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# Thallium uptake by white mustard (*Sinapis alba* L.) grown on moderately contaminated soils—Agro-environmental implications

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ABSTRACT

The work focused on Tl uptake by white mustard (*Sinapis alba* L.) grown on moderately contaminated soils with different characteristics. The data presented here clearly demonstrate the ability of white mustard to (hyper)accumulate Tl. Substantially higher Tl levels were was found in mustard grown on the Arenosol as compared to the carbonate-rich Leptosol; a relationship between the content of labile Tl (adsorbed, bound to carbonates etc.) in soil and its uptake by the plant is suggested. Approximately 3-fold lower concentrations of Tl in roots and stems of the mature mustard (compared to the young plant) indicate a decreasing trend of Tl uptake with the age of the plant. The exchangeable/acid-extractable and reducible Tl fractions were evaluated as the dominant fractions controlling Tl transfer from both contrasting soils. Thallium associated with the residual fraction (e.g., incorporated into silicates) was rather stable in the rhizosphere, proving a negligible influence of root exudates on Tl release from such an operationally defined fraction, despite the anthropogenic origin of Tl. Regarding our results, when mustard is cultivated for nutrition purposes and/or as green manure, it may pose an important source of Tl introduction into the food chain.



## 1. Introduction

Thallium (Tl) is a toxic metal [1,2] included in the US EPA list of priority toxic pollutants. Its toxicological effects are compared with Hg, Cd or Pb [2,3]. Therefore, Tl can be thought as one of the most dangerous elements for the environment. Predominant anthropogenic sources of Tl include emissions or solid wastes from coal combustion and ferrous and non-ferrous mining/smelting activities [3–5]. Moreover, there has been evidence of Tl contamination as a consequence of cement production [6].

The phytoavailability of Tl depends on plant species, its form of binding and content of Tl in soil [7]. Previous investigations found that Brassicaceae plants have a potential to accumulate elevated amounts of Tl [6,8,9]. The highest accumulation rates were reported for several species; *Iberis intermedia* Guers. (candytuft), *Biscutella laevigata* L., *Brassica oleracea acephala* L. (kale) and *Brassica napus* L. (rape) [9–13]. These plants are therefore referred as Tl-hyperaccumulators. Because some members of Brassicaceae are commonly grown as vegetables (kale, kohlrabi, radish, green cabbage, white cabbage, turnip etc.), they pose a hazard with respect to the potential introduction of Tl into the food chain [11,14,15]. Nevertheless, levels of Tl in edible parts (roots and foliage) of such plants differ not only among plant species but also among individual cultivars [16]. According to Tremel and Mench [17], Tl is mostly accumulated by sulfur rich species of Brassicaceae. Thallium uptake is a result of a set of processes, which have not yet been fully explained, in particular considering that Tl is present in different fractions in contaminated 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 a labile complex) [18].

To our best knowledge, there is no data on Tl uptake by white mustard (*Sinapis alba* L.), a crop plant commonly cultivated in Central and Eastern Europe, Canada and northern regions of the USA. Therefore, the aims of this study were (i) to determine Tl concentrations in individual parts (root, stem, leave and seed) of white

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mustard grown on artificially contaminated soils and quantify the soil–plant transfer of Tl of anthropogenic origin, (ii) to evaluate the effect of different soil types on phytoavailability of Tl, (iii) to describe changes in Tl fractionation in the rhizosphere soil (i.e., within the root zone of the investigated plant) and thus to understand the mechanism of Tl uptake from the soil, and (iv) to assess the potential risk of Tl introduction into the food chain associated with the cultivation of white mustard.

## 2. Materials and methods

### 2.1. Soil sampling and preparation

Two sandy soils with different characteristics (originating from the region of Central Bohemia, Czech Republic), a Haplic Arenosol and a Rendzic Leptosol [19], 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 determinations were air-dried, homogenized and sieved through a 2-mm stainless-steel sieve prior to analyses. Soil used for pot experiments was air-dried, homogenized and sieved through a 5-mm stainless-steel sieve.

### 2.2. Soil characterization

Soil pH was measured using a 1:5 (v/v) ratio of soil and water or 1 M KCl solution [20] using a pH-meter Handylab pH 11 (Schott, Germany). The pH at the point of zero charge ($pH_{ZPC}$) was determined using the immersion technique described by Fiol and Villaescusa [21]. The contents of total organic carbon (TOC) and total sulfur ($S_{tot}$) were determined by catalytic oxidation (1350 °C) using a combination of Metalyt CS 500 and Metalyt CS 530 elemental analyzers (Eltra, Germany). The cation exchange capacity (CEC) was computed after saturation of the soil samples with 0.1 M $BaCl_2$ and $Ba^{2+}$ release using $MgSO_4$ [22]. Acid oxalate extraction (0.2 M ammonium oxalate/oxalic acid at pH 3) for amorphous and poorly crystalline Fe-, Mn- and Al-(hydr)oxide content was performed according to Pansu and Gautheyrou [23]. Oxalate-extractable amounts of Fe, Mn and Al were determined by FAAS (AA 280 FS, Varian, Australia). Particle size distribution was determined by the hydrometer method [24].

Soil samples were digested in a mixture of concentrated acids ($HF/HNO_3/HClO_4$) and analyzed for initial Tl and metal (Fe, Mn and Ca) concentrations using ICP-MS and ICP-OES, respectively (See Section 2.5). All chemicals used were of analytical grade (Lach-Ner, Czech Republic; Merck, Germany). Basic physico-chemical parameters of the investigated soils are summarized in Table 1. Complete data on bulk soil mineralogy are given elsewhere [25].

**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 |
| TS (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 |
| 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.

### 2.3. Pot experiments and plant treatment

White mustard (*Sinapis alba* L.) was chosen as the tested plant species because of its high biomass yields and potential capability of extracting significant amounts of Tl.

A 5-kg mass of air-dried and sieved (≤10 mm) soil was put into a 5-L plastic pot. The soils were contaminated with Tl by making a single application of $Tl_2SO_4$ (analytical grade; Fluka, Germany) (100 mL of 250 mg Tl $L^{-1}$) dissolved in water to achieve 5 mg Tl $kg^{-1}$. Such Tl concentration can be thought as a moderate soil contamination. For example, in areas affected by sulfide ore mining/processing (i.e., by Tl-bearing sphalerite, galena, pyrite etc.) the average Tl concentrations in soils commonly exceed 5 mg Tl $kg^{-1}$ [3,9]. The contamination was followed by the wet-dry cycle for 6 months in order to reach approximate chemical equilibrium state of Tl in both soils. The incubation was carried out at a constant temperature of 21 °C in an indoor preparation hall. One thousand mL of deionized water (~60% of water holding capacity, WHC) was applied to the soil at the start of the incubation; 200 mL of deionized water was periodically added to the soil at seven-day intervals. Such watering simulated the real/variable soil moisture conditions. After the wet-dry cycle, pot experiments (with plants) in two vegetation periods were conducted; between June–August and September–October 2009, respectively.

In order to provide a sufficient nutrient supply, the soils were treated with 1 g $pot^{-1}$ Kristalon Superior Soluble fertilizer (Hydro, Netherlands) (20% N; 10% $P_2O_5$; 10% $K_2O$; 2% MgO). Consequently, ten seeds of white mustard (*Sinapis alba* L.) were sown in each pot in June. Four replicates were used for each soil including a control treatment (16 pots in the experiment). Normally developed plants were singled out in July, i.e., the five best-developed plants remained in each pot. The pots were protected against rain during the whole period. Soil moisture was kept at ~60% of WHC by watering with deionized water. Fully mature plants were harvested after 12 weeks (in August). Roots, stems and seed pods (seeds) were collected separately, weighted and stored for analyses. During harvest, the plants were defoliated; therefore, leaves were not sampled in this part of the experiment. After the harvest, soil from all the pots was carefully cleaned, homogenized and reused in the following experiment. Ten seeds of mustard were sown again in September. The treatment and the conditions (water regime, fertilization etc.) were the same as those described for the first pot experiment. The plants were harvested after 8 weeks growth (in October); roots, stems and leaves were sampled. This scheme for the pot experiments was chosen in order to simulate seed and green manure production.

