | 3 | 848 | 0.000 |
| <u>A × B</u> | 2 | 0.27 | 0.768 |
| <u>A × C</u> | 3 | 29.9 | 0.000 |
| <u>B × C</u> | 6 | 11.1 | 0.000 |
| <u>A × B × C</u> | 6 | 4.20 | 0.005 |
| Exchangeable/acid-extractable fraction | | | |
| Soil type (A) | 1 | 109 | 0.000 |
| Soil treatment (B) | 2 | 88.6 | 0.000 |
| <u>A × B</u> | 2 | 40.4 | 0.000 |
| Reducible fraction | | | |
| Soil type (A) | 1 | 90.6 | 0.000 |
| Soil treatment (B) | 2 | 48.5 | 0.000 |
| <u>A × B</u> | 2 | 15.2 | 0.004 |
| Oxidizable fraction | | | |
| Soil type (A) | 1 | 95.3 | 0.000 |
| Soil treatment (B) | 2 | 3.41 | 0.103 |
| <u>A × B</u> | 2 | 1.65 | 0.269 |
| Residual fraction | | | |
| Soil type (A) | 1 | 1.79 | 0.229 |
| Soil treatment (B) | 2 | 1.79 | 0.245 |
| <u>A × B</u> | 2 | 0.86 | 0.471 |

The statistically significant factors A, B and C and their interactions are underlined. Sequential extraction analysis describing Tl fractionation in the soils was tested in scheme with the entire fractions together and each fraction separately to find out the significant fraction versus soil treatment.

Interestingly, the addition of illite to the Leptosol had no influence on Tl levels in mustard and even higher concentrations (2–8%), although statistically insignificant, were found in both roots and shoots (stems and leaves) (Fig. 2), indicating a negligible effect of illite in Tl stabilization in the carbonate-rich soils. Although it is not possible to make conclusions about the exact retention mechanisms involved, Tl coprecipitation with the newly formed carbonates, following partial CaCO_3 dissolution [22], seems to be the main factor controlling Tl uptake from this soil, despite the abundance of illite. In contrast, birnessite added to the Leptosol substantially reduced Tl uptake by the plant; the Tl accumulation rates for roots, stems and leaves dropped by 44%, 50% and 45%, respectively, as compared to the control treatment (i.e., non-amended soil) (Fig. 2).

3.3. Thallium dynamics in the rhizosphere

The rhizosphere of both studied soils can be characterized by a majority of Tl bound to the reducible fraction (corresponding approximately to soil oxides), reaching 64% (Arenosol) and 56%

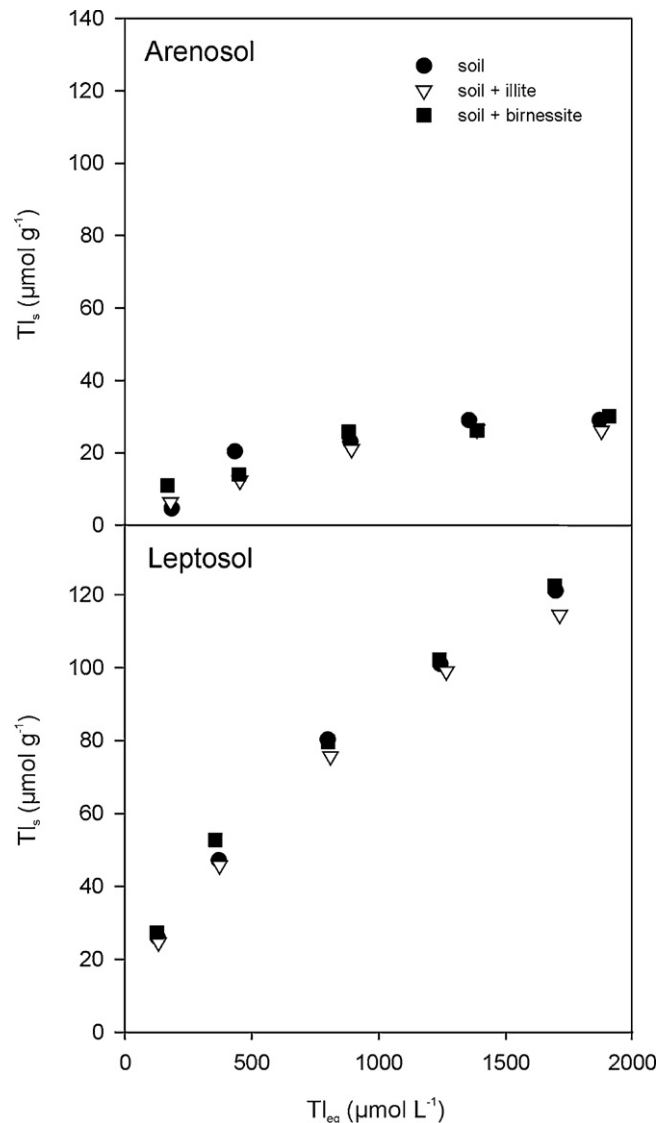


Fig. 4. Sorption isotherms of Tl. Tl_s —sorbed Tl; Tl_{eq} —final solute Tl concentration ($N=3$).

