Thallium at the interface of soil and green cabbage (*Brassica oleracea* L. *var. capitata* L.): Soil–plant transfer and influencing factors

Yanlong Jia [a,b], Tangfu Xiao [a,*], Guangzhu Zhou [a,c], Zengping Ning [a]

[a] *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[b] *Graduate University of Chinese Academy of Sciences, Beijing 100039, China*
[c] *School of Chemistry and Environmental Engineering, Shandong University of Science and Technology, Qingdao 266590,China*

HIGHLIGHTS

► Tl migration at the interface of soil and green cabbage was investigated.
► The leaves of green cabbage had high bioconcentration capacity for Tl.
► The leaves were the main storage site for Tl (greater than 80%) in the green cabbage.
► Enrichment of Tl in green cabbage was influenced by Tl content of soil and mobility in soil.
► Tl mobility was affected by water content, pH, SOM and CEC in rhizospheric soils.

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ABSTRACT

Thallium (Tl) is a non-essential and toxic trace metal found in many plants, but it can accumulate at particularly high concentration in green cabbage (*Brassica oleracea* L. *var. capitata* L.). The aim of this study is to explore the transfer and accumulation of Tl at the interface of rhizospheric soil and green cabbage from a long-term Tl contaminated site in southwestern Guizhou Province, China. Influencing factors such as Tl distribution in various soil fractions and physical–chemical characteristics of rhizospheric soil were also investigated. Our results demonstrated that green cabbage had high accumulation of Tl, with most bioconcentration factor (BF) values exceeding 1, and up to a maximum level of 11. The enrichment of Tl in the green cabbage tissues followed a descending order, i.e. old leaves > fresh leaves > stems ≈ roots. The stems functioned as a channel for Tl transportation to the leaves, where most of the Tl (greater than 80%) was found to accumulate. In the rhizospheric soils, 62–95% of Tl existed in the residual fraction, while lower concentrations of Tl (on average, 1.7% of total T1 in rhizospheric soil) were found in the water and acid soluble fractions. The major fraction of labile Tl was located in the reducible fraction (9%). Our results also suggested that the uptake and enrichment of Tl in green cabbage were affected by Tl concentrations, soil water content, soil pH, soil organic material (SOM) and cation exchange capacity (CEC) in rhizospheric soil.

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1. Introduction

Thallium (Tl), a non-essential and toxic heavy metal that is detrimental to plants (Zitko, 1975; Repetto et al., 1998), is classified as one of the 13 priority pollutant metals (Keith and Telliard, 1979). Due to its toxicity (Kazantzis, 2000; Peter and Viraraghavan, 2005) and pollution occurrence in China, Tl has been regulated as one of the metal pollutants in China (Li et al., 2012; Xiao et al., 2012). Although widely distributed in the natural environment, the average Tl concentration in soil is less than 1 mg/kg all over the world (Fergusson, 1990), and the Tl concentration in the soils in China was in the range of 0.29–1.2 mg/kg (Qi et al., 1992). The Canadian environmental quality guideline for Tl in soil is 1 mg/kg (CCME, 2003). However, high concentration of Tl in soil has been observed in many areas of the world. For instance, high concentrations of Tl (1.54–55 mg/kg) have been reported in the arable soils of France (Tremel et al., 1997a), and elevated levels of Tl (8.8–27.8 mg/kg) in soils from Silesian–Craeowian zinc–lead mine areas have also been recorded (Lis et al., 2003). In China, high Tl soil concentrations ranging from 40 to 124 mg/kg have been reported in regions heavily mineralized with Tl–As–Hg (Xiao et al., 2004a), and concentrations between 5 and 15 mg/kg have been reported from pyrite processing areas (Yang et al., 2005). These high Tl soil concentrations are of either pedogeochemical origin (Tremel et al., 1997a; Xiao et al., 2004b) or anthropogenic (i.e., mining, processing and smelting) origin (Lis et al., 2003; Yang et al., 2005).

Previous studies have illustrated that certain plants are more susceptible to accumulation of Tl from Tl-contaminated sites (Tremel et

* Corresponding author. Tel./fax: +86 851 5895318.
  E-mail address: xiaotangfu@vip.gyig.ac.cn (T. Xiao).

al., 1997b; Al-Najar et al., 2003, 2005; Xiao et al., 2004a). However, little information is available regarding the geochemical behavior of Tl at the soil–plant interface. The soil–plant transfer of Tl is a complex process that may be constrained by certain factors. In addition to physiological and molecular characteristics of plants, several geochemical factors may also control the behavior of Tl in soils and its accumulation in plants. Two key factors are the mobility and bioavailability of Tl in soils. The mobility of Tl can be determined by sequential extraction of soil (Al-Najar et al., 2003; Yang et al., 2005; Vanek et al., 2010a), and a correlation between the content of labile Tl in soil and its uptake by plants is established (Vanek et al., 2010a). The bioavailability of ions largely depends on the physical–chemical and biological characteristics of soils, especially dynamic processes in the rhizosphere (Wenzel, 2009). For example, green rapes, bush beans and rye grass were found to absorb less Tl from weakly acidic soil (pH 6.2) than from highly acidic soil (pH 5.6), and Tl supplied by cement factory dust was more available to be absorbed by plants than Tl in soil from a lead–zinc mining area (WHO/IPCS, 1996).

Green cabbage (*Brassica oleracea* L. *var. capitata* L.) has been identified as a plant prone to high accumulation of Tl (LaCoste et al., 2001; Xiao et al., 2004a; Al-Najar et al., 2005; Pavlickova et al., 2005). However, only limited research has addressed the geochemical process associated with transfer of Tl from the rhizospheric soil to green cabbage. Al-Najar et al. (2005) have examined the effect of origin (anthropogenic vs. geogenic) and mobility of Tl in the rhizosphere on Tl uptake by plants, and pointed out that most of the uptaken Tl was derived from the so-called "easily accessible" fractions. Tl accumulation and factors may constrain these processes. In the present study, our objective was to determine Tl concentrations in individual parts (root, stem, young leaves and old leaves) of green cabbage grown on Tl-polluted soils and to quantify the Tl transfer capacity between soil and plants. In addition, we also aimed to investigate the environmental factors that may influence the accumulation of Tl in green cabbage. The results of this study provide useful information for improved understanding of the geochemical processes associated with Tl transfer from soils and Tl accumulation in plants.