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 seeds were used without grinding. The samples (0.2–0.5 g) were digested in 60-mL PTFE beakers (Savillex, USA) with 3–10 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).

**Table 2**
Thallium concentrations (mg kg$^{-1}$) in different plant parts of white mustard grown on Tl-spiked Arenosol and Leptosol (with 5 mg Tl kg soil$^{-1}$ added) after 12 and 8 weeks, respectively.

| Soil type | | Vegetation period/weeks | | | | | |
|---|---|---|---|---|---|---|---|
| | | June–August/12 | | | September–October/8 | | |
| | | Roots | Stems | Seeds | Roots | Stems | Leaves |
| Arenosol | Control | $0.07^{a} \pm 0.01$ | $0.09^{a} \pm 0.01$ | $0.12^{a} \pm 0.01$ | $0.19^{a} \pm 0.02$ | $0.31^{a} \pm 0.10$ | $0.17^{a} \pm 0.01$ |
| | Tl-spiked | $9.65^{de} \pm 2.20$ | $19.9^{f} \pm 3.3$ | $13.4^{e} \pm 0.5$ | $34.8^{c} \pm 1.5$ | $65.0^{e} \pm 7.1$ | $47.8^{d} \pm 1.5$ |
| Leptosol | Control | $0.06^{a} \pm 0.01$ | $0.05^{a} \pm 0.01$ | $0.11^{a} \pm 0.01$ | $0.09^{a} \pm 0.01$ | $0.09^{a} \pm 0.01$ | $0.10^{a} \pm 0.002$ |
| | Tl-spiked | $1.84^{ab} \pm 0.61$ | $4.42^{bc} \pm 1.41$ | $6.62^{cd} \pm 0.37$ | $5.54^{ab} \pm 0.59$ | $8.43^{b} \pm 0.64$ | $7.01^{ab} \pm 0.10$ |

Data shown are means ± SD ($n = 4$). Same letters represent statistically identical values according to the Duncan test ($p < 0.05$). Data from each harvest were treated separately.

### 2.4. Chemical fractionation of Tl in the rhizosphere soils

In order to understand Tl uptake from the soil, the chemical fractionation of Tl in the rhizosphere soils was studied. For this purpose, soils at a close distance (0–5 mm) to rhizoplanes, with a maximum concentration of root exudates [6], were analyzed. The soils were sampled using a stainless-steel tube (5-mm diameter) at the end of the second vegetation season (in October). As a control treatment, an unplanted soil (contaminated with 5 mg Tl kg$^{-1}$; subjected to the same fertilization/watering regime) was used.

The Tl fractionation in both soils was determined using the optimized BCR sequential extraction procedure by Rauret et al. [26]. Extraction solutions were prepared using analytical grade chemicals (Lach-Ner, Czech Republic; Merck, Germany). The fractions determined were as follows: (i) exchangeable/acid-extractable fraction (0.11 M $CH_3COOH$-extractable); (ii) reducible fraction (0.5 M $NH_2OH{\cdot}HCl$-extractable); (iii) oxidizable fraction (8.8 M $H_2O_2$/1 M $CH_3COONH_4$-extractable); (iv) residual fraction (total digestion of the residue using a mixture of concentrated $HF/HNO_3/HClO_4$). The extraction was performed in four replicates and the sum of individual extraction steps was in a good agreement with total Tl concentration (recovery differences were less than 10%). Thallium concentrations in all digests were determined using ICP-MS (see Section 2.5).

