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

$$BCF = \frac{Cvegetable}{Csoil}$$

where C_{soil} (mg/kg) and $C_{vegetable}$ (mg/kg) refer to the total Tl contents in the soil and the edible part of the vegetable, respectively.

The estimated daily intake (EDI) of Tl depended on both the Tl content in vegetables and the quantity of vegetables consumed. The EDI (ng/kg/day) of Tl was estimated by the following equation (Zhuang et al., 2009):

$$EDI = \frac{CTl \times Wvegetable \times Cfactor}{BW} \times 10^6$$

where C_{Tl} (mg kg^{-1}, on dry weight basis) is the content of Tl in the vegetable matter, C_{factor} is a conversion factor used to convert the fresh vegetable weight to dry weight (0.05 was adopted in this study based on the water contents of flowering cabbages and lettuces (Chen et al., 2014; Pei et al., 2015)), $W_{vegetable}$ represents the daily average vegetable consumption in the PRD, and BW is the average body weight. The average daily consumption rates for leafy vegetables were 173 g/person/day for adults and 125 g/person/day for children in the PRD (Chang et al., 2014b). The average body weights of the local adults and children were 55.9 kg and 32.7 kg, respectively.

The health risks from vegetable consumption by the local population were assessed based on the target hazard quotient (THQ), which is a ratio of a determined dose of a pollutant to a reference dose level. If the ratio is less than 1, the exposed population is unlikely to experience obvious adverse effects. The method of estimating risk using THQ is based on the equation below (Zhuang et al., 2009):

$$THQ = \frac{EFr \times ED \times Wvegetable \times CTl \times C_{factor}}{RfD \times BW \times AT} \times 10^{-3}$$

where $W_{vegetable}$, C_{Tl}, BW and C_{factor} are the same as above, EFr is the exposure frequency.(365 days $year^{-1}$), ED is the exposure duration (70 years); RfD is the oral reference.dose (mg kg^{-1} d^{-1}, 8.5×10^{-5}) (Wang et al., 2013), and AT is average time for non-carcinogens (365 days $year^{-1}$ $\times$ number of exposure years; in this study, 70 years was assumed).

To evaluate the factors affecting the bioavailability of Tl in vegetables, random forest (RF), an accurate learning algorithm, was used (Breiman, 2001a; Breiman, 2001b). Statistical analyses of the experimental data were performed using the SPSS® 10.0 software (SPSS, USA). The correlation analysis was conducted using Pearson's correlation test (two-tailed) with a significance level of $P < 0.05$.

3. Results and discussion

3.1. Content levels of Tl in soils and vegetables

The total Tl contents of the soils ranged from 0.12 to 1.7 mg kg^{-1} with a mean ± SD value of 0.79 ± 0.36 mg kg^{-1} (Fig. 1), which is similar to the range reported in a recent study (0.89–1.8 mg kg^{-1}) (Liu et al., 2017a). Of these soil samples, 30% and 29% had lower levels of Tl than the medians of background values for soil in China (range: 0.292–1.172 mg kg^{-1}, median: 0.58 mg kg^{-1}) (Qi et al., 1992) and in Guangdong Province (range: 0.036–1.430 mg kg^{-1}, median: 0.54 mg kg^{-1}) (The Chinese Environmental Monitoring Station, 1990), respectively. At the upper end, Tl contents in 27% of the total soil samples exceeded the critical trigger limit (1 mg/kg) set for agricultural soil in China (Liu et al., 2017a). To evaluate the mobility of Tl, four Tl fractions extracted with different extractants were also analyzed. The average content levels of the amorphous Fe oxide-bound fraction (Tl_{Ox}), the chelated fraction (Tl_{DTPA}), the carbonate-bound fraction (Tl_{NaOAc}), and the exchangeable fraction (Tl_{CaCl2}) were 0.016 mg kg^{-1}, 0.0010 mg kg^{-1}, 0.0034 mg kg^{-1} and 0.0011 mg kg^{-1}, respectively, meaning that the Tl contents of the fractions were in the order $Tl_{Ox} > Tl_{NaOAc} > Tl_{DTPA} \approx Tl_{CaCl2}$. Generally, Tl within the exchangeable and carbonate-bound fractions is more available to plants compared with the other fractions (Yu et al., 2016).

The content of Tl in the lettuces ranged from 0.0022 to 0.39 mg kg^{-1} dry weight with a mean value of 0.051 mg kg^{-1} (Fig. 1), which was considerably lower than that of the lettuce collected from the Yunfu Sulfuric Acid Plant (22.2 mg kg^{-1} dry weight) in western Guangdong Province, China (Wang et al., 2013). Similarly, for flowering cabbages, Tl levels varied between 0.0062 and 0.42 mg kg^{-1} dry weight with a mean value of 0.13 mg kg^{-1} (Fig. 1). In particular, 69% of the studied flowering cabbages and 27% of the lettuces showed higher levels of Tl than the background level (0.01–0.06 mg/kg) for vegetables grown in areas without Tl contamination in China (Zhou et al., 2008). In addition, Tl levels in 75% of the studied flowering cabbages and 30% of the lettuces were higher than the natural content usually found in plants (approximately 0.05 mg/kg) (Karbowska, 2016). These results indicate that the studied flowering cabbages and lettuces were moderately contaminated with Tl. The bioconcentration factors in all the vegetable samples were lower than 1 and fell within the ranges of 0.0027–0.99 and 0.0077 to 0.99 for lettuces and flowering cabbages, respectively, indicating the low accumulation capacity of Tl for the studied vegetables. However, leafy vegetables showed obvious accumulation capacity for Tl in the rhizospheric soils near a steel factory in northern Guangdong Province, China (Liu et al., 2017a). This discrepancy suggested that many factors affect the bioavailability of Tl in soils, such as the soil type, plant species, sampling site or extraction method (de Caritat and Reimann, 2017).

3.2. Spatial distributions of soil and vegetable (flowering cabbages and lettuces) Tl across the PRD

According to the distribution of the river basin that enters the PRD, the PRD can be divided into five regions, i.e., the East River, North River, West River, Liuxi River and river networks. The East River is the largest of these regions with an area of 31840 km^2. The production, drinking and ecological water supplies in Huizhou, Dongguan, Guangzhou, Shenzhen and Hong Kong are all sourced from the East River. The contents of Tl in soils growing lettuces from the river networks were significantly higher than those in soils from the West River and comparable to those from the East River (Fig. 2). In contrast, Tl contents in lettuces from the river networks were significantly lower than those in soils from the West River and comparable to those from the East River (Fig. 2). There was no significant difference for Tl contents in the soils growing flower cabbages from the five river basins, nor in the flower cabbages. Soil samples with high Tl contents are primarily distributed in the river networks, whereas the Tl content in vegetables showed a different trend. For the lettuces, high Tl levels were found in the West River and for the flower cabbages, the Liuxi River was more polluted with Tl (Fig. 2). In general, high contents of Tl usually occurred in sulfide minerals, and there are two Tl-rich ore deposits, namely, the Shaoguan Pb/Zn deposit and the Yunfu pyrite deposit, in Guangdong Province (Xiao et al., 2012). These two Tl-rich ore deposits are located in the upper regions of the North River and West River, respectively. Mining and smelting activities have resulted in increased levels of Tl from the mining areas into the catchment of the Pearl River, and consequently, soils in the river networks are more polluted by Tl (Xiao et al., 2012).

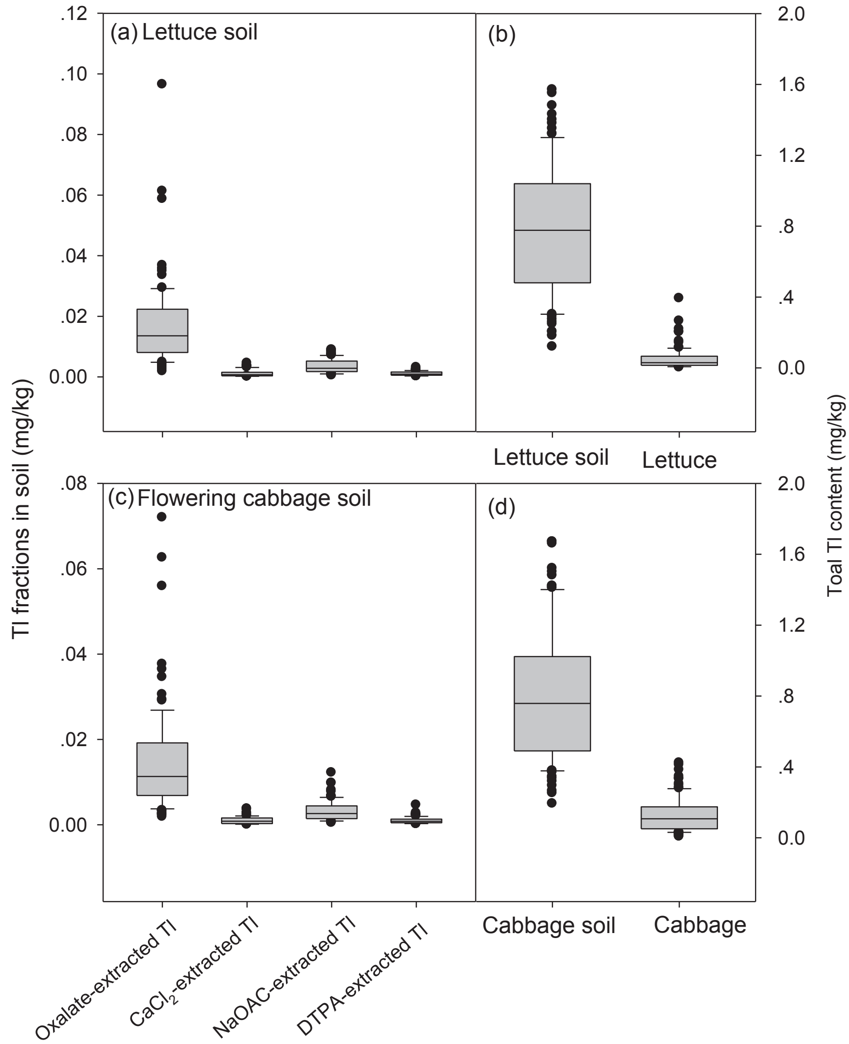

Fig. 1. Total thallium (Tl) content in soils and vegetables (flowering cabbage and lettuce) and Tl fractions (oxalate-extractable Tl, diethylenetriaminepentaac -etic acid (DTPA)-extractable Tl, NaOAc-extractable Tl, and $CaCl_2$-extractable Tl extracted with oxalic acid-ammonium oxalate buffer solution 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) in soils.