2. Materials and methods

2.1. Site description

The study area for sampling is located in Lanmuchang (105°30′23″E, 25°31′28″N), a small town of approximately 1000 inhabitants in southwest Guizhou Province, China. The local residents have reportedly exhibited symptoms associated with chronic Tl poisoning, including weakness, muscle and joint pain, disturbance of vision, hair loss, and high Tl levels in urine. These symptoms are induced by Tl contaminations in local soils, waters and crops (Zhou and Liu, 1985; Xiao et al., 2007), which appears to be due to local sulfide mineralization of Tl, arsenic (As) and mercury (Hg), and mining activities. For example, local Tl concentrations have been measured at 100–35,000 mg/kg in sulfide minerals, 40–124 mg/kg in soils, 0.8–495 mg/kg in crops, 13–1966 μg/L in groundwater and 1.9–8.1 μg/L in stream water (Xiao et al., 2003, 2004a,b,c). The local concentrations of Tl have been elevated to high levels, due in part to anthropogenic factors and consequently present a severe threat to the public health of the local population (Xiao et al., 2007, 2012).

Geologically this area is karst topography, exhibiting a higher elevation in the northwest and a lower elevation in the southeast. The average altitude is 1400 m, and the relative relief is 100–200 m. The local outcropping rocks are composed of limestone, argillite and siltstone formed during the Permian and Triassic periods. Previous studies have described the local geology and sulfide mineralization in detail (Xiao et al., 2003, 2004a). The Lanmuchang area has been widely developed for agricultural and residential purposes.

2.2. Sampling and preparation

Nineteen green cabbage samples were collected in the study area. At each sampling site, rhizospheric soil was also collected (Fig. 1). The soil samples were kept in polyethylene bags and air-dried in the laboratory pending final processing. The soils were processed for geochemical analysis by disaggregation to pass through a 2-mm sieve. The sieved fractions were then ground in a Bico ceramic disc grinder followed by reduction to 80-mesh (<180 μm) powder in a ceramic ball mill. The plant samples were partitioned into roots, stems, young leaves and old leaves. Plant materials were cleaned using de-ionized water to exclude any Tl contaminations by dusts or soil particles on the plants, and air-dried in labeled paper bags. All the plant samples were crushed using a crushing machine (FZ102, TAISITE, China) to fragments capable of passing thorough a 60-mesh sieve.

The soil pH was measured after suspending soil in de-ionized water in a ratio of 1:2.5 (v/v) using a pH meter (AISI pHB9901, Taiwan). The concentration of soil organic materials (SOM) was determined by catalytic oxidation (1350 °C) using a combination of Metalyt CS 500 and Metalyt CS 530 elemental analyzers (Eltra, Germany). The cation exchange capacity (CEC) was computed after saturation of the soil samples with 0.005 M EDTA, 1 M ammonium acetate mixture, and a standard titration solution of ammonia acid. Approximately 50 mg of the sieved soil sample (<180 μm) was digested using a heated acid mixture (15 mL of 15 M HNO$_3$ and 5 mL of 10 M HF) to determine Tl, Fe and Mn. Additionally, 100 mg of the powdered plant samples was digested with a 10-mL mixture of strong acids (8 mL of 15 M HNO$_3$ and 2 mL of 12 M HClO$_4$) for Tl determination. Milli-Q water (18.2 MΩ cm) was used for all experiments, and reagents used were of super pure grades.

2.3. Sequential extraction of soil

The full protocol for sequential extraction of Tl in soil samples was performed in accordance with the modified BCR procedure (Rauret et al., 1999) and consisted of the water soluble, weak acid soluble, reducible, oxidizable, and residual fractions (Table 1). The water soluble fraction was supplemented as the initial stage, which provides information concerning the immediately available Tl in the soil (Jakubowska et al., 2007), and the residual fraction was through digestion using a heated acid mixture (15 mL of 15 M HNO$_3$ and 5 mL of 10 M HF) (Qi et al., 2000). Two soil samples (S102 and S205) were analyzed in triple in order to assess the uncertainty of the extraction procedure for Tl determination, and the coefficients of variation (CVs) were 7%, 3%, 1%, 3%, 3% for S102, and 5%, 2%, 6%, 1%, 2% for S205 for all the five sequential extraction fractions (steps 1 to 5), respectively. To evaluate the intensity of experimental contamination, blank experiments were performed under the same conditions, and the results suggested that no significant Tl contamination was introduced during the sequential extraction. The recovery of Tl was determined by comparing the amount of Tl extracted with the total amount indicated by its total digestion concentration: (sum/total)×100%. In this study, the recovery rate of Tl was found to be within the range of 91–117% (Table 2).