### 2.5. Analyses and quality control

The concentrations of K, Ca, Fe and Mn were determined using ICP-OES (iCAP 6500, Thermo Scientific, Germany) under standard analytical conditions. The Tl concentrations in the mineralized plant materials, the sequential extraction solutions and total digests were determined using ICP-MS (X Series 2, Thermo Scientific, UK) under the standard 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 calibrations of ICP-MS and ICP-OES measurements were performed against the multi-element 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).

### 2.6. Statistical treatment

The dry biomass data (Fig. 1) and Tl concentrations in different plant parts (Table 2) for individual vegetation periods were tested using Analysis of Variance (ANOVA) statistical test at a probability level of 5%. The post hoc Duncan test was used to find differences in biomass yield and Tl concentration in various plant parts (roots, stems, leaves, seeds). The chemical Tl fractions in the rhizosphere soils were tested using ANOVA with post hoc Duncan test ($p < 0.05$) as well. Each soil type was tested separately (Fig. 2). All the statistical tests presented in this study were performed using Statistica 6.0 software package [27].

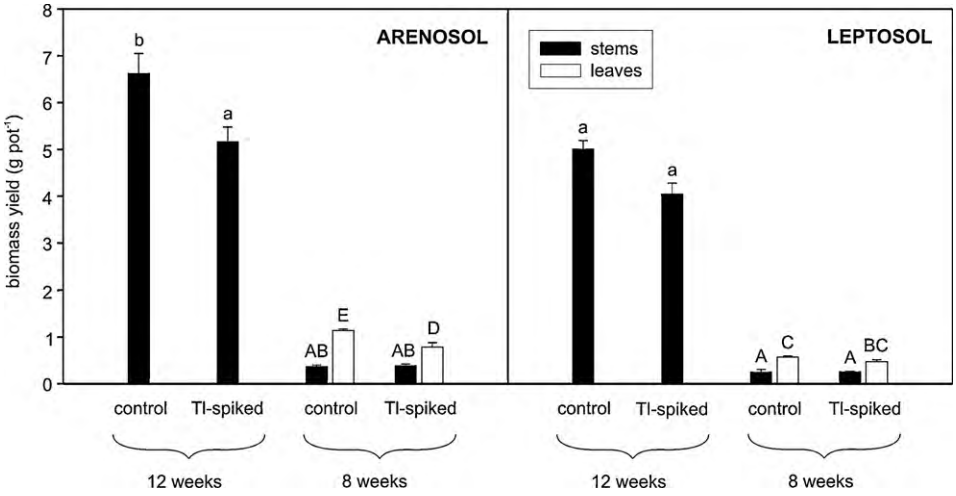


**Fig. 1.** Dry biomass yields of white mustard grown on Tl-spiked Arenosol and Leptosol after 12 and 8 weeks (corresponding to June–August and September–October vegetation periods, respectively). Data shown are means ± SD ($n = 4$). Same letters represent statistically identical values according to the Duncan test ($p < 0.05$). Data from each harvest were treated separately.

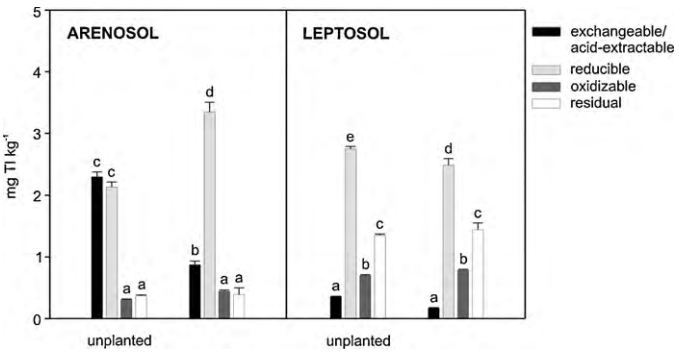


**Fig. 2.** Chemical distribution of Tl in the rhizosphere after 8 weeks of mustard growth as compared to the unplanted soil. Data shown are means ± SD ($n = 4$). Same letters represent statistically identical values according to the Duncan test ($p < 0.05$); each soil was treated separately.

## 3. Results and discussion

### 3.1. Plant yields and Tl uptake by white mustard

The average dry weight (above-ground) yields of mustard after the two vegetation periods are summarized in Fig. 1. In general, the absolute yields of mustard biomass were higher for plants grown on the Arenosol, resulting probably from an increased nutrient availability in this soil. Thallium uptake significantly reduced the stem yield of the mature plants (harvested after the first vegetation period) from the Arenosol. A similar trend, although statistically insignificant, was observed for mustard grown on the Leptosol. In the case of the immature plants (harvested after the second vegetation period), decreased leaf biomass by dry weight was noted for both contaminated soils (Fig. 1).

Thallium concentrations in different plant parts are given in Table 2. Generally higher Tl levels were found in mustard grown on the Arenosol, the soil with a large portion (~45%) of labile Tl (see Section 3.3). The maximum concentration of Tl (65 mg $kg^{-1}$) was detected in stems of young mustard shoots (i.e., associated with the Arenosol), followed by leaves (47.8 mg $kg^{-1}$) and roots (34.8 mg $kg^{-1}$) (Table 2), respectively. Approximately 3-fold lower concentrations of Tl (19.9 mg $kg^{-1}$, in maximum) were observed in roots and stems of the mature plants in this soil. These findings indicate that the rate of Tl uptake is decreasing with the age of the plant. Such Tl behavior can be interpreted by enhanced nutrient uptake (mainly of K) by young mustard shoots [28] and the tendency of Tl to substitute K in biogeochemical reactions/cycling [29]. Furthermore, a significant correlation ($R = 0.955$, $p < 0.05$) between Tl and K concentrations in different parts of the mustard plants was found. The substitution of Tl for K in plants has been described by many researchers [8,30,31]. In biochemical processes, Tl occurs as a singly charged, weakly hydrated cation ($Tl^+$) with ionic radius similar to $K^+$, and is expected to interfere competitively with K-dependent biological reactions [30]. It is believed that the $Na^+/K^+$–ATPase plays the main role in uptake of $Tl^+$ [32].

For the Leptosol, significantly lower Tl uptake by mustard was identified; the average Tl concentrations in the individual plant parts (roots, stems and leaves) were 5–8-fold lower as compared to the Arenosol. The Tl concentrations in roots and stems of the mature mustard accounted for 1.8 and 4.4 mg $kg^{-1}$, respectively, and were thus 3- and 2-fold lower than the concentrations in the immature plants (as in the Arenosol) (Table 2).

**Table 3**
Translocation factors (TF) of Tl in individual plant parts of white mustard.

| | | Leaves/stems | Seeds/stems |
|---|---|---|---|
| Arenosol | Tl-spiked | 0.74 | 0.67 |
| Leptosol | Tl-spiked | 0.83 | 1.50 |

The concentrations of Tl determined in mustard seeds were rather high reaching 13.4 and 6.6 mg $kg^{-1}$ for the Arenosol and the Leptosol, respectively, proving that Tl is effectively accumulated in the reproductive organs of the plant. Moreover, the Tl content in the mustard seeds grown on the Leptosol exceeds Tl levels in other plant organs (roots and stems) (Table 2). Comparable rates of Tl accumulation in seeds exceeding its content in soil were reported for rape [8,13], suggesting a similar physiology of Tl cycling in these Brassicaceae plants.

The calculated transfer coefficients (TC; a ratio of Tl concentration in the plant to total Tl concentration in the soil [12]) clearly demonstrate a different pattern of Tl accumulation in mustard for each soil type. In the case of the Arenosol, the TC values related to green parts (stems, leaves and seeds) were in the range of 3–13. The TC values for the Leptosol were substantially lower (0.9–1.7), as expected. The translocation factors (TF; ratio of Tl in individual plant parts) are given in Table 3.

The results suggest that soil mineralogy and/or content and quality of soil organic matter (SOM) are the main factors influencing Tl availability and consequently both the uptake and distribution of anthropogenic Tl between different parts of mustard plant.