(Leptosol) of total Tl content (Fig. 3). Moreover, the Arenosol contained a higher portion (~14%) of labile Tl (associated with the exchangeable/acid-extractable fraction). Regarding the low CEC value (Table 1), suggesting a poor sorption efficiency of this soil, the presence of easily soluble or desorbed Tl is proposed. Retention of labile Tl in the Leptosol is most probably affected by the presence of CaCO_3 , as the preferential association of Tl with carbonates in alkaline soils is known [31]. Thallium bound to the oxidizable fraction attributed to strong binding sites on the soil organic matter (SOM) seems to be overestimated (Fig. 3). Considering that Tl complexation with most low-molecular weight organic acids ($\log K=0.5$ – 2.0), and fulvic acids ($\log K=3.3$ – 4.8) is weak [32], the formation of organic complexes is unlikely. On the other hand, Tl association with humic acids present in SOM cannot be neglected, as it has not been studied before.

The addition of illite to the Arenosol resulted in a decrease of Tl bound to both the exchangeable/acid-extractable and reducible fractions, corresponding to ~42% and 15% of the individual fractions, respectively. Additionally, an increase of the residual Tl fraction was found (Fig. 3). This shift in Tl equilibrium confirms its effective fixation by illite. Birnessite added to the Arenosol caused the complete depletion of labile Tl in the rhizosphere

(Fig. 3) with corresponding increase (~14%) of the reducible TI content. A similar trend, with a TI shift (~6%) towards the reducible fraction, was found for the Leptosol. Such TI behavior proves a distinct role of Mn oxides in TI dynamics in soil–plant systems. For the illite-amended Leptosol, no changes in distribution of TI fractions were observed (Fig. 3). These findings are in good agreement with data on plant uptake (Fig. 2) and clearly demonstrate a relationship between the contents of labile TI in soils and TI levels in the plants. In other words, most of the TI taken up was derived from the exchangeable/acid-extractable fraction. Nevertheless, partial dissolution of birnessite within the rhizosphere with consequent reducible TI release in the presence of root exudates is supposed. Increased Mn concentrations in roots of plants grown on the birnessite-amended soils (up to 10 times higher than in the non-amended soils) support this statement. The application of individual amendments had almost no effect on soil pH (<0.2 unit) due to the pH-buffering capacity of both soils. However, the low pH_{ZPC} of birnessite (<4) [10] implies the tendency of the Mn oxide to increase the pH (due to the prevailing surface protonation).

3.4. Thallium sorption onto the soils

Higher sorption of TI (Fig. 4) was observed for the Leptosol with elevated pH, total organic and inorganic C and Fe, Mn-(hydr)oxides resulting into an increased CEC value (28.3 cmol kg^{-1} vs. 10.1 cmol kg^{-1}) (Table 1). Additionally, the Arenosol was composed predominantly with sand (92.3%). Both the Freundlich and the Langmuir equation described sufficiently TI sorption onto the soils (model efficiencies $E=0.985\text{--}0.999$); nevertheless, the Freundlich equation yielded slightly higher efficiencies, which is in accordance with other works conducted on soils [25]. All isotherms fitted the L-type, which is a typical shape of the Freundlich model [33,34]. No significant differences of TI sorption were observed after the addition of illite or birnessite to the soils (Fig. 4), which highlights the importance of the entire soil sorption complex. However, the highest calculated values of the Freundlich parameter K_f , describing the affinity of the adsorbate for the adsorbent, were obtained after the addition of birnessite. This confirms again the high affinity of TI for Mn oxides [9,11].

4. Conclusions

Data presented in this work demonstrate that the application of birnessite ($\delta\text{-MnO}_2$) to the contaminated soils can effectively transform TI from the labile (easily mobilizable) fraction to its reducible form, thus lowering TI bioavailability and accumulation by plants. Birnessite added to the soils reduced substantially TI uptake by the plants (i.e., white mustard), compared to the control treatment. The effect of illite on the immobilization and uptake of TI was less pronounced, and in the carbonate-rich Leptosol it has not been proved at all. Therefore, the general applicability of illite for TI 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 TI. Although our experiment was conducted only on circum-neutral soils, due to the relative stability of birnessite at lower pHs, this amendment can be potentially used also for moderately acidic soils.

Acknowledgements

This research was funded by the grants of Czech Science Foundation (GAČR P210/11/1597 and GAČR P503/11/0840) and the project of Ministry of Education of the Czech Republic MSM 6046070901. The ICP-MS/OES analyses were supported by MSM 0021620855.

Two anonymous reviewers are thanked for improving the quality of the paper.

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