3.3. Main factors affecting the bioavailability of Tl in vegetables

To further quantitatively evaluate the relative contribution of soil properties to the bioavailability of Tl in vegetables, the RF model was adopted. As forest building progresses, RF generates an internal unbiased estimate of the generalization error to assure unbiased variable selection and employs pruning to avoid overfitting (Hothorn et al., 2006); therefore, it is superior to conventional and correlation-based regression analyses. For our datasets, the BCF of Tl was used as the dependent variable, and all other parameters were used as independent variables (including pH_{H2O}, pH_{KCl}, TOC, SOM, CEC, clay, silt, sand, total N, total P, total K, available N, available P, rapidly available K, Fe_2O_3, Al_2O_3, MnO, MgO, Na_2O, K_2O, CaO, SiO_2, WI-1, WI-2, WI-3, WI-4, WI-5, CIW, CIA, Fe fractions (Fe_{Ox}, Fe_{Co}, Fe_{DCB}, Fe_{DTPA}, Fe_{Ac}), and Tl fractions (Tl_{CaCl2}, Tl_{Ox}, Tl_{DTPA}, and Tl_{Ac})). The results from RF showed that the rapidly available K, K_2O, total K, CaO, Na_2O, silt, WI-5, and CIW were the greatest contributors to BCF in the flowering cabbages with corresponding importance scores of 10.8%, 5.4%, 5.3%, 5.3%, 4.7%, 4.0%, 3.8%, and 3.7%, respectively (Fig. 3). Similarly, the top contributors to BCF in the lettuces were K_2O, total K, SiO_2, TOC, Na_2O, WI-1, Al_2O_3, MgO, CIW, and CaO, with corresponding importance scores of 16.9%, 14%, 13%, 11%, 5.0%, 4.2%, 3.6%, 3.5%, 2.2% and 2.1%, respectively (Fig. 3). For some soil characteristics, their relative contributions to Tl accumulation in the flowering cabbages and lettuces showed differences. This may be related to the differences of plant physiology between cabbages and lettuces and soil properties between cabbage and lettuce soil (Figs. S2–S6). The difference in accumulation of Tl between cabbages and lettuces was also reported by previous studies (LaCoste et al., 2001; Wang et al., 2013). For example, Wang et al. (2013) found that the average bioconcentration factor of Tl in green cabbage was two times that of lettuce. The content of rapidly available K in cabbage soil from the East River was significantly lower than that in lettuce soil from the East River. In contrast, in the West River, the content of rapidly available K in cabbage soil was significantly higher than that in lettuce soil. Accordingly, the difference in soil properties, such as rapidly available K content, between cabbage and lettuce soil may also affect the relative contributions of soil characteristics to Tl accumulation in the flowering cabbages and lettuces.

For both the flowering cabbages and lettuces, K_2O and total K were the most important factors affecting Tl bioavailability, which is consistent with the findings reported in previous studies (Kazantzis, 2000; Hassler et al., 2007). Due to a similar valency and

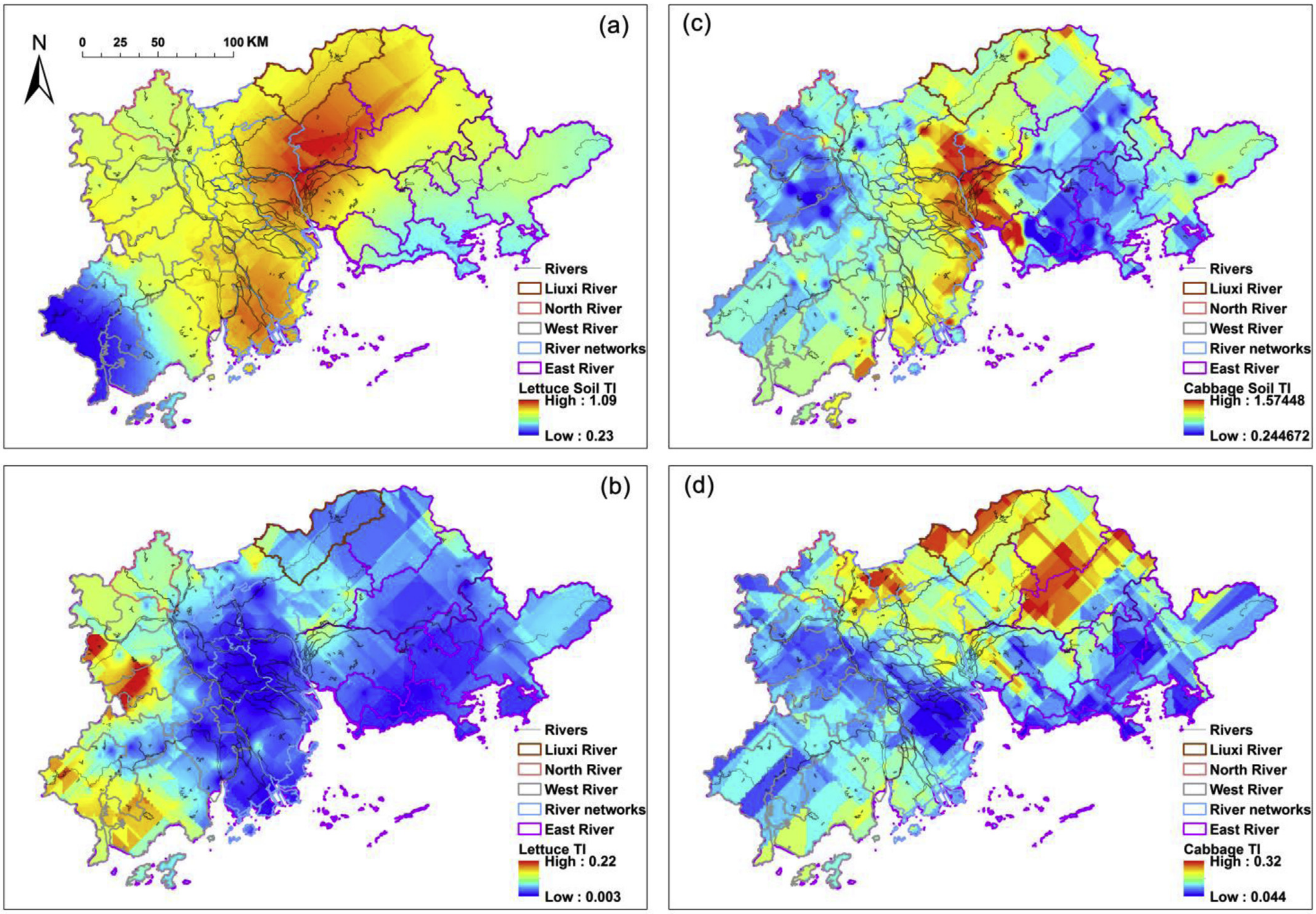

Fig. 2. Spatial distributions of total thallium (Tl) in soils ((a) lettuce soil and (c) flowering cabbage soil) and vegetable ((b) lettuce and (d) flowering cabbage) Tl across the Pearl River Delta (PRD). According to the distribution of the PRD river basin, the PRD is divided into five regions, i.e., the East River, North River, West River, Liuxi River and river networks.

radius, Tl and K can interchange in mineral crystal lattices and cellular membrane ion-transport channels (Zhou and MacKinnon, 2004). For example, a significant positive correlation between Tl and K in rocks/ores was reported (Xiao et al., 2004). Similarly, in our results, significant positive correlations between the content of total Tl and total K were found in both the cabbage and lettuce soils (Figs. S7 and S8). However, no significant correlation between Tl fractions (Tl_{Ox}, Tl_{NaOAc}, Tl_{DTPA}, and Tl_{CaCl2}) and the contents of rapidly available K, total K and K_2O in vegetable soil was found, except that total K and K_2O in lettuce soil were significantly and negatively correlated with the carbonate-bound Tl, indicating little impact on Tl mobility from soil K (Fig. S9). Previous studies (Hassler et al., 2007; Renkema et al., 2015) have indicated that K showed a competitive effect on Tl uptake and that predicting Tl accumulation using a K accumulation model with a correction factor may be possible for some plants. In the present study, based on a field experiment, significant negative correlations between the BCF of Tl in flowering cabbages and rapidly available K, total K and K_2O in cabbage soil and between the BCF of Tl in lettuces and total K and K_2O in lettuce soil were found (Figs. 4 and 5). The contents of Tl in the flowering cabbages and lettuces were also significantly and negatively correlated with the rapidly available K in soils (Figs. 4D and 5C), but no correlation was found with total K and K_2O. All these results confirmed the competition between K and Tl uptake obtained by previous studies under control conditions and suggested that the competitive effect was mainly derived from rapidly available K, which was consistent with the fact that rapidly available K is the most available portion of K in soil. As mentioned above, the soil weathering in the PRD was high under the warm and moist climate. During the weathering process, the most mobile elements, such as K, Na, Ca, and Mg, were readily leached in the form of carbonates or sulfates, while the low mobility elements, such as Si, Al, Fe, and Mn, were liable to be accumulated as either oxides or hydroxides. Therefore, the soil weathering indices derived from the ratio of the oxide contents of various elements were used to assess the degree of soil weathering (Chang et al., 2014a). Chemical weathering is the main cause of the release of Tl from rocks and ores (Peng et al., 2004; Xiao et al., 2004). As a result, in the PRD, where numerous Tl-bearing sulfide mineral deposits have been found, the release of Tl from Tl-rich sulfide minerals through weathering processes poses a high risk to the soil, sediment and water safety of this region (Xiao et al., 2012; Liu et al., 2016a; Li et al., 2017). Accordingly, for both the flowering cabbages and lettuces, the soil weathering indices, such as WI-5, CIW, and WI-1, and the related oxides, such as CaO, Na_2O, SiO_2, Al_2O_3, and MgO, contributed substantially to Tl accumulation in the vegetables. A previous study (Vaněk et al., 2015a) indicated that rhizospheric conditions, such as root exudation, enhanced the sulfide mineral dissolution associated with Tl release; however, this was invalid in soils enriched in carbonates (mainly $CaCO_3$), and/or that had a higher soil pH.