2.4. Analysis and quality control

The concentrations of Fe and Mn in soils were determined using inductively coupled plasma optical emission spectrometry (ICP-OES) (iCAP 6500, Thermo Scientific, Germany), while Tl concentrations in plants and soils were determined using inductively coupled plasma mass spectrometry (ICP-MS) (Perkin-Elmer, ELAN DRC-e, USA) (Qi et al., 2000). The detection limit is calculated as average of ten times the standard deviation of the ion counts obtained from the individual procedural reagent blanks (prepared in the same way as the sample decomposition), divided by the sensitivity of standard solution. The detection limit for Tl was 0.01 mg/kg, which is largely lower than the Tl contents in this study. The analytical precision,
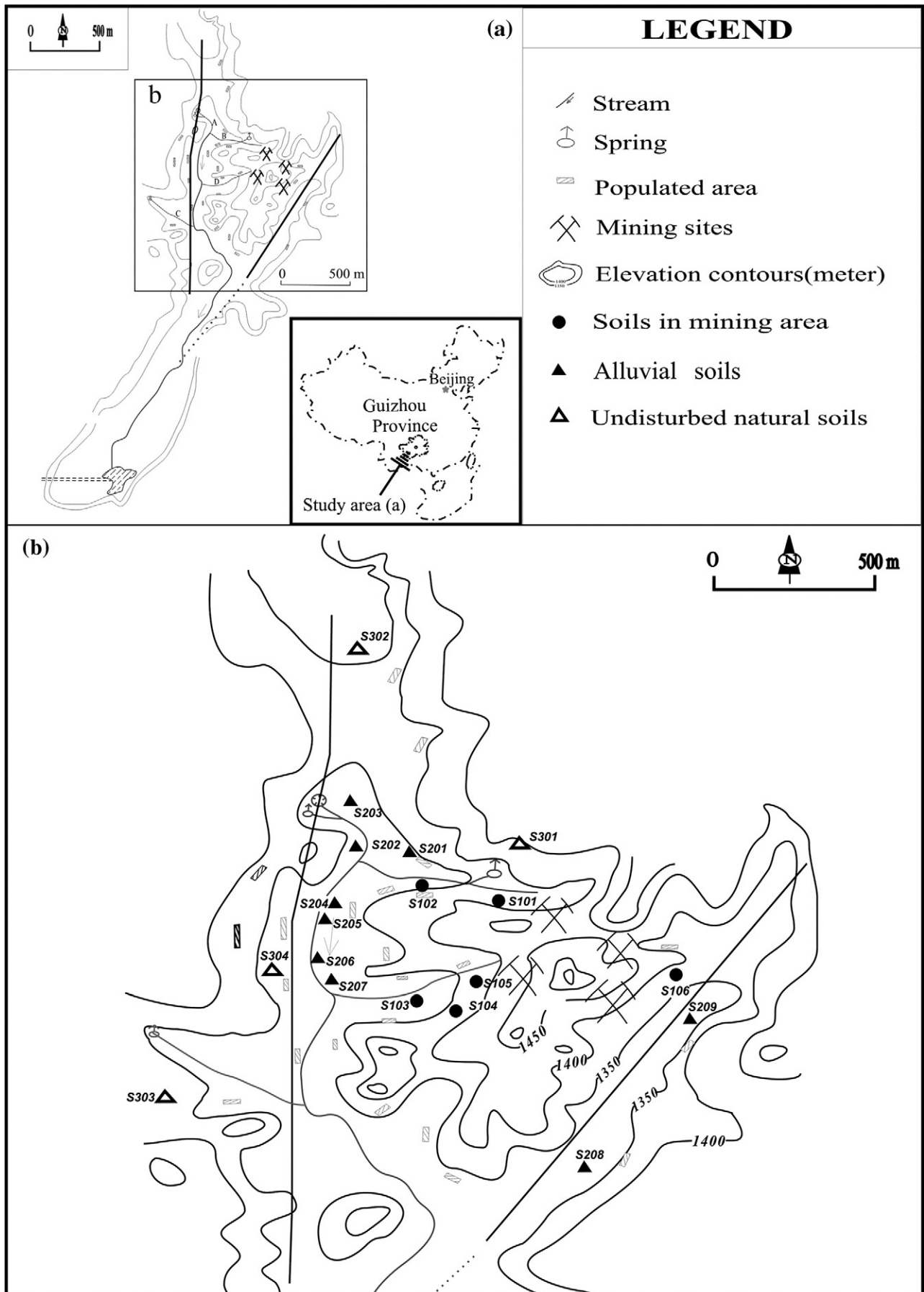
Fig. 1. Map of the sampling sites.

Table 1

Reagents and operation conditions for the modified BCR sequential extraction procedure.

Step	Operationally-defined phase	Reagent	Stirring time and temperature
1	Water soluble [a]	30 mL of H_2O	1 h at 22 ± 5 °C
2	Weak acid soluble [b]	40 mL of 0.11 M HOAc	16 h at 22 ± 5 °C
3	Reducible [b]	40 mL of 0.5 M $NH_2OH \cdot HCl$	16 h at 22 ± 5 °C
4	Oxidizable [b]	10 mL of 8.8 M H_2O_2	1 h at 22 ± 5 °C
		10 mL of 8.8 M H_2O_2	1 h at 85 ± 5 °C
		50 mL of 1 M NH_4Ac	16 h at 22 ± 5 °C
5	Residual [c]	$HNO_3 + HF$	As described in Section 2.2

[a] Jakubowska et al., 2007.
[b] Rauret et al., 1999.
[c] Qi et al., 2000.

determined based on the standard quality control procedures using internationally certified reference materials (OU-6, AMH-1, GBPG-1 and NIST 2711), internal standards (Rh at 500 μg/L), and duplicates, was better than ±10%. The standard reference material NIST 2711 (Montana Soil) was used for analytical quality control. The average total Tl concentration of the NIST 2711 was 2.42 ± 0.13 mg/kg (n = 6), which is comparable with the certified value of 2.47 ± 0.15 mg/kg. The relative percentage differences of sample replicates for soil and plant were <7% (n = 3) and <5% (n = 3), respectively. The determined data for plants were reported as dry weight (DW).

