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Thallium in flowering cabbage and lettuce: Potential health risks for local residents of the Pearl River Delta, South China☆

Huan-Yun Yu [a, b], Chunying Chang [c], Fangbai Li [a, *], Qi Wang [a], Manjia Chen [a], Jie Zhang [d]

[a] Guangdong Key Laboratory of Integrated Agro-Environmental Pollution Control and Management, Guangdong Institute of Eco-Environmental Science and Technology, Guangzhou 510650, China
[b] Guangzhou Key Laboratory of Environmental Exposure and Health, School of Environment, Jinan University, Guangzhou 510632, China
[c] Guangdong Key Laboratory of Contaminated Sited Environmental Management and Remediation, Guangdong Provincial Academy of Environmental Science, Guangzhou 510045, China
[d] Camda New Energy Equipment Co., Ltd., China

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ABSTRACT

Thallium (Tl), a rare metal, is universally present in the environment with high toxicity and accumulation. Thallium's behavior and fate require further study, especially in the Pearl River Delta (PRD), where severe Tl pollution incidents have occurred. One hundred two pairs of soil and flowering cabbage samples and 91 pairs of soil and lettuce samples were collected from typical farmland protection areas and vegetable bases across the PRD, South China. The contamination levels and spatial distributions of soil and vegetable (flowering cabbages and lettuces) Tl across the PRD were investigated. The relative contributions of soil properties to the bioavailability of Tl in vegetables were evaluated using random forest. Random forest is an accurate learning algorithm and is superior to conventional and correlation-based regression analyses. In addition, the health risks posed by Tl exposure via vegetable intake for residents of the PRD were assessed. The results indicated that rapidly available potassium (K) and total K in soil were the most important factors affecting Tl bioavailability, and the competitive effect of rapidly available K on vegetable Tl uptake was confirmed in this field study. Soil weathering also contributed substantially to Tl accumulation in the vegetables. In contrast, organic matter might not be a major factor affecting the mobility of Tl in most of the lettuce soils. Fe and manganese (Mn) oxides also contributed little to the bioavailability of Tl. A risk assessment suggested that the health risks for Tl exposure through flowering cabbage or lettuce intake were minimal.

1. Introduction

Thallium (Tl) is a soft, malleable heavy metal that is listed as a high priority toxic pollutant by the United States Environmental Protection Agency. In nature, Tl is primarily present in sulfide ores of zinc, copper and lead and in coal, silicates, pyrite and soils containing large amounts of clay, organic matter, and iron (Fe) and manganese (Mn) oxides (Kazantzis, 2000; Gomez-Gonzalez et al., 2015; Vaněk et al., 2015b). In the past, Tl was widely used as a rodenticide and a pesticide, and currently, Tl is primarily used in the electrical and electronics industries (Kazantzis, 2000). Approximately 2000–5000 tons of Tl per year are released by industrial processes (Kazantzis, 2000). Thallium is more toxic to humans, animals, microorganism and plants than many other heavy metals, such as mercury, cadmium, lead, copper and zinc (Kazantzis, 2000; Peter and Viraraghavan, 2005). The toxicity of Tl mainly results from the similarity of its ionic radius to that of potassium, which can cause the malfunction of potassium-associated metabolic processes (Kazantzis, 2000). Stomach and intestinal ulcers, alopecia and polyneuropathy have been reported as classic symptoms of thallium poisoning (Karbowska, 2016). In addition, Tl poisoning can cause astral disorders, insomnia, paralysis, loss of body mass, internal bleeding, myocardial injury and death (Karbowska, 2016). Human exposure to Tl occurs primarily via the consumption of contaminated foods or drinking water. Vegetable consumption is considered a particularly important pathway for Tl exposure in humans (Kazantzis, 2000). It is notable that although Tl is universally present in the environment with high toxicity and

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* Corresponding author.
E-mail address: cefbli@soil.gd.cn (F. Li).

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accumulation, the behavior and fate of Tl still merit further study (Vaněk et al., 2016).

The Pearl River Delta (PRD), located in South China within Guangdong Province, is one of the most rapidly growing economic regions in China. The PRD is also the largest plain in the subtropical zone of China with a typical subtropical monsoon climate that is mild and humid with abundant rainfall; thus, the PRD has become an important base of grain, vegetable, fruit and livestock production. Due to the rapid development of industrial and agricultural production, the contamination of heavy metals has become a serious concern in the PRD, especially since the low soil pH further aggravates this situation (Zhang et al., 2015). The natural background values of Tl for soil based on 853 soil samples across China ranged from 0.29 to 1.17 mg kg^{-1} (Qi et al., 1992). In contrast, in the Tl-rich sulfide mineral area, elevated levels of Tl were often found (Xiao et al., 2012). In a recent study, widespread contamination of Tl was observed in the sediments of the PRD (Liu et al., 2016a); however, a limited amount of data on Tl is currently available for the PRD.

Previous studies have demonstrated that the bioavailability of Tl is significantly affected by soil properties, such as pH, organic matter, cation exchange capacity (CEC), Fe and Mn oxides (Martin et al., 2004; Xiao et al., 2012; Jia et al., 2013; Grosslova et al., 2015), and plant species (Pavlícková et al., 2005). In acid soil, a particularly high proportion of Tl is adsorbed into amorphous or poorly crystallized Fe oxides (Martin et al., 2004). Moreover, the soils in the PRD, located in subtropical areas, have high levels of Fe oxides and relatively low pH levels. Therefore, Fe oxides may play an important role in Tl mobility in the soils of the PRD. The region's climate, e.g., high rainfall precipitation and warm temperature, can facilitate the release of Tl from sulfide minerals and rocks through weathering processes (Xiao et al., 2012). The soils in the PRD developed under a subtropical and tropical monsoon climate. This climate is typically warm, temperate, and moist; thus, there is substantial soil weathering in this region (Wei, 1979). Consequently, Tl dispersion in the PRD through the weathering processes may be more pronounced.

