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UPTAKE AND FRACTIONATION OF THALLIUM BY *BRASSICA JUNCEA* IN GEOGENIC THALLIUM-AMENDED SUBSTRATE

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Abstract

This study shows thallium (Tl) concentrations in *Brassica juncea* (Indian mustard) tissue are over an order of magnitude higher (3830 $\mu\text{g/kg}$) than the substrate (100 $\mu\text{g/kg}$) and are strongly influenced by the underlying mineralogy, i.e., Tl bioaccessibility depends on the mineral structure: K-feldspar > Mn-nodule > hendricksite mica. The majority of Tl for all substrates is contained in edible parts of the plant, i.e. leaves (41% of total Tl, on average) > flower stems (34%) > seed pods (11%) $\approx$ stems (10%) > flowers (3%). We also show that Tl isotope fractionation induced by *B. juncea* is substantial, at nearly 10 $\epsilon^{205}\text{Tl}$ units, and generates systematic plant-specific patterns. Progressive plant growth strongly fractionates Tl isotopes, discriminating against ^{205}Tl as the plant matures. Thus, ^{205}Tl values are systematically higher in the early-formed stem ($\epsilon^{205}\text{Tl}_{\text{avg}} = +2.5$) than in plant elements formed later ($\epsilon^{205}\text{Tl}_{\text{avg}} = -2.5$ to $+0.1$), which demonstrates the large degree of translocation and the associated effects during plant growth. This study establishes the potential of Tl isotopes as a new tool in understanding heavy metal (re-)distribution during anthropogenic and geologic processes and the utility of such information in environmental and health-related planning, as well as phytomining or bioprospecting.

Graphical Abstract

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Keywords

thallium; *Brassica juncea*; Indian mustard; stable isotope fractionation

INTRODUCTION

Thallium (Tl) is a heavy metal that is enriched in certain geologic environments, notably some ore-forming systems, coals, and black (organic carbon-rich) shales. It is on the US EPA list of priority toxic pollutants and has a drinking water maximum contaminant level of 2 $\mu\text{g/L}$. It has been estimated that the world average daily intake of Tl is 2 $\mu\text{g/day}$ and that plants are safe for human consumption if they contain less than 0.3 mg Tl/kg plant on a dry weight basis.¹ Exposure to or consumption of Tl may bring with it adverse health effects including gastroenteritis, polyneuropathy, and alopecia, which can ultimately precede death.^{2,3} The toxicity of Tl is enhanced by the fact that, because of a chemical behavior similar to that of K^+ , biologic systems have the ability to accumulate, and in some cases hyperaccumulate, Tl within their tissue.⁴

Thallium occurs in two oxidation states (Tl^+ and Tl^{3+}), with associated differences in ionic size and bonding. In the reduced state, Tl^+ is the same charge and comparable in size to K^+ , with ionic radii at 1.76 Å and 1.60 Å, respectively. This allows Tl^+ to substitute for similar-sized alkali element K^+ in rock-forming minerals, including silicates and sulfates,^{5,6} as well as in biologic systems.^{7,8} Although Tl is highly toxic to humans, certain plant species have been shown to bioaccumulate this element in their tissues at relatively high concentrations with no adverse effects^{4,7,9–11}. One such family of plants is Brassicaceae, which contains species that have previously been shown to accumulate Tl within their tissues.^{4,9} Several members of this crucifer plant family are commonly raised as food crops (e.g., mustard, broccoli, Brussels sprouts, cabbage, cauliflower, kale). The combination of being active Tl bioaccumulators and food crops presents both environmental and human health risks.

While posing a significant health risk to humans, these same plants present other opportunities, such as the potential for phytomining or bioprospecting. A species within the Brassicaceae, *B. juncea*, commonly referred to as Indian mustard, has been identified as a plant capable of withstanding high concentrations of Tl via bioaccumulation and thereby has

the potential for utilization in phytomining, bioprospecting and phytoremediation, and other geochemical exploration techniques.^{10,12,13} The potential benefits of utilizing *B. juncea* are three-fold: 1) plant-based extraction of metals with economic or environmental benefit, such as Tl; 2) sustainable soil management and risk minimization; and 3) long-term (multi-seasonal or multi-generational), less labor intensive geochemical sampling techniques during exploration for ore deposits.^{10,14,15}