3. Results and discussion

3.1. Migration of Tl in the interface of rhizospheric soil and green cabbage

The parameters relating to soil properties and Tl concentrations in the rhizospheric soils were summarized in Table 2. The soil pH indicated acidic soils in the mining site (pH 5.1–6.3) and in the alluvial soils (pH 4.9–6.5), while the undisturbed natural soils were relatively neutral (pH 5.7–7.3). The SOM contents varied from 50 to 146 g/kg (average of 86 g/kg). The low SOM contents in soils at the mining

sites resulted in high CEC values. Tl levels ranged from 1.5 to 109 mg/kg in the rhizospheric soils, far above the median value (0.58 mg/kg) of Chinese soils (Qi et al., 1992). In the study area, Tl ranged from 37.4 to 109 mg/kg with an average of 71.4 mg/kg in the rhizospheric soils of the mining sites; 1.5 to 42.2 mg/kg (average of 21.5 mg/kg) in the alluvial soils; and 2 to 26.2 mg/kg in the undisturbed natural soils. The mining activity and the erosion of natural soils from the Tl mineralized area have both been identified as factors responsible for the distributions of high Tl concentrations in the soils (Xiao et al., 2004a).

The concentrations of Tl measured in the green cabbages are summarized in Table 3. Very high accumulation of Tl was observed in green cabbage growing on the Tl-polluted soils of the study area, ranging from 3.7 to 818 mg/kg. Tl ranged from 0.8 to 71.1 mg/kg (average of 20.8 mg/kg) in roots, 1 to 39.4 mg/kg in stems (average of 15.3 mg/kg), and 1.6 to 658 mg/kg in young leaves (average of 57.4 mg/kg), thus exhibiting much higher accumulation in the leaves. However, Tl displayed much higher contents in the old leaves than the young leaves, i.e. 6.1 to 1503 mg/kg with an average of 238 mg/kg in old leaves. This rural area is far away from urban and industrial zones, except for several small coal and Hg-Tl mines that have been abandoned for decades. The possible Tl contamination by dusts or soil particles on the green cabbage leaves is negligible. The pre-treatment using de-ionized water to clean the plants also excludes such possible Tl contamination. The results clearly indicated that Tl in the rhizospheric soils transferred through roots and stems to the leaves that stored more than 80% of Tl in green cabbage. The accumulation capacity of green cabbage planted in the study area is similar with green cabbage planted around the cement factory (mean value 28 mg/kg Tl in leaf, fresh weight) (WHO/IPCS, 1996).

The transfer coefficient (TC) is defined by the ratio of an element concentration in plant tissue aboveground to its concentration in the roots, and is thus used to assess the ability of aboveground plant tissue to transfer the element from the roots. The bioconcentration factor (BF) is defined by the ratio of an element concentration in plant tissue to its concentration in rhizospheric soils, and is used to

Table 2

Characteristics of rhizospheric soil, total Tl and Tl in extracted fractions in rhizospheric soils.

Samples	pH	SOM [a] (g/kg)	CEC [b] (cmol/kg)	Fe (g/kg)	Mn (mg/kg)	Tl_{Total} (mg/kg)	Tl in sequential fractions (mg/kg)					Recovery [c] (%)
							Water soluble	Weak acid soluble	Reducible	Oxidizable	Residual	
Soils at mining site												
S101	5.1	99	23	43.8	987	71	0.04	0.18	1.47	1.82	64.6	97
S102	5.4	101	21	40.8	268	87.5	0.14	0.82	3.95	3.53	78.7	100
S103	5.1	65	33	42.4	3276	37.4	0.06	0.76	11.8	1	22.6	97
S104	5.5	109	20	31.7	3781	80.9	0.08	1.03	14.4	1.62	58	93
S105	6.3	119	18	42.3	280	109	0.12	0.81	2.23	3.33	102	100
S106	5.8	76	22	114	685	42.4	0.04	0.41	1.59	0.72	40.4	102
Alluvial soils												
S201	5.1	54	27	54.4	1110	7.6	0.08	0.61	1.34	0.47	6.36	117
S202	4.9	76	20	40.4	267	7.9	0.05	0.32	1.1	0.28	6.74	108
S203	5.0	63	27	50.3	399	1.5	0.01	0.06	0.3	0.06	1.3	116
S204	5.8	146	20	47.5	726	41.1	0.11	0.6	3.2	1.63	37.3	104
S205	6.5	72	34	62.6	987	42.2	0.07	0.66	5.92	1.01	30.8	91
S206	5.8	77	25	52.5	881	36.5	0.07	0.55	3.24	1.58	29.9	97
S207	5.9	59	24	63.5	1236	15.4	0.06	0.68	1.74	0.55	14.5	114
S208	5.7	76	25	46.4	578	28.4	0.16	0.85	2.46	1.26	23.8	100
S209	5.8	62	32	43.9	597	13.3	0.03	0.26	1.65	0.57	10.5	98
Undisturbed natural soils												
S301	5.7	112	25	50	1038	25	0.01	0.54	1.27	1.07	23.4	105
S302	7.0	113	30	50.5	1078	19.6	0.04	0.26	1.2	0.69	18.7	107
S303	7.0	50	29	45.6	2005	2	0.01	0.05	0.2	0.09	1.6	97
S304	7.3	113	22	58.7	959	26.2	0.11	1.3	3.34	1.11	23.8	113

[a] SOM: soil organic materials.
[b] CEC: cation exchange capacity.
[c] Recovery = [($Tl_{Water\ soluble}$ + $Tl_{Weak\ acid\ soluble}$ + $Tl_{Reducible}$ + $Tl_{Oxidizable}$ + $Tl_{Residual}$)/Tl_{Total}]∗100.

Table 3
Concentrations of Tl in green cabbage (unit in mg/kg, dry materials) and the biomass (g, dry materials) of each plant part of green cabbage.