### 3.2. Thallium removal from the contaminated soils

As a rule, the Tl uptake (per pot) was higher for mustard grown on the Arenosol (Table 4); the maximum uptake rate achieved 107 μg Tl $pot^{-1}$ by the mature plants (including seeds) and represented approximately 0.5% of total Tl content in the pot. Nevertheless, it must be highlighted that the mature plants were defoliated. Therefore, the rates of Tl removal were reduced by its amount in leaves. As consequence of lower biomass yields for the second vegetation period (resulting from shorter vegetation time and different climatic conditions), the Tl removal from both the Arenosol and Leptosol decreased (Table 4). It is probable, that the total Tl uptake by mustard under field conditions, as reported by Kurz et al. [16] for rape, will be higher compared to the pot experiment. This is because biomass production is generally reduced when plants are grown in pots.

Al-Najar et al. [9] and LaCoste et al. [11] mentioned that Brassicaceae species have a potential for Tl phytoextraction. Nevertheless, as Tl generally accompanies other metals/metalloids (primarily of Zn, Pb, Cd and As), which predominate in anthropogenically affected soils (e.g., contaminated by mining/smelting activities), their toxicity and inhibition effect on

**Table 4**
Average uptake of Tl by white mustard from the experimental pots after individual vegetation periods.

| Vegetation period/weeks | Plant part | Arenosol | | Leptosol | |
|---|---|---|---|---|---|
| | | μg Tl $pot^{-1}$ | % | μg Tl $pot^{-1}$ | % |
| June–August/12 | Stems | 104 ± 23 | 0.42 | 18 ± 7 | 0.07 |
| | Seeds | 3 ± 0 | 0.01 | 1 ± 0 | 0.00 |
| September–October/8 | Stems | 26 ± 4 | 0.10 | 2 ± 0 | 0.01 |
| | Leaves | 38 ± 6 | 0.15 | 4 ± 1 | 0.02 |

plant growth are probably more important than when Tl is the sole contaminant. For this reason, the use of white mustard (and other Tl-accumulating species) for Tl phytoextraction in real conditions (i.e., with multi-element contamination) is questionable.

### 3.3. Mechanism of Tl uptake from the rhizosphere soil

Both the Arenosol and Leptosol can be characterized as soils with a majority of Tl bound to the reducible fraction (corresponding approximately to soil oxides), reaching 42% and 53% of total Tl content, respectively (Fig. 2). Moreover, the Arenosol contained a large portion (~45%) of labile Tl (associated with the exchangeable/acid-extractable fraction). Regarding the low CEC value (Table 1), indicating a poor sorption efficiency of this soil, the presence of easily soluble and desorbed Tl (present as free $Tl^+$ or $TlNO_3{}^0$) is proposed. Retention of labile Tl in the carbonate-rich Leptosol is most probably controlled by Tl coprecipitation with the newly formed carbonates following partial $CaCO_3$ dissolution. Thallium bound to the oxidizable fraction (attributed to strong binding sites on the soil organic matter) seems to be overestimated. Considering that Tl complexation with most organic ligands ($\log K = 0.5–2.0$), and fulvic acids ($\log K = 3.3–4.8$) is weak [33], the formation of organic complexes is unlikely.

Although, the absolute Tl uptake by mustard from the soils was lower in the second vegetation season (as compared to the first one) (Table 4), Tl depletion from the rhizosphere soil (0.3 mg $kg^{-1}$, in maximum) was observed. In addition, a shift in Tl equilibrium between particular chemical fractions in the rhizosphere was detected (Fig. 2).

For the Arenosol, the amount of labile Tl dropped significantly (~60%), compared to the unplanted soil. A similar trend (although insignificant) was found for the Leptosol, suggesting preferential Tl uptake from the easily soluble species (desorbed, adsorbed, bound to carbonates etc.). The Tl associated with the reducible fraction decreased (~10%) in the Leptosol, thus, the contribution of this fraction to plant uptake is likely. On the other hand, the Arenosol showed a substantial increase (~55%) of the reducible Tl (Fig. 2). This fact implies the tendency of labile Tl to be transformed into the reducible species (e.g., associated with Mn(III,IV) oxides [34]) in the presence of root exudates. The strong affinity of Mn oxides (mainly birnessite, δ-$MnO_2$) for Tl is well known [34,35]. However, the influence of ageing of anthropogenic Tl cannot be fully excluded. Surprisingly, residual Tl contents were similar (compared to the control) in both soils, indicating a greater stability of this fraction in the rhizosphere of circumneutral soils.