Typically, Tl occurs in bedrock in relatively low concentrations, with a crustal average of 0.5 – 0.7 mg/kg.^{5,6,16,17} However, some geologic and anthropogenic processes can concentrate Tl by several orders of magnitude, such as coal formation, epithermal gold mineralization, magmatic differentiation, and certain types of hydrothermal alteration, among others. For example, as a result of fossil fuel combustion, ferrous and non-ferrous metal smelting, and other industrial processes (e.g., cement production), an estimated annual flux of 2,000 – 5,000 tons per year of Tl is released to the atmosphere, resulting in localized high Tl concentrations (or [Tl]) reaching tens or hundreds of mg/kg, and in some cases weight percent concentrations.^{1,17–20} These processes can also isotopically fractionate Tl, which occurs as two stable isotopes, ²⁰³Tl (29.5%) and ²⁰⁵Tl (70.5%). The relative abundance of ²⁰⁵Tl versus ²⁰³Tl is by convention expressed in the ε-notation:

$$\epsilon^{205}\text{Tl} = \left(\frac{\left(\frac{^{205}\text{Tl}}{^{203}\text{Tl}} \right)_{\text{sample}}}{\left(\frac{^{205}\text{Tl}}{^{203}\text{Tl}} \right)_{\text{NIST 997}}} - 1 \right) \times 10,000 \quad (1)$$

where $\epsilon^{205}\text{Tl}$ is the deviation of the sample ²⁰⁵Tl/²⁰³Tl ratio compared to that in the NIST 997 standard. The natural variability in size, charge, bonding properties, and redox of Tl can lead to a considerable fractionation in some geologic and anthropogenic systems, with natural isotopic variations spanning more than 35 $\epsilon^{205}\text{Tl}$ units.^{20–23} Previous studies have shown a strong mineralogical control on both [Tl] and $\epsilon^{205}\text{Tl}$ values in geologic environments and soil genesis.^{4,20,24–26} These controls mainly involve the substitution of Tl⁺ for K⁺ in K⁺-bearing silicate minerals, such as potassium feldspar (K-feldspar) and mica, however, Tl is also commonly found, to a lesser extent, associated with sulfide minerals. Sulfide minerals have lower [Tl] but have consistently higher $\epsilon^{205}\text{Tl}$ values compared with other coexisting silicate minerals.²⁰ Thus, the weathering of K-feldspars and micas along with the oxidation of exposed sulfide minerals are processes which may control Tl mobilization rates and isotopic values in surrounding soils, water, and plant tissues.

In the present study, our objective was to determine [Tl] and report $\epsilon^{205}\text{Tl}$ values in individual plant parts (stem, leaves, flower stems, flowers, and seed pods) of *B. juncea* grown on various Tl-amended substrates with unique Tl geochemical signatures. Our experiments were designed to examine the effects of differences in the soil substrates and Tl sources on the distribution of [Tl] and $\epsilon^{205}\text{Tl}$ values in plants during the course of their development.

MATERIALS AND METHODS

Plant cultivation conditions

Thallium uptake into plants was determined using pot experiments with all treatments and sub-treatments performed in triplicate. Plant cultivation was carried out in a greenhouse at The University of Arizona Controlled Experiment Agriculture Center. Seeds of *B. juncea* were sown into four-quart pots containing a mixture of pure silica sand, Osmocote Plus 15-9-12 fertilizer, and water-absorbing polymer crystals for moisture retention. All containers were watered via a drip irrigation system daily. Five Tl treatments were used, along with a control: (1) a NIST 997 Tl standard solution added to a final concentration of 20 µg Tl/kg soil within each container; (2) a NIST 997 Tl standard solution added to a final concentration of 100 µg Tl/kg soil within each container; (3) powdered Tl-bearing K-feldspar [amazonite ($K(AlSi_3O_8)$) from Amelia Courthouse, VA] with a final concentration of 20 mg Tl/kg soil within each container; (4) powdered Tl-bearing mica [hendricksite ($K(Zn,Mg,Mn^{2+})_3(AlSi_3O_{10})(OH)_2$) from Sterling Hill, NJ] with a final concentration of 20 mg Tl/kg soil within each container; (5) powdered Tl-bearing manganese nodule NOD-A-1 from the USGS reference standards with a final concentration of 20 mg Tl/kg soil within each container; and (6) a control with no Tl-bearing amendments. All Tl-bearing mineral amendments have been previously characterized for both [Tl] and $\epsilon^{205}Tl$ values (Table 1).²⁰ Thallium recovery from certified materials was 85–95%.

In treatments 1 and 2, Tl as a solution was added gradually (1–5 mL per plant weekly) until reaching the final concentration of either 20 µg/kg or 100 µg/kg Tl per container of mixed sand, fertilizer, and water-absorbing polymer crystals. The Tl isotope standard solution used in these treatments was prepared with the certified stable isotope standard reference material NIST 997 Tl. NIST 997 Tl metal (350 mg) was accurately weighed and dissolved into 75 mL of doubly distilled HNO_3 (8 mol/L) in a 500 mL Teflon bottle. Following complete dissolution of the metal chunks, the solution was diluted with 375 mL reagent grade deionized water (MQ) (18.2 MΩ Milli-Q water) and 50 mL HNO_3 to obtain a NIST 997 stock solution with a concentration of 649 µg/g Tl in HNO_3 (2 mol/L).