Samples	Roots	Stems	Young leaves	Old leaves	Whole plant
In soils of mining sites					
B101	12.1 (11) [a]	12.7 (19.2)	12.6 (40.7)	90.9 (30)	35.9 (100.9)
B102	33.2 (5.4)	38.1 (11.2)	658 (20.9)	1503 (23.8)	818 (61.3)
B103	15.9 (9.8)	15.9 (9.5)	51.8 (10.1)	164 (38.3)	105 (67.7)
B104	33.3 (8.9)	10.7 (28.4)	9.8 (37.9)	77.6 (38.5)	34.8 (113.7)
B105	7.7 (19.6)	7.9 (24.3)	5.9 (52)	76.3 (52.1)	31.3 (148)
B106	21 (10.6)	16.4 (18.4)	5.5 (41.6)	58 (55.1)	31.4 (125.7)
In alluvial soils					
B201	12.4 (8.7)	16.4 (13.6)	39.6 (41.1)	48 (51.2)	38.5 (114.5)
B202	7.5 (5.2)	7.7 (17.2)	3.2 (35.8)	32.1 (57.6)	18.4 (115.8)
B203	2.1 (13.4)	2.8 (21.7)	5.3 (33.5)	37.9 (43.7)	17.1 (112.3)
B204	20.7 (11.6)	14.1 (14.4)	45.5 (28.4)	422 (36.1)	188 (90.4)
B205	71.1 (13.3)	36 (19.3)	84.5 (25)	818 (45.5)	397 (103.1)
B206	55.9 (14.5)	31.9 (27.1)	25.1 (38.4)	228 (50.6)	108 (130.5)
B207	29.6 (12)	17.3 (23.1)	33.1 (27.6)	115 (45.2)	63.6 (107.9)
B208	10.6 (11.6)	15.1 (12)	55.8 (39.1)	534 (35.5)	219 (98.1)
B209	49.4 (9.6)	39.4 (10.5)	41.6 (40)	231 (45.7)	124 (105.8)
In undisturbed natural soils					
B301	4 (7.2)	3.6 (17)	4.6 (23.1)	23.3 (31.2)	11.8 (78.4)
B302	3.1 (8.9)	1.5 (21.4)	1.6 (29.3)	6.1 (47.8)	3.7 (107.4)
B303	0.8 (8.7)	1 (11)	2.4 (21.2)	48 (32.5)	22.2 (73.3)
B304	4.3 (9.6)	2.8 (11.9)	4.1 (28.6)	13.5 (41.7)	8.2 (91.8)

[a] Numbers in parentheses represent the biomass of plants (g, dry materials).

evaluate the ability of the plant to accumulate the element. The corrected bioconcentration factor (corrected-BF) of Tl by green cabbage is defined in this study using the following equation:

$$corrected-BF = \frac{Tl\ in\ each\ plant \times M\ (yield\ of\ each\ green\ cabbage\ biomass)}{Tl\ in\ soils \times M\ (average\ yield\ of\ green\ cabbage\ biomass)}.$$

We observed that the biomass of B105 was 2.4 fold of B102, but the concentration of Tl in B102 was 25 fold higher than that in B105 (Table 3). Biological dilution can be eliminated by corrected-BF. The

TC, BF and corrected-BF values for green cabbage in the study area are summarized in Table 4. Higher TC values (>1) were observed in the old leaves, far in excess of those observed in the young leaves and stems. The average value of TC was 0.9 in stems, which implied that stems, which are full of xylems and transmission catheters, were the transport channels for Tl from roots to leaves. The average value of TC in the young leaves was 2.4, indicating high mobility of Tl from roots to leaves. It is interesting to observe that larger amounts of Tl transferred to old leaves, compared to young leaves exhibiting higher TC values. This suggested that the transfer and accumulation of Tl in leaves of green cabbage increased over time.

Similarly, green cabbage showed higher BF and corrected-BF values in leaves compared with roots or stems, with the highest BF and corrected-BF values observed in old leaves. This suggested that the leaves are the major storage sites for Tl and that the accumulation of Tl in leaves increased over time. Most of the BF and corrected-BF values for whole green cabbage were greater than 1, indicating that green cabbage has a strong propensity to accumulate Tl from rhizospheric soils. The BF values were lower than those (maximum at 35, edible part) determined by LaCoste et al. (2001), which may be contribute to stronger toxic effects of Tl at higher concentrations.

3.2. Geochemical fractionation of Tl in rhizospheric soils

The geochemical fractionation of Tl in rhizospheric soils, determined by sequential extraction, was quantified in terms of concentration (Table 2). Tl concentrations in the water soluble fractions were low, within the range of 0.01–0.16 mg/kg in the rhizospheric soils, and averaged at 0.2% of the total Tl. Concentrations from 0.05 to 1.3 mg/kg were found in weak acid extracted fraction, and averaged 1.6% of the total Tl. Comparatively, Tl was found to present higher proportions in the reducible fraction (9%) and the oxidizable fraction (3%), respectively. The presence of Tl in the reducible fraction suggested its potential association with easily and moderately reducible iron and manganese oxide in soils. In the study area, the weathering process of the Tl-rich sulfide minerals may produce increasing amounts of iron and manganese oxide that contributed to higher Tl release into

Table 4
Transfer coefficient (TC), bioconcentration factor (BF) and corrected-BF for green cabbage.