The solubilization mechanism of soil Tl by simple organic acids, simulating root exudates, was previously evaluated as indirect [25]. Data obtained by speciation modeling suggest that complexation of organic ligands with major elements (mainly Ca, Mg, Al) originating from various soil phases (e.g., carbonates, oxides) is the prevailing process of Tl mobilization. The effect of $H^+$-promoted dissolution seems to be of a minor importance [25]. Although, soil pH is considered to be an important chemical factor controlling metal uptake by plants, no significant pH variation was detected between rhizosphere and unplanted soils (data not shown). Accumulation of Tl by mustard might thus not be related to acidification of the rhizosphere.

In conclusion, root exudation combined with root uptake resulted changes in the distribution of less stable Tl fractions, i.e., those primarily formed by the exchangeable/acid-extractable and reducible species. Therefore, these fractions are assumed to have the highest potential for Tl depletion in the contaminated rhizosphere, as also noted by Al-Najar et al. [9].

### 3.4. Agro-environmental implications

Our findings proved the tendency of white mustard (*Sinapis alba* L.) to accumulate high amounts of Tl, particularly within the green parts of the plant. However, the rate of Tl uptake was strongly dependent on the portion of labile Tl in soil; therefore, CEC, $pH/pH_{ZPC}$, soil mineralogy and content and quality of SOM are suggested as critical parameters influencing Tl uptake by mustard (and probably other Brassicaceae) from the moderately contaminated soils. It is probable that long-term (repeated) cultivation of mustard will result in reduction of total Tl uptake, following the lower yields and Tl concentration in plant biomass [16]. These aspects must be taken into account prior to general agro-environmental recommendations in areas affected with Tl.

Due to the high Tl levels (up to 13 mg $kg^{-1}$) detected in mustard seeds, intensive consumption of mustard-derived food products may be a potential pathway of Tl introduction into the food chain; mustard seed is used as raw material for producing table mustard, mustard oil or spice mixtures. Because of high toxicity of Tl, cultivation of mustard (as well as other Tl-accumulating species) should be thus monitored and alternatively excluded from growing for human nutrition in areas with high anthropogenic or natural Tl inputs. Although, Tl of geochemical origin is considered as relatively "insoluble" (e.g., incorporated into silicates or sulfides), previous investigations found [8,13,15] that even such Tl may be to a great extent taken up by different Brassicaceae plants. When mustard is used as green manure, accumulation of Tl in topsoil is supposed. The effect of (bio)degradation of Tl-rich plant parts with consequent Tl release into soil favors such prediction. It must be noted that there are no threshold limits for Tl in soils and foodstuffs in most countries. The remaining question is to what extent can Tl be accumulated by other mustard crops such as *Brassica nigra* L. or *Brassica juncea* L.

## 4. Conclusions

The data presented in this work clearly demonstrate the ability of white mustard (*Sinapis alba* L.) to accumulate large amounts of Tl. Substantially higher Tl uptake was found in mustard grown on the Arenosol as compared to the carbonate-rich Leptosol; a relationship between the content of labile Tl in soil and its uptake by the plant is suggested. The exchangeable/acid-extractable and reducible Tl fractions were probably the dominant fractions controlling Tl uptake from both contrasting soils. Thallium associated with the residual fraction (e.g., incorporated into silicates) was rather stable in the rhizosphere, proving a negligible influence of root exudates on Tl release from such an operationally defined fraction. Regarding our results, when mustard is cultivated for nutrition purposes and/or as green manure, it may pose an important source of Tl introduction into the food chain.

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