Speciation and Distribution of Thallium in *Iberis intermedia*: An In-vivo Synchrotron Study

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INTRODUCTION

Thallium (Tl) is an element with greater toxicity to mammals than Hg, Cd, Pb or Cu (Nriagu, 1998) and is listed among the 13 priority metals by the USEPA (Keith and Telliard, 1979). Environmental accumulation of Tl is the result of both geogenic and anthropogenic inputs (Nriagu, 1998). The major pathway of exposure to humans is the ingestion of vegetables grown in Tl-contaminated soils. Thallium can be readily taken up by plants because it is generally present in soil as thermodynamically stable Tl(I) and, as such, is an analogue of potassium. Little is known regarding the chemical speciation of Tl in plants (Nriagu, 1998). However, this information is important because Tl has two oxidation states, monovalent Tl(I) and trivalent Tl(III), which differ in terms of toxicity and chemical reactivity. In this work we investigated *in vivo* Tl speciation and distribution in leaves of the Tl hyperaccumulator *Iberis intermedia* (Scheckel et al., 2004). The ability of *I. intermedia* to accumulate extremely large concentration of Tl in the above ground biomass (up to 13 429 mg kg^{-1}) makes this plant interesting in terms of phytomining. Currently, Tl is the fourth most expensive metal after Pt, Au and Pd. Determining the oxidation state of Tl in this plant is essential to assess disposal options and/or recycling possibilities of the metal-loaded plant biomass. In our work we assessed both Tl speciation and compartmentation in *I. intermedia* leaves using an innovative *in vivo* synchrotron technique.

METHODS

I. intermedia plants in 20 ppm Tl-spiked potting soil were grown in controlled environment growth chambers to simulate approximately one-third sunlight (photosynthetically active radiation (PAR) of approximately 1100 μmoles m^{-2} s^{-1}) with an average temperature of 25 ^{o}C. The *I. intermedia* plants were grown for ten weeks (reaching an average height of 23 cm) prior to examination by μ-XANES and μ-XRF.

RESULTS AND DISCUSSION

Figure 2 shows the μ-XRF maps for Tl and Ca for the area encompassing the main central vein of a mature *I. intermedia* leaf. It is evident from Figure 2 that Tl and Ca are closely associated and localized within the vascular system of the leaf. Identical results were obtained for other leaves and sections of leaves including minor veins between the main central vein and the edge of the leaf (Figure 3). Regardless of leaf maturity, Tl and Ca were localized to veins (primary and smaller secondary veins) within the leaves of *I. intermedia*. This distribution of Tl in leaves is comparable to that reported for K in a number of hyperaccumulator plants (Küpper et al., 2001), and likely results from the chemical similarity of K(I) to Tl(I).

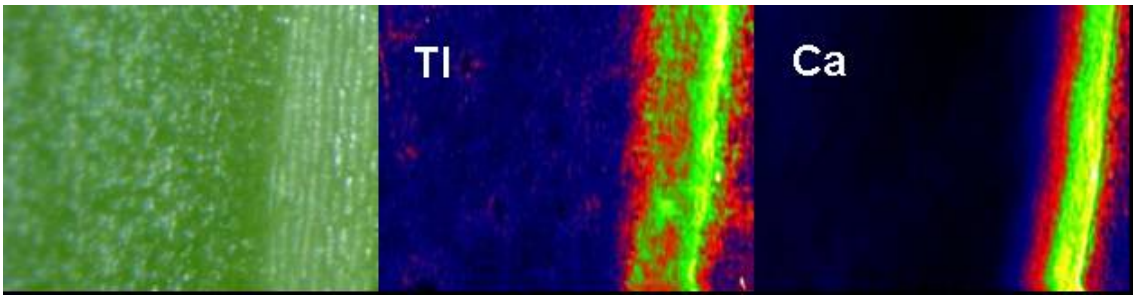

FIGURE 1. Optical image and XRF maps showing the direct correlation of Tl and Ca within the main central vein of *I. Intermedia* basal leaf. Image and maps cover an area of 660 x 500 μm. Dark to light color scale represents increasing Tl signal intensity.

The XANES spectra are shown in Figures 2 for results of Tl speciation in two μ-XANES investigations and one bulk XANES sample of *I. intermedia*. The bulk XANES sample was prepared and examined by placing approximately 10 leaves from one plant in a stack, so as to align the main central vein of each leaf. The bundle of leaves were taped together, using Kapton film, and placed in line with the electron beam for bulk XANES analysis in transmission mode. The spectra shown in Figures 2 for the μ-XANES samples are the collection, reduction, and average of 50 individual μ-XANES scans in close proximity on the same central vein of two separate leaves from different plants grown in 20 mg kg^{-1} spiked soil. The reference spectrum for aqueous $Tl(I)NO_3$ is shown in Figures 2 as the best representation of the data collected for the speciation of Tl in the plant tissues. Consistent with results of Nolan et al. (Nolan et al., 2004), the XANES results indicate the Tl speciation in *I. intermedia* is aqueous Tl(I).

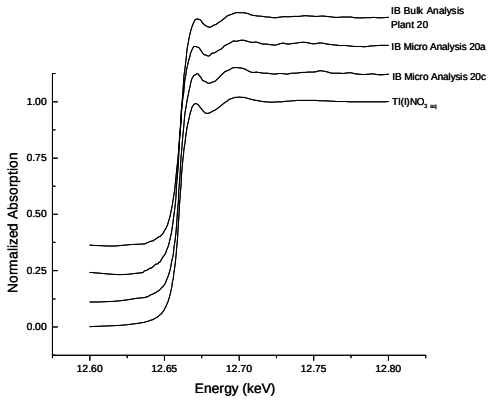

FIGURE 2. Normalized XANES (L_{III} edge) spectra of *I. intermedia* bulk- and micro-XANES samples with aqueous $Tl(I)NO_3$.

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