Samples	Transfer coefficient (TC) [a]			Bioconcentration factor (BF) [b]					Corrected-BF [c]
	Stems	Young leaves	Old leaves	Roots	Stems	Young leaves	Old leaves	Plants	
In soils of mining sites									
B101	1.1	1	7.5	0.2	0.2	0.2	1.3	0.5	0.5
B102	1.2	20	45	0.4	0.4	7.5	17	9.3	5.6
B103	1	3.3	10	0.4	0.4	1.4	4.4	2.8	1.9
B104	0.3	0.3	2.3	0.4	0.1	0.1	1	0.4	0.5
B105	1	0.8	9.9	0.07	0.1	0.1	0.7	0.3	0.4
B106	0.8	0.3	2.8	0.5	0.4	0.1	1.4	0.7	0.9
In alluvial soils									
B201	1.3	3.2	3.9	1.6	2.2	5.2	6.3	5.1	5.7
B202	1	0.4	4.3	1	1	0.4	4.1	2.3	2.6
B203	1.3	2.5	18	1.4	1.9	3.5	25	11	13
B204	0.7	2.2	20	0.5	0.3	1.1	10	4.6	4
B205	0.5	1.2	12	1.7	0.9	2	19	9.4	9.5
B206	0.6	0.5	4.1	1.5	0.9	0.7	6.3	3	3.8
B207	0.6	1.1	3.9	1.9	1.1	2.2	7.5	4.1	4.4
B208	1.4	5.3	50	0.4	0.5	2	19	7.7	7.4
B209	0.8	0.8	4.7	3.7	3	3.1	17	9.3	9.6
In undisturbed natural soils									
B301	0.9	1.2	5.8	0.2	0.1	0.2	0.9	0.5	0.4
B302	0.5	0.5	2	0.2	0.1	0.1	0.3	0.2	0.2
B303	1.3	3	60	0.4	0.5	1.2	24	11	7.9
B304	0.7	1	3.1	0.2	0.1	0.2	0.5	0.3	0.3

[a] TC = concentration of Tl in aboveground of plants / concentration of Tl in root of plants.
[b] BF = concentration of Tl in each plant part / concentration of Tl in soils.
[c] Corrected-BF = concentration of Tl in each plant*M (yield of each green cabbage biomass) / concentration of Tl in soils / M (average yield of green cabbage biomass).

the reducible fraction (Xiao et al., 2004a). It is interesting to observe a significantly positive correlation between total Mn in rhizospheric soils and Tl in the reducible fraction ($r = 0.79$, $p < 0.01$) (Fig. 2a), but no similar correlation was observed for Fe versus Tl. This may be attributed to increasing enrichment of Tl in Mn nodules as a result of Tl^+ oxidation to Tl^{3+} at the δ-MnO_2 interface (Bidoglio et al., 1993). The presence of Tl in the oxidizable fraction suggested an association with the SOM and sulfides. A significantly positive correlation between SOM in the rhizospheric soils and Tl in the oxidizable fraction ($r = 0.66$, $p < 0.01$) (Fig. 2b) was observed, and reflected the likelihood that Tl in the oxidizable fraction was bound with SOM. The local soils are characterized by high concentrations of sulfur (0.1–3%) that are attributed to the abundance of local sulfide minerals (Xiao et al., 2004a). The majority of Tl (62–95% of total Tl) was found predominantly in the residual fraction. The local soils show very similar mineralogical compositions in all soil types, characterized by the clay mineralogy composed of quartz, kaolinite, illite and goethite (Xiao et al., 2004a). Thus, the majority presence of Tl in the residual fraction indicated that Tl was mainly bound in silicate minerals, from which the release of Tl is unlikely under surface of environmental conditions.

3.3. Factors influencing accumulation of Tl in green cabbage

The enrichment of Tl in green cabbage is generally related to Tl concentrations in rhizospheric soils, and is more closely related to the alluvial soils. Significantly positive correlation was observed between Tl concentrations in green cabbage and in the alluvial rhizospheric soils along the stream bank ($r = 0.87$, $p < 0.01$) (Fig. 3a). This can likely be attributed to Tl concentrations in the water and weak acid soluble fractions, which are more exchangeable and bioavailable. The enrichment of Tl in green cabbage positively correlated

Fig. 2. Correlations between the reducible fraction of Tl and Mn and between the oxidizable fraction of Tl and SOM in rhizospheric soils.

with Tl concentrations in the water and weak acid soluble fractions Tl in the alluvial rhizospheric soil ($r = 0.64$, $p < 0.05$) (Fig. 3b), but no similar correlations were observed for the disturbed soils in the mining sites and the undisturbed natural soils (Fig. 3c). The alluvial soils along the stream bank originated from washed materials derived from upstream Tl-rich sulfide mine debris and rocks, and displayed more fine particles (Xiao et al., 2004a). In addition, the alluvial soils at the study site were observed to have higher moisture content in general. These two factors likely contributed to higher proportions of Tl in the water and weak acid soluble fractions of the alluvial rhizospheric soils.

Water contents in the rhizospheric soils may also contribute to the accumulation of Tl in green cabbage. Comparing the 3 groups of soil samples, Tl concentrations in the alluvial soils were lower than those in soils of the mining sites, but they contributed to higher BF and corrected-BF in green cabbages (Table 4). In the study area, the alluvial soils along the local stream bank (include S102, S103 at mining site) exhibited lower groundwater levels (0.5 m below surface) and higher water content, which may facilitate mobility of Tl in soils and transfer to green cabbage. A significantly positive correlation was observed between Tl concentrations in green cabbage and in the alluvial rhizospheric soils along the stream bank (include S102, S103 at mining site) ($r = 0.91$, $p < 0.01$) (Fig. 3d). Similar findings by Pascual et al. (2004) suggest that transfer of some metals from soil to plant is reduced under dry conditions. In addition, transport of metals from the external solution into the plant cell walls is basically a non-metabolic, passive process, driven by diffusion or mass flow (Epstein, 1972). This process is facilitated by water fluxes in the soil–plant continuum, which are ultimately caused by loss of water to the atmosphere via transpiration. With low soil water content, the above process was limited and caused low corrected-BF values for green cabbage.