To fully understand the environmental behavior and fate of Tl in the PRD, in the present study, 102 pairs of soil and flowering cabbages and 91 pairs of soil and lettuces were collected from typical farmland protection areas and vegetable bases across the PRD. The objectives of this study were (i) to investigate the contamination levels and spatial distributions of soil and vegetable (flowering cabbages and lettuces) Tl across the PRD, (ii) to identify the primary factors affecting the bioavailability of Tl in the vegetables, and (iii) to assess the health risks posed by Tl exposure via vegetable intake for residents of the PRD.

2. Materials and methods

2.1. Sampling and soil property analyses

Soil and vegetable samples were collected from typical farmland protection areas and vegetable bases away from cities and industrial areas across the PRD region between May and October of 2012 (Fig. S1). Soil samples were collected from the surface layer (0–20 cm) using a bamboo shovel and gently shaken off from the vegetable roots. At each sampling point, one paired soil and plant sample was collected, and 102 pairs of soil and flowering cabbages and 91 pairs of soil and lettuces were finally obtained. All the soil and vegetable samples were sealed in polyethylene bags and transported to the laboratory within 6 h. After gravel, leaves and roots were manually removed, soils were air-dried at room temperature, ground and passed through an 80-mesh sieve (0.2 mm). Soil properties, including pH in water (pH_{H2O}), pH in a KCl extraction (pH_{KCl}), total organic carbon (TOC), soil organic matter (SOM), cation exchange capacity (CEC), soil texture (clay, silt, sand), Total N, available N, rapidly available K, total P, available P, Fe fractions (oxalate-extractable Fe (Fe_{Ox}), complexed Fe (Fe_{Co}), dithionite-citrate-bicarbonate (DCB)-extractable Fe (Fe_{DCB}), diethylenetriaminepentaacetic acid (DTPA)-extractable Fe (Fe_{DTPA}), NaOAc-extractable Fe (Fe_{Ac})), Al fractions (oxalate-extractable Al (Al_{Ox}), complexed Al (Al_{Co}), DCB-extractable Al (Al_{DCB}), DTPA-extractable Al (Al_{DTPA}), and NaOAc-extractable Al (Al_{Ac})), and total Fe, Al, Ca, Mn, Mg, Na, K, and Si contents were determined. In addition, soil weathering indices indicating changes in the chemical composition and contents before and after weathering were also calculated. The detailed methods for these analyses and data are provided in the supporting information (Tables S1 and S2). For the vegetable samples, decayed and withered tissues were removed, and the edible parts were later washed twice with tap water, repeatedly rinsed in deionized water and dried at 60 °C until their weight was stable. Next, all vegetable samples were crushed with a wooden hammer in a carnelian mortar, passed through an 80-mesh sieve, and packed for subsequent analyses. Further descriptions and details regarding sampling information are provided in a previous study (Liu et al., 2017b).

2.2. Thallium content in soils and vegetables

Approximately 0.5 g of each soil sample were digested in HNO_3/$HClO_4$/HCl (87:13:10, v/v/v) at 80–130 °C. In addition, approximately 0.3 g of each vegetable sample were digested in a mixture of HNO_3/$HClO_4$/H_2O_2 (87:13:10, v/v/v) at 80–130 °C until a clear solution was obtained. All the digested samples were adjusted to 50 ml, passed through a 0.45-mm filter and then analyzed for total Tl using an inductively coupled plasma mass spectrometer (ICP-MS, NexION™ 300X, Perkin Elmer, USA). All reagents were of analytical grade or better and were obtained from Guangzhou Chemical Co., China. An ICP-MS was used to measure the following different Tl fractions: oxalate-extractable Tl (Tl_{Ox}), DTPA-extractable Tl (Tl_{DTPA}), NaOAc-extractable Tl (Tl_{Ac}), and $CaCl_2$-extractable Tl (Tl_{CaCl2}). These fractions were extracted with an oxalic acid-ammonium oxalate buffer solution at pH 3.2, DTPA-$CaCl_2$-triethanolamine (TEA) at pH 7.3, acetic acid-sodium acetate buffer solution at pH 4.0 and 0.01 M $CaCl_2$, respectively. The reporting limits (Yu et al., 2011), operationally defined as the lowest concentration of the calibration curve of Tl, were 2.4×10^{-4} mg/kg and 0.4×10^{-4} mg/kg for total Tl and Tl fractions, respectively, for 1 kg of soil on a dry weight basis and 4.0×10^{-4} mg/kg for 1 kg of the vegetables on a dry weight basis. To verify the accuracy of the metal analysis, certified reference materials (GBW07451 for soil and GBW10020 for vegetables) from the National Research Center for Standards in China were used. The certified values of GBW07451 and GBW07451 were 0.61 ± 0.05 and 0.060 ± 0.008 mg/kg, respectively. The results of our study provided mean values of 0.64 ± 0.032 and 0.051 ± 0.0042 mg/kg for GBW07451 and GBW10020, which were 104% and 84% of the target values, respectively. Reagent blanks and analytical duplicates were also used to ensure accuracy and precision in the analysis.

2.3. Statistical analyses

The bioconcentration factor (BCF) has commonly been used to evaluate the potential for transfer of a metal from the soil to a plant and is calculated as follows: