



## Microcolumn-based speciation analysis of thallium in soil and green cabbage

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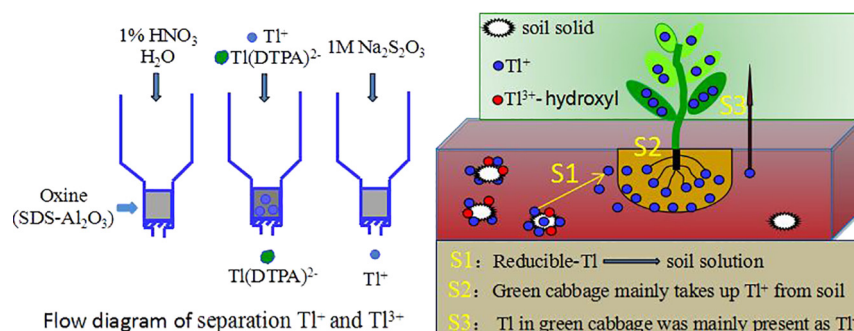
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### HIGHLIGHTS

- An efficient method separating and detecting Tl species for soil and plant samples was elaborated.
- Tl in green cabbage was mainly present as Tl(I).
- Green cabbage mainly takes up Tl(I) from soil.
- The reducible fraction was the main carrier for Tl in soil.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Thallium (Tl) is a toxic trace metal, whose geochemical behavior and biological effects are closely controlled by its chemical speciation in the environment. However, little tends to be known about this speciation of Tl in soil and plant systems that directly affect the safety of food supplies. In this context, the objective of the present study was to elaborate an efficient method to separate and detect Tl(I) and Tl(III) species for soil and plant samples. This method involves the selective adsorption of Tl(I) on microcolumns filled with immobilized oxine, in the presence of DTPA (diethylenetriaminepentaacetic acid), followed by DTPA-enhanced ultrasonic and heating-induced extraction, coupled with ICP-MS detection. The method was characterized by a LOD of 0.037 µg/L for Tl(I) and 0.18 µg/L for Tl(III) in 10 mL samples. With this method, a second objective of the research was to assess the speciation of Tl in pot and field soils and in green cabbage crops. Experimental results suggest that DTPA extracted Tl was mainly present as Tl(I) in soils (>95%). Tl in hyperaccumulator plant green cabbage was also mainly present as Tl(I) (>90%). With respect to Tl uptake in plants, this study provides direct evidence that green cabbage mainly takes up Tl(I) from soil, and transports it into the aboveground organs. In soils, Tl(III) is reduced to Tl(I) even at the surface where the chemical environment promotes oxidation. This observation is conducive to understanding the mechanisms of Tl isotope fractionation in the soil-plant system. Based on geochemical fraction studies, the reducible fraction was the main source of Tl getting accumulated by plants. These results indicate that the improved analytical method presented in this study offers an economical, simple, fast, and sensitive approach for the separation of Tl species present in soils at trace levels.

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## 1. Introduction

Thallium (Tl) is a nonessential trace metal. It is more toxic to mammals than cadmium, lead and even mercury (Nriagu, 1998), and is therefore categorized by many countries and international agencies as one of 13 priority metal pollutants (Keith and Telliard, 1979). Worldwide, the Tl content of soils seems to depend largely on the geological origin of the parent material (Sager, 1998; Jacobson et al., 2005). Some soils have a naturally high background concentration of Tl, like the clayey soils developed on the Sinemurian limestone in France, with natural Tl contents as high as 55 mg/kg (Tremel et al., 1997; Escarre et al., 2011; Resongles et al., 2014), but in general, Tl concentrations in uncontaminated surface soils range from 0.1 to 2 mg/kg, with most reported concentrations <1 mg/kg (Fergusson, 1990; Heim et al., 2002). In anthropogenically-contaminated soils, Tl concentrations can vary substantially, as high in some cases as, e.g., 15 mg/kg in soils near cement factories in Germany, 61 mg/kg in mine tailings-impacted soils in China, 73 mg/kg in soils near old mines in Germany (Sholl, 1980; Zhou and Liu, 1985), 8.8–27.8 mg/kg in soils from Silesian–Craeowian zinc-lead mine areas in Poland (Lis et al., 2003), and 3.0–27.6 mg/kg in soils from abandoned Pb–Zn–Cu mining area in Turkey (Sasmaz et al., 2007).

Such high concentrations of Tl, in soils that may be used for the production of food crops, cause serious concerns in terms of food safety. Indeed, when grown on Tl-contaminated soils, certain crops take up high levels of Tl (Xiao et al., 2004; Pavlickova et al., 2006; Vanek et al., 2010). For instance, *Brassica oleracea* L. var. *capitata* L. (green cabbage) accumulates large amounts of Tl (LaCoste et al., 2001; Al-Najar et al., 2005; Pavlickova et al., 2005).