The soil pH and SOM appear to be the major factors that control the solubility, mobility and transport of trace elements (Carrillo-Gonzalez et al., 2006). The concentration of soluble Tl revealed a decrease with the increase of pH, which were 8.0, 2.0 and <0.15 mg/kg at soil pH of 1–2, 3–4 and 6–7, respectively (Zhou and Liu, 1985). In this study, the lower corrected-BF values seemed to correspond to higher pH in the rhizospheric soils (Tables 2 and 4), which indicated that weak mobility Tl in the soils and low Tl uptake by green cabbages were the result of high pH in the rhizospheric soils. This may be attributed to soil colloids with higher pH that increase the negative charge and decrease the mobilization of Tl (Vanek et al., 2010b). Soil pH may also affect the solubility of SOM (Lebourg et al., 1998; Appel and Ma, 2002), and higher pH may improve the solubility of SOM, resulting in the adsorption of metals onto soils (Catlett et al., 2002). In this study, the samples of S302 and S303 exhibited the same pH (7.0), but the corrected-BF value for B303 was approximately 40 times higher than that for B302. This was likely due to higher SOM content at S302 (113 g/kg) resulting in increased adsorption and retention of Tl within soils, and consequently, reduced transfer to the plants. A similar conclusion was reached by Jacobson et al. (2005). For those alluvial soils with similar pH, higher CEC values seemed to facilitate the accumulation of Tl in green cabbage (Tables 2–4).

4. Conclusions

This study revealed the capacity of Tl transfer at the interface of soil and green cabbage. The distribution pattern of Tl concentration in green cabbage followed a descending order of old leaves > fresh leaves > stems ≈ roots. The stems functioned as a channel for Tl transportation to the leaves, and the leaves were the major storage site (greater than 80%) for Tl. In the rhizospheric soils, the majority of Tl was observed in the residual fraction bound to silicate minerals, while the majority of the labile Tl was located in the reducible fraction in which manganese oxide played important roles. SOM was evaluated as the dominant phase responsible for the retention of Tl bound to
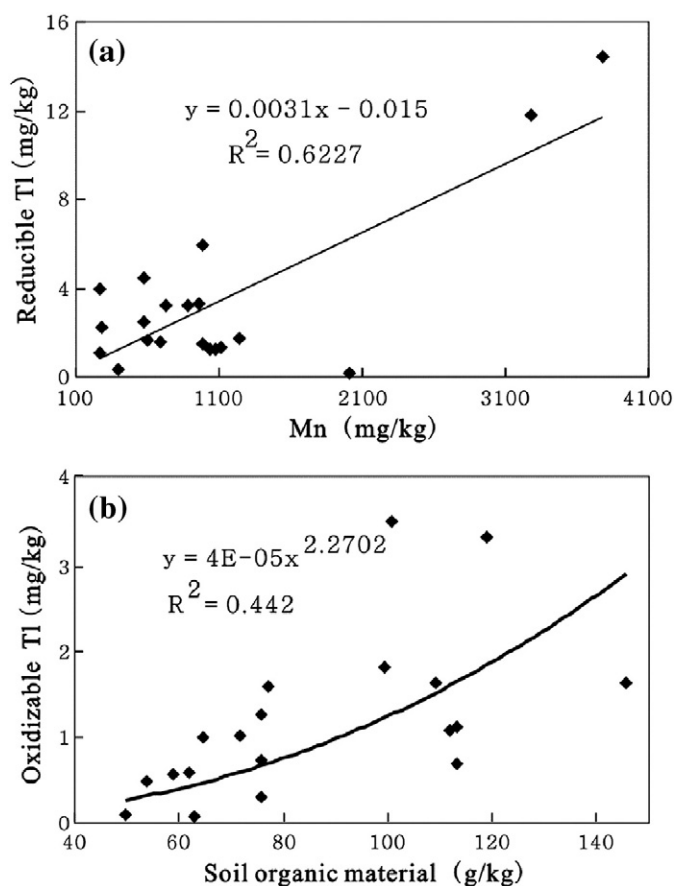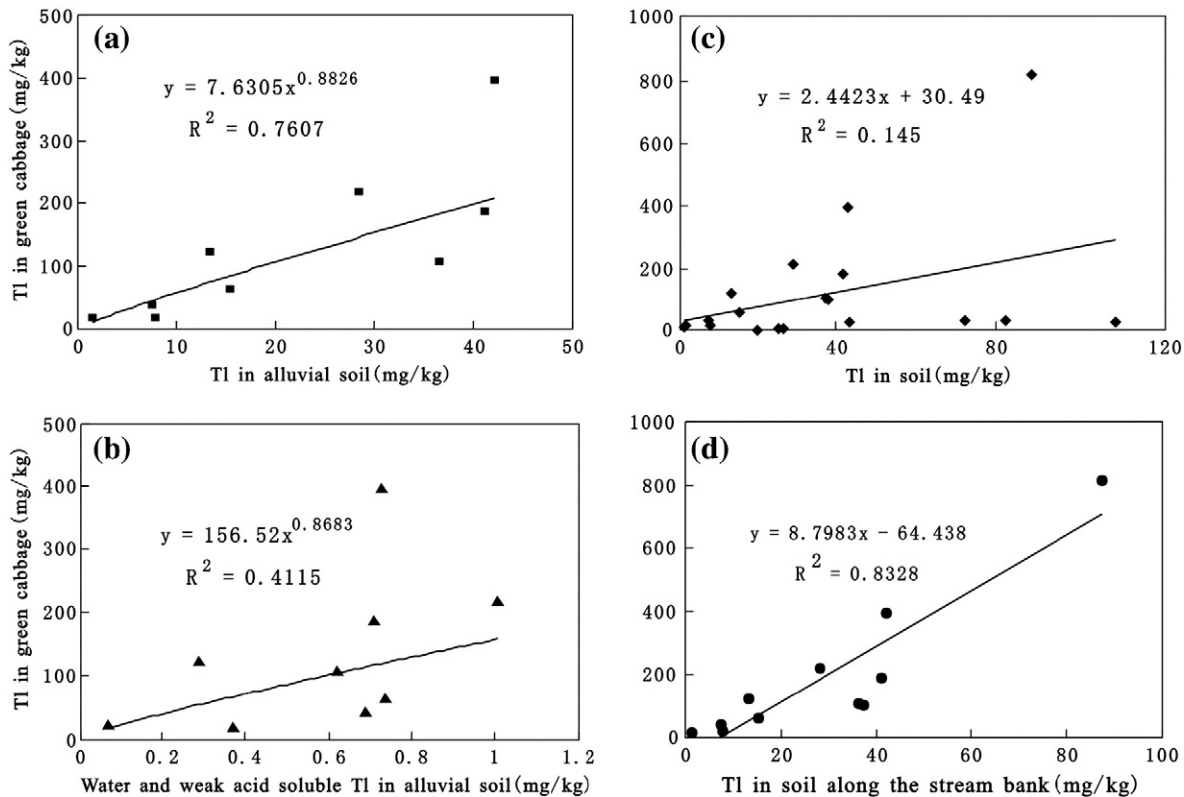
Fig. 3. Correlations between Tl in green cabbage and in different Tl fractions in rhizospheric soils.