In addition to Tl-bearing minerals, organic matter can also act as

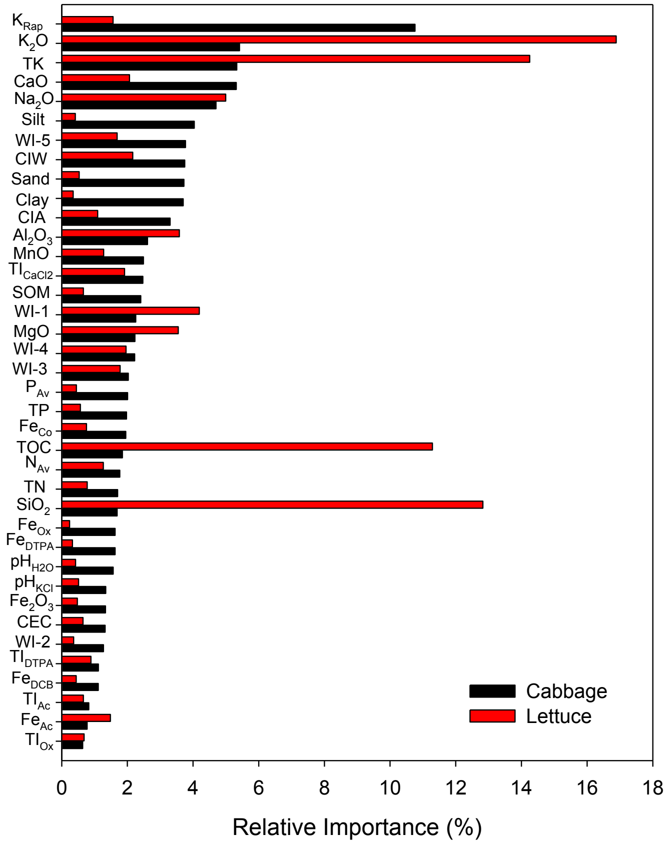

Fig. 3. Variable importance scores of the individual predictors for estimating the Tl accumulation in cabbages and lettuces based on random forest (RF). The importance scores of the independent variables were rescaled by setting their sum to 100%. K_{Rap}: rapidly available K; TK: content of total K in soil; WI-5: soil weathering indices presented as the molecular ratio $(K_2O + Na_2O + CaO + MgO)/Al_2O_3$; CIW: soil weathering indices presented as the molecular ratio $[Al_2O_3/(Al_2O_3+CaO + Na_2O)] \times 100$; CIA: soil weathering indices presented as the molecular ratio $[Al_2O_3/(Al_2O_3+CaO + Na_2O + K_2O)] \times 100$; Tl_{CaCl2}: Tl fraction extracted with 0.01 mol L^{-1} $CaCl_2$; SOM: soil organic matter; WI-1: soil weathering indices presented as the molecular ratio SiO_2/Al_2O_3; MgO: content of MgO in soil; WI-4: soil weathering indices presented as the molecular ratio $(K_2O + Na_2O)/Al_2O_3$; WI-3: soil weathering indices presented as the molecular ratio $(Al_2O_3+Fe_2O_3)/SiO_2$; P_{Av}: available P; TP: total P content in soil; Fe_{Co}: Fe extracted with 0.1 mol L^{-1} sodium pyrophosphate (g/kg); N_{Av}: available N content; TN: total N content in soil; Fe_{Ox}: Fe extracted with 0.2 mol L^{-1} ammonium oxalate; Fe_{DTPA}: Fe extracted with 0.005 mol L^{-1} diethylenetriaminepentaacetic acid (DTPA)+0.01 mol L^{-1} $CaCl_2$+0.1 mol L^{-1} triethanolamine (pH = 7.3); WI-2: soil weathering indices presented as the molecular ratio Al_2O_3/Fe_2O_3; Tl_{DTPA}: Tl fraction extracted with 0.005 mol L^{-1} diethylenetriaminepentacetate acid (DTPA)+0.01 mol L^{-1} $CaCl_2$+0.1 mol L^{-1} triethanolamine (pH = 7.3); Fe_{DCB}: Fe extracted with dithionite–citrate–bicarbonate (DCB); Tl_{Ac}: Tl fraction extracted with NaOAc/HOAc buffer solution (pH = 4); Fe_{Ac}: Tl fraction extracted with NaOAc/HOAc buffer solution (pH = 4); and Tl_{Ox}: Tl fraction extracted with 0.2 mol L^{-1} ammonium oxalate (pH = 3.2).

a major sink for metals (Grybos et al., 2007). In the present study, soil TOC and SOM were the fourth and twenty-fifth largest contributors to Tl accumulation in lettuces, respectively (Fig. 3). Notably, soil TOC seems more important than SOM for Tl accumulation in lettuces (Fig. 3). As indicated by previous studies (Kogel-Knabner, 2002; Tamburini et al., 2017; Cotching, 2018), both TOC and SOM are defined as the total amount of the organic carbon-containing part in the soil, consisting of living organisms, slightly altered plant and animal residues, and well-decomposed organic residues. In fact, TOC is an integral component of SOM, and generally, it accounts for 58% of the total amount of SOM (Liu, 2017). The difference in the contributions of TOC and SOM may be related to the composition of organic matter. Based on the Tl distribution in soils from a smelter-impacted area, the content and quality of SOM, especially the ratio between fulvic and humic acids, were thought to be key parameters affecting Tl mobility and bioavailability (Vaněk et al., 2013). Generally, the interaction of organic matter with metal ions can mobilize or immobilize metal ions through the formation of more or less stable complexes, which depends on the metal ion itself, the composition of organic matter and pH (Hattab et al., 2014). For example, humic substances, one important component of organic matter, can immobilize Pb, Cu and Mo while mobilizing Zn and As through the formation of soluble Zn- and As-humic substance complexes (Hattab et al., 2014). Previous studies have indicated that weak complexation of Tl occurs with most organic ligands, fulvic acids and humic acids (Jacobson et al., 2005; Gomez-Gonzalez et al., 2015; Vaněk et al., 2016). In addition, the amount of Tl associated with organic matter fractions was relatively low based on the results of the sequential extractions of Tl in soils (Vaněk et al., 2010; Gomez-Gonzalez et al., 2015). In this study, significant negative correlations between the BCF of Tl in lettuces and soil TOC was found (Fig. S10). Similarly, the lettuce Tl also showed a significant negative correlation with TOC in the lettuce soil (Fig. S10). In addition, in the lettuce soil, significant positive correlations between the amorphous Fe oxide-bound Tl and TOC and SOM, between the chelated Tl and TOC and SOM and between the carbonate-bound Tl and TOC were found (Table S3). These results indicated that to a certain extent, organic matter could affect Tl mobility and further affect Tl bioavailability in lettuces. Notably, when TOC was lower than 1%, the BCF of Tl in lettuces and lettuce Tl decreased exponentially with increasing TOC and later became steady when TOC was higher than 1% (Fig. S10). In the present study, more than 70% of soil TOC was higher than 1%; thus, organic matter might not be a major factor affecting the mobility of Tl in most lettuce soils.

Many previous studies have demonstrated that soil minerals, especially Fe and Mn oxides, play an important role in the bioavailability of Tl (Grosslova et al., 2015; Liu et al., 2016b; Antić-Mladenović et al., 2017). On one hand, Tl can be immobilized by Fe and Mn oxides through sorption or precipitation at the mineral surface (Duan et al., 2010; Zhuang and Gao, 2015). On the other hand, Fe and Mn oxides enriched in Tl can also behave as a potential source of Tl under reductive conditions (Duan et al., 2012; Grosslova et al., 2015). Thallium exhibits a higher tendency toward sorption to Mn oxides than to Fe oxides (Antić-Mladenović et al., 2017). Hence, Tl was more easily immobilized by Mn oxides, and soil treatments containing Mn oxides were considered an efficient and environmentally friendly solution for the remediation of soil systems contaminated with Tl (Vaněk et al., 2011; Wan et al., 2014). However, in the present study, the contributions of Fe and Mn oxides to Tl availability were minor, which is related to the mechanism of Tl retention by oxides. Previous studies (Bidoglio et al., 1993; Antić-Mladenović et al., 2017) have indicated that Tl can be immobilized by oxides through a sequence of adsorption, surface oxidation of Tl(I) to Tl(III), and the sorption or precipitation of Tl_2O_3 at the mineral surface. The immobilization of Tl by oxides was affected by many factors, such as the valence state of Tl, pH, the characteristics of oxides and the Tl/oxides ratio (Antić-Mladenović et al., 2017). Furthermore, under the actual environmental conditions, oxides and their associations with other soil constituents in soils make this process more complex. Hence, this subject needs further study from microcosm and field experiments.