In treatments 3, 4, and 5, Tl-bearing minerals were crushed to < 700 µm and weighed out for a final concentration of 20 mg/kg Tl per container and mixed with sand, fertilizer, and water-absorbing polymer crystals prior to planting. All plants were grown for 12 weeks, after which they were harvested. All harvested plants were separated into stems, leaves, flowers, flower stems, and seed pods, placed into labeled paper bags, and air-dried in an oven at 55–60 °C for 3 days. The dried samples were homogenized by either grinding with a silica mortar and pestle or milling in a Wiley Mill to 30-mesh sieve.

Sample digestion and preparation

Homogenized plant samples were weighed into microwave digestion vessels and predigested with 2 mL of doubly distilled concentrated HNO_3 and 2 mL MQ for 2–3 days. Samples were then sealed and further digested using a MARS 6 microwave digestion system, where they were incrementally heated over a 25-minute period to 200 °C, then held at 200 °C for an additional ten minutes. Procedural blanks were included with each batch of plant

products. These blanks were consistently below the detection limit of this method (0.02 µg/L Tl in solution). After microwave digestion, the solutions were transferred to 15 mL Savillex screw-cap vessels where they underwent further preparation necessary for the chemical isolation of Tl from the sample matrix for accurate isotopic analysis.²⁰ During this additional process, samples were evaporated to dryness on a hotplate (80–90 °C) then refluxed overnight in doubly distilled HCl (6 mol/L). The refluxed samples were evaporated to dryness on a hotplate (80–90 °C) and refluxed again in a doubly distilled HCl (1 mol/L)-5% Br₂ solution for 24 hours. Thallium in these final solutions was chemically isolated using a multi-stage chromatographic extraction procedure as described by Rehkämper and Halliday,²⁷ and Nielsen et al.²⁸ and later modified by Rader et al.²⁰

[Tl] measurements by MC-ICP-MS

Once Tl was chemically isolated, 100 µL of the purified solution was diluted to 1 mL using doubly distilled 2% HNO₃, which was used for [Tl] measurements. Sets of five samples were bracketed by a mixed NIST 997-NIST 981 solution standard (20 µg/kg Tl [NIST 997]; 20 µg/kg Pb [NIST 981]), for external correction for mass fractionation. Both [Tl] and $\epsilon^{205}\text{Tl}$ values were collected using a Thermo Scientific/GV/Micromass IsoProbe MC-ICP-MS located in the Geosciences department at the University of Arizona. The raw data were processed offline in MS Excel. [Tl] were calculated based on the voltage in relation to the NIST 997-NIST 981 standard solution through monitoring ²⁰⁵Tl. Using this method, concentrations can be estimated to a precision of ± 10% or better. All samples from the control experiments were below the detection limit of this method for Tl. Residual Pb remaining in purified Tl separates would greatly impact later Tl isotope composition measurements (section 2.4.) and as such ²⁰⁸Pb was also monitored, confirming that negligible. None of the processed samples contained measurable Pb. All concentrations are reported in µg/kg relative to dry plant weight.

Thallium isotope ratios measurements by MC-ICP-MS

Sets of three unknown samples were bracketed with the mixed NIST 997-NIST 981 Tl and Pb isotope solution standard (20 µg/kg Tl [NIST 997]; 20 µg/kg Pb [NIST 981]). For each analysis bracketing unknowns, five blocks of NIST 997-NIST 981 were analyzed in sequence to monitor instrumental stability and drift; each unknown analysis consisted of three blocks of each sample analyzed in sequence for reproducibility. For further details regarding the analytical setup, refer to Rader et al. 2018.²⁰ Total procedural blanks for Tl were below our detection limit, or < 0.02 µg/kg, well below the Tl processed for samples (20 µg/kg).

Mass balance of Tl within plants

Mass balance calculations relating individual plant parts to the overall Tl isotopic signature of the plant were carried out to investigate whether the initial uptake of Tl from the underlying substrate could be responsible for the Tl isotopic patterns observed here. The mass balance of the entire plant was derived using the following relationship:

$$\epsilon^{205}\text{Tl}_{\text{substrate}} = \frac{(m_s * \epsilon^{205}\text{Tl}_s) + (m_l * \epsilon^{205}\text{Tl}_l) + (m_{f.s.} * \epsilon^{205}\text{Tl}_{f.s.}) + (m_f * \epsilon^{205}\text{Tl}_f) + (m_{s.p.} * \epsilon^{205}\text{Tl}_{f.p.})}{m_{\text{total}}} \quad (2)$$

where m = molar quantities of plant parts and $\epsilon^{205}\text{Tl}$ = isotopic ratio of plant parts and the subscripts are s = stem, l = leaves, f.s. = flower stems, f = flowers, and s.p. = seed pods.

RESULTS

NIST 997 and mineralogically Tl-amended substrate [Tl]

The absolute concentration of Tl in individual plant parts varied from 3 µg/kg in flowers from the mica (hendricksite) amendment up to 3800 µg/kg in flower stems from the 100 µg/kg NIST 997 amendment (Figure 1 and Table 1). There is high variation among [Tl] for individual treatments, which we attribute to the low number of replicates (n = 3) and the natural variability in growth conditions for a greenhouse trial (e.g., irrigation consistency, overall plant biomass). Despite overall [Tl] variability, each treatment yielded nearly identical concentration patterns, namely, [Tl] in leaves > flower stems > seed pods ≈ stems > flowers, with only minor amounts of Tl associated with the seed pods, stems, and flowers (Figure 2). Plant accumulation of Tl into all plant parts was much greater for Tl added as NIST 997 solution (Figure 1, A.–B.) than for Tl added as geogenic material (Figure 1, C.–E.) demonstrating the effect of increased bioaccessibility of Tl from the NIST 997 solution than from mineralogical substrates. For example, leaves accumulated 100-fold higher Tl (~3830 µg/kg) in the 100 µg/kg NIST 997 treatment than leaves in the mica (hendricksite) treatment (~38 µg/kg) (Table 1). [Tl] of plants grown in a geogenic substrate decreased in the following order: K-feldspar > NOD-A-1 > mica (Table 1). There was a statistically significant difference between treatment types as determined by one-way ANOVA ($F(4,20) = 6.156$, $p = 0.0021$) and no statistically significant differences between plant parts (across treatment types) as determined by one-way ANOVA ($F(4,20) = 1.203$, $p = 0.34$). Post hoc comparisons between treatment types using the Tukey HSD test indicated that the mean values for plant parts of the NIST 100 µg/kg treatment differed significantly from plant parts of all three mineralogical treatments at $p < 0.05$ (K-feldspar, NOD-A-1, and mica). The NIST 100 µg/kg treatment and NIST 20 µg/kg treatment were not significantly different from one another.

NIST 997 Tl-amended substrate $\epsilon^{205}\text{Tl}$ values

$\epsilon^{205}\text{Tl}$ values of plant parts from *B. juncea* vary from $\epsilon^{205}\text{Tl} = -4.3$ to $+2.7$ (Figure 3 and Table 1) and display some consistent features. First, plant stems grown in the 20 µg/kg and 100 µg/kg amendments yield significantly higher $\epsilon^{205}\text{Tl}$ values ($+2.7$ and $+2.3$, respectively), than the source material, in this case NIST 997 ($\epsilon^{205}\text{Tl} = +0.0$). Second, later-developing plant parts yield successively lower $\epsilon^{205}\text{Tl}$ values than the stem. Finally, $\epsilon^{205}\text{Tl}$ values increase from source to stems, then decrease from stems to leaves, from leaves to flower stems, and finally from flower stems to flowers and seed pods (Figures 3 and 4). The [Tl] of plants grown in geogenic Tl-amended substrate were too low to allow accurate measurement of $\epsilon^{205}\text{Tl}$ values. Overall, there is more than 7 $\epsilon^{205}\text{Tl}$ difference between stems and flowers and/or seed pods for plants analyzed in this study.

DISCUSSION

Plant part [Tl]; Comparison of Tl amendments

Average plant part [Tl] for all Tl amendments studied varied by greater than two orders of magnitude between the hendricksite (9–38 µg/kg) and the 100 µg/kg NIST (213–3832 µg/kg) amendments, controlled by bioaccessibility (Figure 1). Bioaccessibility is defined here as the fraction of Tl that is available to the plant for uptake and incorporation into tissues. Presumably, this difference reflects Tl being immediately available from solution versus being in solid form and thus requiring a kinetically-limited dissolution step. The NIST 997 amendment was added as a solution, allowing the Tl to be more easily partitioned into the soil pore water phase and thereby directly absorbable by the plants' root systems. In contrast, mineralogical amendments (i.e., amazonite, hendricksite, NOD-A-1) contained similar [Tl] at the beginning of the experiments but Tl was associated with the mineral matrices of the respective amendments and not as a dissolved constituent in the soil pore waters. The release of this form of Tl is dependent upon dissolution or desorption of the bound Tl by soil pore water (i.e., chemical weathering) and the physiological activities at the mineral surfaces by microorganisms (i.e., biogeochemical weathering).

Due to differences in bioaccessibility dependent upon the underlying Tl amendment, plants grown in the different Tl amendments produced variable ranges of Tl enrichment. However, the various Tl amendments yielded nearly identical plant Tl distribution patterns, regardless of substrate or uptake potential (Figure 2). Although the mechanism through which plants are able to bioaccumulate and detoxify Tl is not completely resolved, there is evidence that members of the Brassicaceae safely sequester the metal into compartments within their vascular systems (e.g., leaf vacuoles) via cationic transporter systems.²⁹ Furthermore, the adsorption, distribution, and sequestration of Tl through root systems, xylem, and within leaves and other plant parts can also be attributed to a family of potassium (K⁺) channels and symporter systems. Potassium is transported symplastically to the xylem from all regions of the root, where it then becomes particularly concentrated in growing tissues, such as the leaves, as the delivery of K⁺ is largely determined by transpirational water flows.³⁰ These K⁺ channels and symporter systems cannot readily discriminate between K⁺ and Tl⁺ due to their both being univalent and having similar ionic radii (1.60 Å and 1.76 Å, respectively)^{9,29} resulting in indiscriminate uptake of Tl⁺. The persistent uptake of Tl over time ultimately leads to higher Tl concentrations in those earlier developing plant tissues which have higher water and nutrient demands for photosynthesis,⁷ similar to the Tl distribution in plant parts observed in this study.

Although the distribution patterns of Tl are the same across all substrates, there is a noticeable decrease in [Tl] of plant parts for mineralogically amended substrates. This progression of decreasing [Tl] in plant parts observed for the various mineral amendments is in line with trends in silicate mineral stability under soil conditions. It might also reflect crystal chemical effects related to K-Tl substitution within interlayer crystal structures, such as micas, or, alternatively, surface adsorption and resultant incorporation within Mn-oxides. For example, measured weathering rates of silicate minerals under natural conditions at the saprolite-bedrock interface have shown K-feldspar reacts at much faster rates ($k_r = -16.8$ to

$-11.8 \text{ mol/m}^2 \text{ s}^1$) than sheet silicates ($k_r = -16.4$ to $-14.0 \text{ mol/m}^2 \text{ s}^1$) such as biotite and muscovite mica.^{31,32} Furthermore, adsorption studies have confirmed that Tl^+ is readily adsorbed at the frayed edges of micaceous phyllosilicates, but that desorption kinetics are extremely slow or, in some cases, could be inhibited by structural fixation of Tl^+ ,³³ further enhancing the stability of sheet silicate phases.

Additionally, the mica used here is hendricksite, a sheet silicate rich in Mn, which has previously been shown to have a strong affinity for Tl,^{26,34,35} thus further impeding the bioaccessibility of Tl within this substrate. Manganese oxides have a strong affinity for Tl in environments ranging from ore-forming systems to ocean floor nodules, as well as subsurface and soil environments.^{20,23,26,34–36} In these environments, Mn-oxides are capable of transforming Tl from the labile fraction to its reducible form, thus lowering Tl bioavailability in soil and subsequent accumulation by plants by up to 50%.^{24,37} We therefore propose the low [Tl] in plant parts from this study grown in Mn-rich mica- and Mn nodule-amended soils is a result of the initial stability of these phases coupled with the stabilization of Tl following its desorption during mineral weathering by secondary mineral phases, such as micaceous clays, or by incorporation of Tl within Mn-oxides.

In synthetic soil experiments, soils were rich in Tl bound to the exchangeable/acid-extractable fraction, indicating preferential Tl uptake from easily exchangeable/surface positions or more relatively unstable Tl phases.²⁵ However, even though silicates, such as feldspar, are traditionally considered to be rather stable in the rhizosphere, results from previous work indicate that even this Tl may be biologically accumulated to a great extent after chemical dissolution from exudate solutions, while soils enriched in Mn-oxides greatly reduce the potential of biologic plant uptake.²⁴ Nevertheless, it must be highlighted that the redistribution of trace metals, such as Tl, is more pronounced in model studies as compared with natural geochemical systems.^{24,25} Therefore, a more comprehensive study of plant uptake and fractionation of Tl from natural soil, including porewater Tl concentrations and variability over time, with the additional investigation of the potential of microbially-mediated Tl availability (which has currently remained unexplored) is warranted in further quantifying the effect of geogenic materials and processes on Tl biosignatures.

NIST 997 Tl-amended substrate $\epsilon^{205}\text{Tl}$ values

Plant parts displayed a systematic isotopic pattern, regardless of substrate [Tl], which is proposed here to be a result of fractionation during translocation coupled with closed-system fractionation. Stem $\epsilon^{205}\text{Tl}$ values were significantly higher for both the 20 $\mu\text{g/kg}$ and 100 $\mu\text{g/kg}$ treatments ($\epsilon^{205}\text{Tl} = +2.7$ and $+2.3$, respectively) compared to the initial $\epsilon^{205}\text{Tl}$ value for the NIST 997 Tl solution ($\epsilon^{205}\text{Tl} = +0.0$). Moreover, the earliest forming plant parts display higher $\epsilon^{205}\text{Tl}$ values than later forming plant parts. $\epsilon^{205}\text{Tl}$ values decrease following: stem > leaves > flower stems > flowers and/or seed pods (Figure 4). There is variability in the Tl isotopic fractionation pattern for the latest-forming plant parts, namely the flowers and seed pods, between the two treatment types. This effect may be controlled by the underlying concentration or may instead be an artifact given the limited number of replicates of samples ($n = 3$) coupled with the low sample mass for the flowers and the small sample

size (only two varying concentrations were studied). Further work with a larger number of replicates may help to elucidate the primary controls on this divergent behavior.