In terms of potential toxicity, the form that Tl has in these crops is not irrelevant. Indeed, of the two oxidation states, monovalent Tl(I) and trivalent Tl(III), that Tl can have in soils or plants, the trivalent form, Tl(III), is out to be approximately 50,000 times more toxic than Tl(I) on a free-ion basis (Ralph and Twiss, 2002). Because of this large difference in toxicity between the two forms of Tl, a thorough understanding of the redox transformations of Tl and of its fate in soils and crops is required in order to evaluate the potential risks associated with the uptake of Tl by crops. Some research has been carried out on the subject in the last few years (Al-Najar et al., 2003, 2005; Xiao et al., 2004), and several aspects of the topic have been elucidated. Tl(I) shows both chalcophile and lithophile character, i.e., small amounts of Tl(I) are often found in metal sulfides, and Tl(I) readily substitutes  $K^+$  in minerals such as K-feldspars or micas due to its similar ionic radius (Lin and Nriagu, 1998). Tl(I) is relatively soluble, mobile and bioavailable, similar to alkali metal cations. In aquatic environment at low Tl concentrations, Tl(I) tends to dominate over Tl(III), due to the high redox potential of Tl(III)/Tl(I) couple ( $E_h = 1.28$  V) and mostly in the form of hydrated  $Tl^+$  due to limited complexation (Casiot et al., 2011). However, photochemically driven reactions to sunlit surface waters or microbiological processes may lead to Tl(I) oxidation (Twining et al., 2003; Karlsson et al., 2006), and Tl(III) may be stabilized by hydrolysis and colloid formation or sorption to Fe(III)-colloids (Lin and Nriagu, 1999; Karlsson et al., 2006). In contact with certain Mn(IV)-oxides, Tl(I) can be oxidized to Tl(III)-complexes and stabilized by incorporation into Mn(IV)-oxide (Peacock and Moon, 2012).

Unlike with some of the other trace metals found in terrestrial environments, information about what controls the redox chemistry of Tl in any given soil, or in plants that grow on it, remains very scanty (Al-Najar et al., 2003, 2005; Xiao et al., 2004). As a result, it is not possible at the moment to predict quantitatively what the chemical speciation of Tl is in soils at specific locations, and therefore to assess satisfactorily what risk may be associated with growing crops (in particular cabbage) on these soils.

Chemical speciation of Tl can be determined directly by chromatographic separation followed by elemental detection, usually with ICP-MS, ICP-OES, ICP-AES, GFAAS or ETAAS (Lin and Nriagu, 1999; Hu,

2002; Coetzee et al., 2003; Nolan et al., 2004; Meeravali and Jiang, 2008; Krasnodebska-Ostrega et al., 2008, 2012; Casiot et al., 2011). Most of those methods needed ion exchange resin chromatography to separate Tl(I) and Tl(III) with high cost (Lin and Nriagu, 1999; Nolan et al., 2004; Casiot et al., 2011). Dadfarnia et al. (2007) proposed a procedure based on the use of microcolumns of immobilized oxine in order to pre-concentrate and separate the different forms of Tl. In this method, in the presence of EDTA, only Tl(I) is retained in the microcolumn, leading to the successful separation of Tl(I) and Tl(III) in solution. The preparation of the microcolumns themselves is straight forward and economical. However, both Tl(I) and Tl(III) can form complexes with EDTA ( $\log K_{Tl(I)-EDTA} = 5.3$ ,  $\log K_{Tl(III)-EDTA} = 22.5$ ) (Lin and Nriagu, 1998), this lowers the separation efficiency. In addition, the presence of organic substances in complex matrix samples may also influence the separation efficiency, especially for soil and plant matrices. For example, humic acid complex with Tl(III) has a similar stability constant with EDTA (Bidoglio et al., 1997). Compared to EDTA, more stable complexes are formed by Tl(III) with DTPA ( $\log K = 46$ ), whereas Tl(I) cannot be complexed at all by DTPA (Inczyedy, 1976; Lin and Nriagu, 1998). Therefore, use of DTPA as the chelant can help improve the separation efficiency and stabilize Tl(III) (Biaduń et al., 2016; Sadowska et al., 2016).

For the determination of Tl speciation in solid samples (plant, soil, etc.) to have maximum efficiency (Sadowska et al., 2016), the extraction of Tl(I) and Tl(III) from the sample matrix should be carried out in such a way that the original speciation remains unaltered. For the determination of total Tl from solid environmental samples, nitric acid, hydrofluoric acid or chloroacetic acid are usually used as extracting agents. However, they cannot be used to prepare samples for Tl species analysis, because they tend to change the original speciation of Tl in samples. In earlier laboratory Jia (2013) found that 28% and 100% of Tl(I) would be oxidized to Tl(III) by nitric acid and chloroacetic acid, respectively, so that only neutral extraction agents should be considered for Tl species extraction from solid samples. However, the extraction efficiency in this case is low (Jia, 2013). Some complementary techniques are often used to improve the chemical extraction efficiency. For example, ultrasonic extraction for solid samples can significantly improve metal extraction efficiency, and is preferred in the context of element speciation (Marin et al., 2001).

In this general context, the first objective of the research described in the present study was to devise a microcolumn-based method and DTPA as the chelant to determine quantitatively the concentration of Tl(I) and Tl(III) in soil and plant samples. A new extraction technology with ultrasonic was also developed for extraction Tl(I) and Tl(III) from soil and plant samples. This method was then used to determine the chemical speciation of Tl in Tl-rich soil and green cabbage samples to better understand redox transformations of Tl in the soil-plant system.

## 2. Method and materials

### 2.1. Microcolumn separation of Tl(I) and Tl(III)

#### 2.1.1. Preparation of the sorbent and microcolumn

Fifty milliliters of a solution (pH  $\approx$  5) containing 100 mg SDS (Sodium dodecyl sulfate) was added to 1.5 g of alumina (10–50  $\mu$ m,  $\gamma$ -type chromatography grade). The solution was mixed with a magnetic stirrer for 10 min. The supernatant was decanted and the SDS-coated alumina was washed thoroughly with several portion of water. Then  $\sim$ 20 mL of water and 5–7 mL of oxine solution (0.1 g dissolved in acetone) were added. The solution was shaken for 15 min. The mixture was then filtered through Millipore filter, washed, air-dried and was kept in close bottle before use (Dadfarnia et al., 2007).

A microcolumn made of a 4 cm-long PTFE tube (BIO-RAD, USA) with a 6 mm inner diameter was used. The microcolumn was full of oxine immobilized in surfactant-coated alumina ( $\sim$ 400 mg). The tube bottom was fitted with foam to retain the sorbent.

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