3.4. Potential health risks associated with the consumption of vegetables

The estimated dietary intakes (EDI) of Tl for adults and children

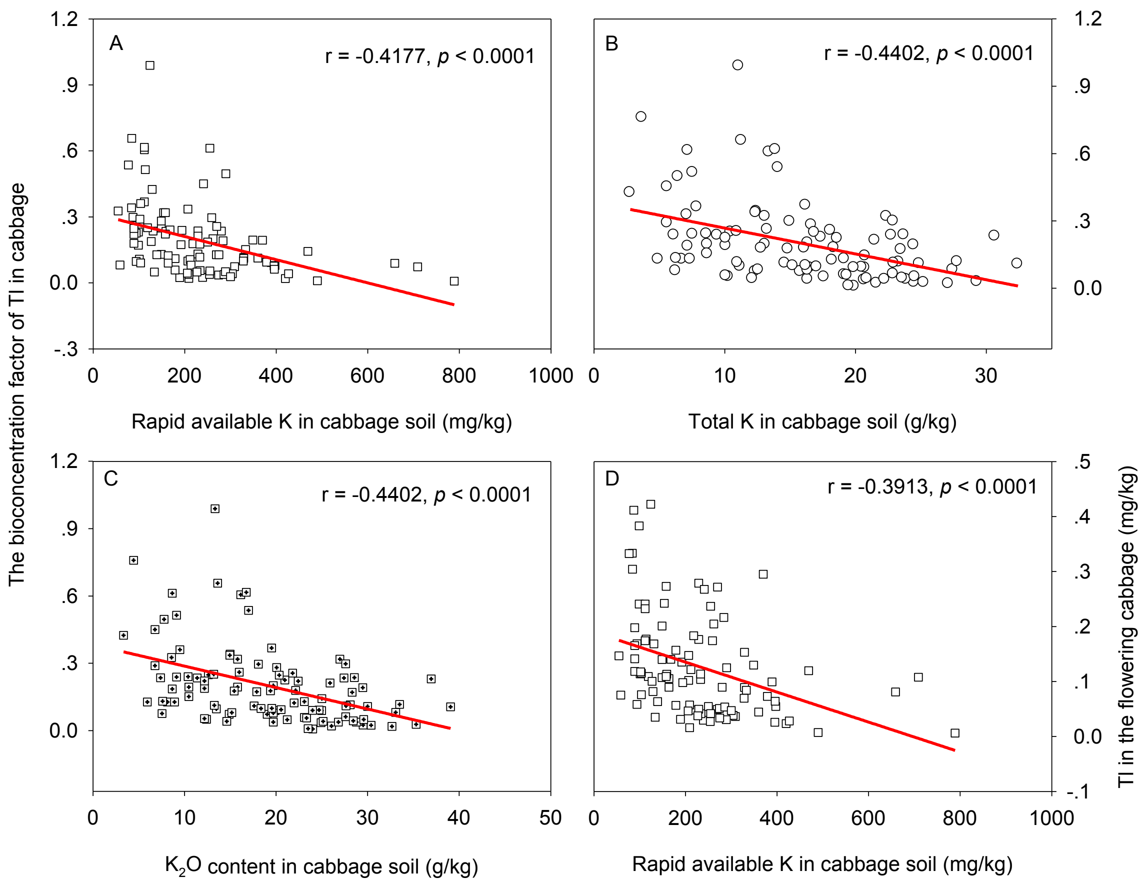

Fig. 4. Correlation analyses between the bioconcentration factor (BCF) of Tl in the flowering cabbages and contents of rapidly available K, total K and K_2O in cabbage soil and between the content of Tl in the flowering cabbages and rapidly available K.

via flowering cabbage consumption varied in the ranges of 0.96–65 ng/kg/day and 1.2–81 ng/kg/day with mean values of 20 ng/kg/day and 24 ng/kg/day, respectively (Fig. 6). Similarly, the EDI of Tl for adults and children via lettuce consumption were in the ranges of 0.35–41 ng/kg/day and 0.43–50 ng/kg/day with mean values of 6.8 ng/kg/day and 8.4 ng/kg/day, respectively (Fig. 6). By comparison, the average estimated amount of Tl intake via consumption of green cabbage and lettuce collected near the Yunfu sulfuric acid factory were 0.98 μg/kg/day and 0.63 μg/kg/day for local adults, respectively, and 0.59 μg/kg/day and 0.38 μg/kg/day for local children, respectively (Wang et al., 2013). Similarly, the average EDI of Tl for people via consumption of Chinese lettuce and romaine lettuce were 0.48 μg/kg/day and 1.3 μg/kg/day, respectively, as reported by another study also conducted near the Yunfu sulfuric acid factory (Liu et al., 2012). In addition, the average calculated daily ingestion amounts of Tl for adults via flowering cabbage and lettuce consumption were 1.1 μg/day and 0.8 μg/day, respectively. It is generally believed that a total intake of Tl of less than a 5 μg/day does not pose a threat to human health based on a report from a previous study (Kazantzis, 2000). Accordingly, there is no immediate health threat arising from the consumption of flowering cabbage and lettuce in the study area for local people. In addition, the target hazard quotient (THQ) of Tl through the consumption of the flowering cabbages for adults and children varied in the ranges of 0.012–0.82 and 0.015 to 1.01, respectively with only one THQ value higher than 1.0. In addition, the TEQ values of Tl through lettuce consumption were in the ranges of 0.0044–0.51 and 0.0054 to 0.63 for adults and children, respectively. By comparison, the average TEQ values of Tl via green cabbage and lettuce collected near the Yunfu sulfuric acid factory were 10.9 and 7.9 for local adults, respectively, and 7.4 and 4.8 for local children, respectively (Wang et al., 2013). Similarly, another study conducted near the Yunfu sulfuric acid factory reported that the average TEQ values of Tl via consumption of Chinese lettuce and romaine lettuce were 5.95 and 16.3, respectively (Liu et al., 2012). Both the EDI and TEQ values from our results were much lower than those from the sampling areas near the Yunfu sulfuric acid factory, indicating minimal health risks from Tl exposure through flowering cabbage or lettuce intake. The EDI and THQ of Tl via flowering cabbage consumption for children were significantly higher than those for adults ($P < 0.05$), revealing that children are more sensitive to Tl exposure through flowering cabbage consumption.

4. Conclusions

High contents of soil Tl are primarily distributed in the river networks due to the mining and smelting activities in the upper regions of the North River and West River. The results from RF indicated that rapidly available K and total K were the most important factors affecting Tl bioavailability, and the competitive effect of rapidly available K on vegetable Tl uptake was confirmed through a field study. Soil weathering also contributed substantially to Tl release in the study area and thus affected Tl accumulation in the vegetables. Organic matter might not be a major factor affecting the mobility of Tl in most of the lettuce soils. Although previous studies have demonstrated the important role of Fe oxides in Tl mobility, the contributions of Fe oxides to the bioavailability of Tl in vegetables were minor in our results, which may require

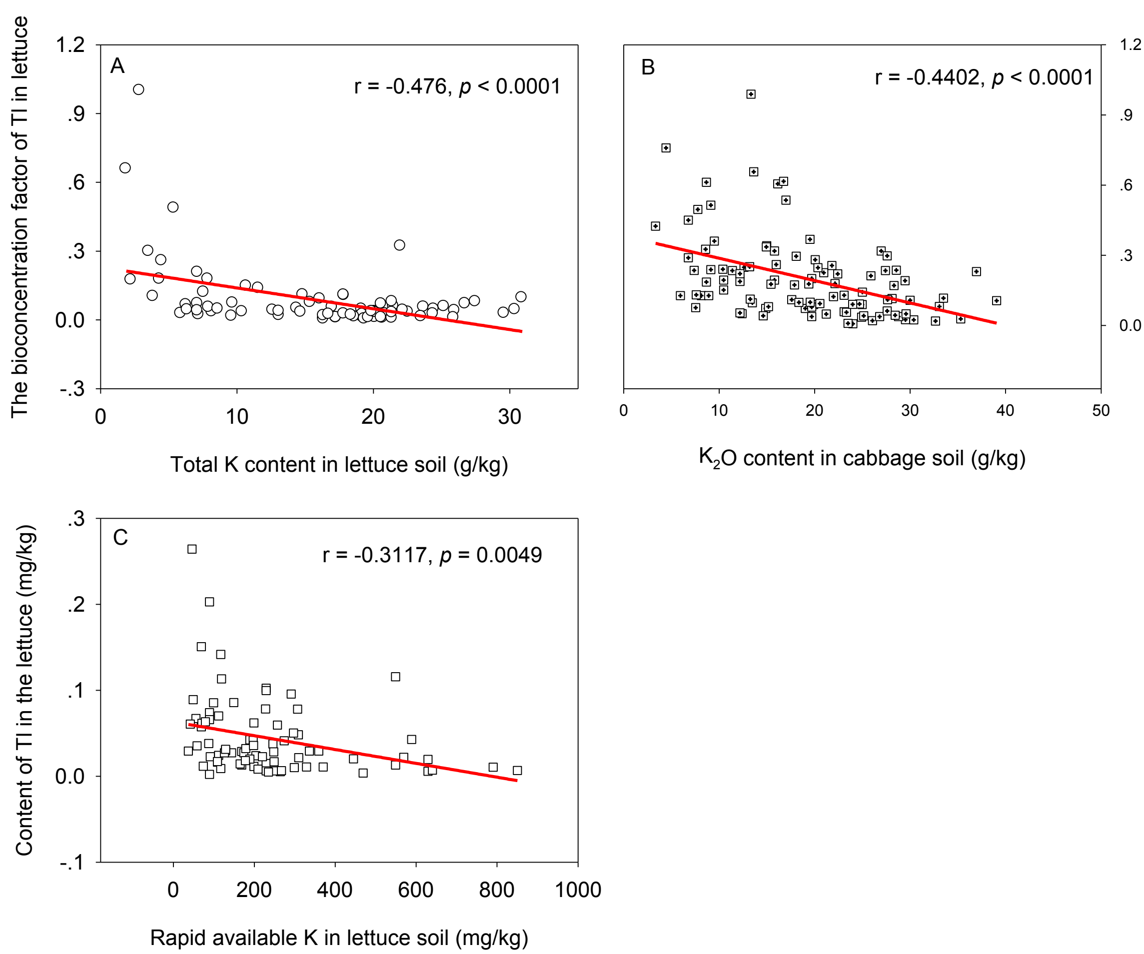

Fig. 5. Correlation analyses between the bioconcentration factor (BCF) of Tl in the lettuces and total K and K_2O in lettuce soil and between the content of Tl in the lettuces and rapidly available K.

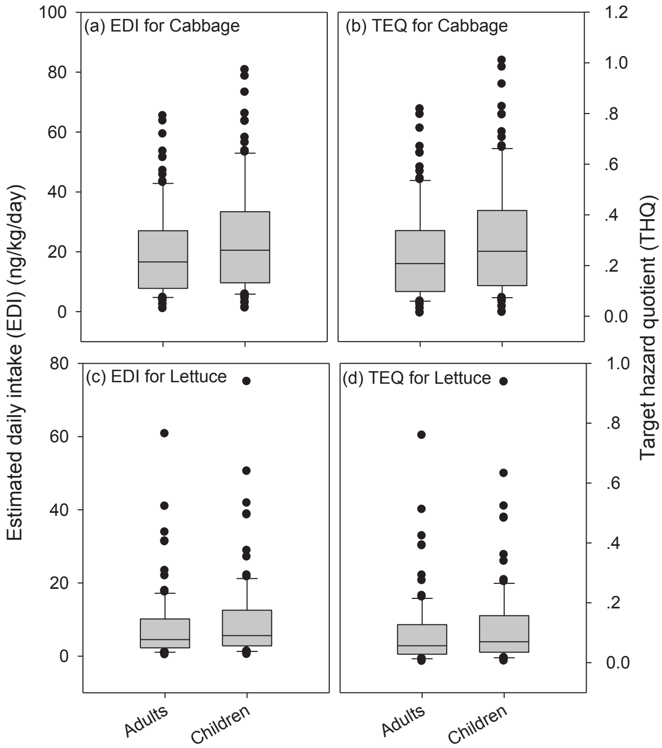

Fig. 6. Estimated dietary intakes (EDI) and the target hazard quotients (THQ) of Tl for adults and children via the consumption of flowering cabbages and lettuces.

further study. A risk assessment based on EDI and THQ suggested that the health risks posed to local people by Tl exposure through flowering cabbage or lettuce intake were minimal.

Conflicts of interest

The authors declare no competing financial interests.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.05.090.

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