Our results show stem $\epsilon^{205}\text{Tl}$ values that are two to three ϵ units higher than initial substrate $\epsilon^{205}\text{Tl}$ values ($\epsilon^{205}\text{Tl} = +2.7$ and $+2.3$ for 20 $\mu\text{g/kg}$ and 100 $\mu\text{g/kg}$ NIST 997, respectively). Previous work in the geologic realm has demonstrated that elevated $\epsilon^{205}\text{Tl}$ values can be associated with the presence of Tl^{3+} .^{20,23,34,36} Therefore, organic ligand complexation with, and the resultant passive uptake of, Tl^{3+} may influence the initial $\epsilon^{205}\text{Tl}$ value of the Tl reservoir within the plant. Other Tl bioaccumulating plants oxidize some Tl^+ to Tl^{3+} during uptake: *Sinapis alba* contained up to 10% of Tl^{3+} within the plant structure, thought to be a result of either leaching Tl^{3+} from its immobile compounds or oxidizing Tl^+ to Tl^{3+} , which forms much more thermodynamically stable complexes with organic ligands, such as the sulfur-containing amino acids cysteine or glutathione.^{7,38}

Tl^{3+} complexation, however, may not be the only process which could explain the fractionation pattern observed here, with much higher $\epsilon^{205}\text{Tl}$ values in the stem relative to the substrate and lower $\epsilon^{205}\text{Tl}$ values in younger plant parts. Epstein³⁹ demonstrated that the initial transport of metals from the external solution or soil into the plant cell walls is a non-metabolic, passive process, driven by diffusion gradients and mass flow. Additionally, Jia et al.⁹ found that stems of other Brassicaceae plants function as a channel for Tl transportation to later plant parts, thereby decreasing stem [Tl]. As such, Tl may be initially enriched in the plant stem with an isotopic composition similar to the underlying substrate with later translocation and metabolic processes isotopically fractionating Tl from this initial pool in the stem, resulting in the patterns observed here. A similar behavior has been demonstrated for other metal isotope systems in plant tissue, such as Fe, where the light Fe isotope is preferentially remobilized during translocation into younger plant tissue, resulting in higher Fe isotopic values in the stems, with systematically lower isotopic values in later plant parts.^{40–42} The higher $\epsilon^{205}\text{Tl}$ values for our stems may therefore be the result of the preferential partitioning of ^{203}Tl into the younger plant parts during growth and not during initial uptake from the underlying substrate.

Our results seem to point to this conclusion, where Tl is isotopically fractionated during growth, and not during initial uptake. By calculating a translocation factor which quantifies the extent Tl is partitioned from the stem to later plant parts, expressed using the following equation, we can see that the stem may act as an initial Tl reservoir that gets depleted during growth: Our stems contain less than 10% of the total [Tl] for all but one Tl amendment (100 $\mu\text{g/kg}$ NIST 997), and even in this case the stem contained less than 20% of the total [Tl], and every plant part except for the flowers, and in some cases the seed pods, display $\text{TF}_{\text{stem}} > 1$ (Table 2). Using the principles of fractionation during translocation coupled with closed-system fractionation during plant growth, a mass balance for the entire plant can be derived (see *Mass balance of Tl within plants*). The plant part values from the 20 $\mu\text{g/kg}$ and 100 $\mu\text{g/kg}$ NIST 997 amendments can be used to reproduce $\epsilon^{205}\text{Tl}_{\text{substrate}}$ values to within error of the original solutions in soils (calculated $\epsilon^{205}\text{Tl} = 0.6$ and -0.2 ± 0.5 , respectively; NIST 997 $\epsilon^{205}\text{Tl} = 0.0 \pm 0.3$), suggesting there was passive uptake of Tl from the underlying substrate with no induced isotopic fractionation during that step. Instead, biologic processes during growth must be responsible for the isotopic patterns demonstrated here.

Phytoremediation potential of *Brassica juncea*

The high concentrations and relative accumulation factors in *B. juncea* afford the possibility of using this plant for phytoremediation of Tl-contaminated soils, such as those in the Lanmuchang area in southwestern Guizhou Province, China.¹ A typical plant of *B. juncea* weighs 80 g dry weight. Based on planting specifications, it can be anticipated that 20 plants can be grown in 1 m² of soil, which we assume here is contaminated and contains 10 mg Tl/kg soil. We can estimate, conservatively, an overall biomass production of 15 t/ha.

It is difficult to assign a [Tl] average for plants grown in typical soil conditions from this current study. Here, we demonstrate the high bioaccumulation potential when using Tl solutions, which are fully bioaccessible, and the mineralogical control on Tl uptake by utilizing crushed, pristine mineral separates; neither of these scenarios is realistic. However, based on the accumulation factors for the two end-member circumstances presented here combined with measured bioaccumulation factors for other *Brassica* species grown in Tl-sulfate contaminated soils by Pavlíková et al.⁴, we assume a plant bioaccumulation factor of 50, meaning whole plants grown in this contaminated soil would contain, on average, 500 mg Tl/kg plant material. This equates to one crop yield providing around 7.5 kg Tl. If we were to remediate soil, with a density of 1.3 g/cm³, to a depth of 20 cm, one hectare of soil would contain 26 kg Tl and would require three to four sequential crop cycles of *B. juncea* to lower [Tl] to acceptable levels, assuming the plant-available fraction of Tl remains constant for each successive crop cycle.

When considering the distribution of Tl for all plant parts, the majority of the Tl accumulated in the later developing edible plant parts, particularly the leaves and the flower stems, regardless of underlying substrate (Figure 2). These results have implications for this type of environmental planning and remediation and demonstrate the need to understand and quantify the underlying geology and stability of Tl-bearing mineral phases in agricultural and water catchment areas. Understanding the distribution of Tl into leaves and flower stems of *B. juncea* is advantageous for phytoremediation efforts because these plant parts can be harvested while leaving the root system in place, thereby allowing for multi-seasonal remediation campaigns.

Additionally, the ability to mass balance the plants isotopic composition from both the 20 µg/kg and 100 µg/kg NIST 997 amendments coupled with the consistent fractionation patterns across varying [Tl] substrates can be used during remediation planning and bioprospecting. Even as [Tl] decreases, the isotopic fractionation pattern within the plant should remain constant, as there is no isotopic fractionation induced during initial Tl uptake, permitting the ability to identify new Tl sources or influxes during a remediation campaign. As new sources of Tl are introduced, presumably with a different or unique isotopic composition, the isotopic composition of the plant material should also change accordingly. Being able to recognize variations in plant isotopic fractionation patterns across space may be able to be linked directly to changes in the underlying geogenic substrate, aiding exploration of ore deposits associated with specific geologic controls.

IMPLICATIONS

Our results establish that most Tl (>80%) bioaccumulates within edible parts of *B. juncea*, with nearly identical enrichment patterns, regardless of substrate material or [Tl] content. The ability of *B. juncea* to accumulate high levels of Tl within edible plant parts, even when grown on relatively stable and low [Tl] geogenic substrates, means a wide variety of geologic environments or the addition of small amounts of anthropogenic Tl could pose an environmental or human health risk. Some of the primary Tl-bearing minerals are also some of the most common rock-forming minerals, such as K-feldspar and mica, therefore the underlying geology is a primary controlling factor on Tl bioaccessibility. This makes it critical to classify the geogenic substrate, both in terms of mineralogy and relative composition, prior to agricultural or recreational use. There is also a systematic isotopic pattern associated with plant parts, regardless of substrate [Tl]: higher $e^{205}\text{Tl}$ values for stems with lower $e^{205}\text{Tl}$ values in younger plant parts.

This behavior has important implications for tracing anthropogenic Tl contamination, bioprospecting, phytoextraction, and phytoremediation. Seasonal patterns may become apparent if sampling multiple times during a plants growth period, affecting bioprospecting potential. Multiple generations may be necessary for complete phytoextraction, but the isotopic pattern should remain constant, even as [Tl] decrease, helping identify new Tl sources over the course of a remediation strategy. By invoking the principles of fractionation during translocation where we move toward progressively lighter $e^{205}\text{Tl}$ values during growth and translocation, we can explain the Tl fractionation pattern observed here for *B. juncea*.

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Figure 1.

[Tl] of plant parts for various Tl-amended substrates. Numbers next to individual plant parts denote the average [Tl] for that plant part in µg/kg. A.-B. depicts Tl added as a NIST-997 standard solution at two concentrations. C.-E. depicts Tl added as three various mineral substrates. Each mineral substrate was added to a total concentration of 20 mg/kg per pot. Control plants were below detection (not shown here). Note the two scales to more accurately compare high-concentration (A.-B.) and low-concentration (C.-E.) plants.

Figure 2. Distribution of total Tl contents (Table 1) within *Brassica juncea* from five unique Tl-amendments. Amendments shown here include two concentrations of NIST 997 Tl standard solution, amazonite (feldspar) from Amelia Courthouse, VA, hendricksite (mica) from Sterling Hill, NJ, and manganese nodule, NOD-A-1, a USGS reference material.

Figure 3. $\epsilon^{205}\text{Tl}$ values of plant parts for two NIST-997 Tl-amended substrates. NIST-997 $\epsilon^{205}\text{Tl} = +0.0$. Numbers next to individual plant parts denote the average $\epsilon^{205}\text{Tl}$ values for that plant part.

Figure 4. $\epsilon^{205}\text{Tl}$ values measured for various parts of *B. juncea* after 12 weeks of growth in a controlled greenhouse. Tl addition was added incrementally utilizing a NIST 997 Tl standard solution with a known isotopic value of $\epsilon^{205}\text{Tl} = +0.0$. Shown here are the results of both the 20 µg/kg NIST 997 solution and 100 µg/kg NIST 997 solution trials.

Table 1.

[Tl] and $\epsilon^{205}\text{Tl}$ values in various plant parts of *Brassica juncea* grown in various soil amendments, both Tl-bearing solutions (NIST 997) and Tl-bearing minerals (amazonite (feldspar), NOD-A-1 (Mn nodule), and hendricksite (mica)). Amendments used here were previously characterized for [Tl] and Tl isotope compositions.²⁰ Initial Tl values for the various amendments are as follows: NIST 997: [Tl] = 649 $\mu\text{g/g}$ Tl, $\epsilon^{205}\text{Tl}$ = 0.0; amazonite: [Tl] = 22.0 mg/kg, $\epsilon^{205}\text{Tl}$ = -0.1; NOD-A-1: [Tl] = 108 mg/kg, $\epsilon^{205}\text{Tl}$ = +11.0; hendricksite: [Tl] = 20.6 mg/kg, $\epsilon^{205}\text{Tl}$ = -1.9.

plant parts analyzed	soil amendment	n	mean $\pm \sigma$ ($\mu\text{g/kg}$)	range ($\mu\text{g/kg}$)	$\epsilon^{205}\text{Tl} \pm 2\sigma$
seed pods	NIST 997 (100 $\mu\text{g/kg}$)	3	1350 (± 616)	528–2000	-3.3 (± 0.3)
	NIST 997 (20 $\mu\text{g/kg}$)	2	211 (± 193)	18–404	-0.3 (± 0.2)
	amazonite	2	149 (± 76)	73–225	
	NOD-A-1	1	112	-	
	hendricksite	2	14 (± 5)	9–19	
flowers	NIST 997 (100 $\mu\text{g/kg}$)	3	213 (± 112)	54–296	-0.6 (± 0.5)
	NIST 997 (20 $\mu\text{g/kg}$)	3	144 (± 139)	12–336	-4.3 (± 0.9)
	amazonite	2	36 (± 20)	16–57	
	NOD-A-1	2	26 (± 9)	17–35	
	hendricksite	3	12 (± 3)	10–17	
flower stems	NIST 997 (100 $\mu\text{g/kg}$)	3	3830 (± 1100)	2887–5370	-0.5 (± 0.3)
	NIST 997 (20 $\mu\text{g/kg}$)	1	1510	-	+0.2 (± 0.4)
	amazonite	1	409	-	
	NOD-A-1	2	193 (± 99)	94–293	
	hendricksite	2	61 (± 14)	47–74	
leaves	NIST 997 (100 $\mu\text{g/kg}$)	3	3860 (± 2100)	2050–6770	-0.5 (± 0.3)
	NIST 997 (20 $\mu\text{g/kg}$)	3	1150 (± 1060)	205–2630	+0.7 (± 0.3)
	amazonite	2	926 (± 209)	717–1140	
	NOD-A-1	2	373 (± 189)	184–562	
	hendricksite	2	38 (± 2)	36–40	
stems	NIST 997 (100 $\mu\text{g/kg}$)	3	1620 (± 536)	1130–2370	+2.3 (± 0.3)
	NIST 997 (20 $\mu\text{g/kg}$)	2	1000 (± 549)	455–1550	+2.7 (± 0.6)
	amazonite	2	125 (± 27)	98–152	
	NOD-A-1	2	116 (± 8)	108–124	
	hendricksite	3	9 (± 4)	3–13	

Table 2.

Translocation factor (TF) for plant parts, relative to the stem, grown in each Tl amendment. TF was calculated based on the average [Tl] for each plant part. TF ranges were calculated based on the low and high [Tl] for each plant part.

plant parts analyzed	soil amendment	translocation factor (TF)	translocation factor (TF) range
seed pods	NIST 997 (100 µg/kg)	0.8	0.5 – 0.8
	NIST 997 (20 µg/kg)	0.2	0.0 – 0.3
	amazonite	1.2	0.7 – 1.5
	NOD-A-1	1.0	–
	hendricksite	1.5	1.5 – 3.0
flowers	NIST 997 (100 µg/kg)	0.1	0.0 – 0.1
	NIST 997 (20 µg/kg)	0.1	0.0 – 0.2
	amazonite	0.3	0.2 – 0.4
	NOD-A-1	0.2	0.2 – 0.3
	hendricksite	1.4	1.3 – 3.3
flower stems	NIST 997 (100 µg/kg)	1.5	–
	NIST 997 (20 µg/kg)	2.4	2.3 – 2.6
	amazonite	3.3	–
	NOD-A-1	1.7	0.9 – 2.4
	hendricksite	6.7	5.7 – 15.7
leaves	NIST 997 (100 µg/kg)	1.1	0.5 – 1.7
	NIST 997 (20 µg/kg)	2.4	1.8 – 2.9
	amazonite	7.4	7.3 – 7.5
	NOD-A-1	3.2	1.7 – 4.5
	hendricksite	4.1	3.1 – 12