the oxidizable fraction. The water and weak acid soluble fraction of Tl was low. The enrichment of Tl in green cabbage was controlled by both Tl concentrations and the mobility of Tl in rhizospheric soils, and the mobility of Tl was affected by water content, pH, SOM and CEC in rhizospheric soils.

Conflict of interest statement

None.

Acknowledgments

References

Al-Najar H, Schulz R, Romheld V. Plant availability of thallium in the rhizosphere of hyperaccumulator plants: a key factor for assessment of phytoextraction. Plant Soil 2003;249:97–105.

Al-Najar H, Kaschl A, Schulz R, Romheld V. Effect of thallium fractions in the soil and pollution origins on Tl uptake by hyperaccumulator plants: a key factor for the assessment of phytoextraction. Int J Phytoremediation 2005;7:55–67.

Appel C, Ma L. Concentration, pH, and surface charge effects on cadmium and lead sorption in three tropical soils. J Environ Qual 2002;31:581–9.

Bidoglio G, Gibson PN, Ogorman M, Roberts KJ. X-ray-absorption spectroscopy investigation of surface redox transformations of thallium and chromium on colloidal mineral oxides. Geochim Cosmochim Acta 1993;57:2389–94.

Carrillo-Gonzalez R, Simunek J, Sauve S, Adriano D. Mechanisms and pathways of trace element mobility in soils. Adv Agron 2006;91:111–78.

Catlett KM, Heil DM, Lindsay WL, Ebinger MH. Soil chemical properties controlling zinc activity in 18 Colorado soils. Soil Sci Soc Am J 2002;66:1182–9.

CCME (Canadian Council of Ministers of the Environment). Summary of existing Canadian environmental quality guidelines. Available from: http://www.ccme.ca/assets/pdf/e1_062.pdf 2003.

Epstein E. Mineral nutrition of plants: principles and perspectives. New York: John Willey & Sons Inc.; 1972.

Fergusson JE. The heavy elements: chemistry, environmental impact and health effects. Oxford: Pergamon Press; 1990 (614 pp.).

Jacobson AR, McBride MB, Baveye P, Steenhuis TS. Environmental factors determining the trace-level sorption of silver and thallium to soils. Sci Total Environ 2005;345:191–205.

Jakubowska M, Pasieczna A, Zembrzuski W, Swit Z, Lukaszewski Z. Thallium in fractions of soil formed on floodplain terraces. Chemosphere 2007;66:611–8.

Kazantzis G. Thallium in the environment and health effects. Environ Geochem Health 2000;22:275–80.

Keith LH, Telliard W. Priority pollutants. I. A perspective view. Environ Sci Technol 1979;13:416–23.

LaCoste C, Robinson B, Brooks R. Uptake of thallium by vegetables: its significance for human health, phytoremediation, and phytomining. J Plant Nutr 2001;24:1205–15.

Lebourg A, Sterckeman T, Ciesielski H, Proix N. Trace metal speciation in three unbuffered salt solutions used to assess their bioavailability in soil. J Environ Qual 1998;27:584–90.

Li XD, Wang WX, Zhu YG. Trace metal pollution in China. Sci Total Environ 2012;421:1–2.

Lis J, Pasieczna A, Karbowska B, Zembrzuski W, Lukaszewski Z. Thallium in soils and stream sediments of a Zn–Pb mining and smelting area. Environ Sci Technol 2003;37:4569–72.

Pascual I, Antolin MC, Garcia C, Polo A, Sanchez-Diaz M. Plant availability of heavy metals in a soil amended with a high dose of sewage sludge under drought conditions. Biol Fertil Soils 2004;40:291–9.

Pavlickova J, Zbiral J, Smatanova M, Houserova P, Cizmarova E, Havlikova S, et al. Uptake of thallium from artificially and naturally contaminated soils into rape (*Brassica napus* L.). J Agric Food Chem 2005;53:2867–71.

Peter ALJ, Viraraghavan T. Thallium: a review of public health and environmental concerns. Environ Int 2005;31:493–501.

Qi WQ, Chen YL, Cao JS. Indium and thallium background contents in soils in China. Int J Environ Stud 1992;40:311–5.

Qi L, Hu JD, Conrad G. Determination of trace elements in granites by inductively coupled plasma mass spectrometry. Talanta 2000;51:507–13.

Rauret G, Lopez-Sanchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A, et al. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. J Environ Monit 1999;1:57–61.

Repetto G, del Peso A, Repetto M. Human thallium toxicity. In: Nriagu JO, editor. Thallium in the environment. New York: John Wiley & Sons, Inc.; 1998. p. 167–99.

Tremel A, Masson P, Sterckeman T, Baize D, Mench M. Thallium in French agrosystem. I. Thallium contents in arable soils. Environ Pollut 1997a;95:293–302.

Tremel A, Masson P, Garraud H, Donard OFX, Baize D, Mench M. Thallium in French agrosystems. II. Concentration of thallium in field-grown rape and some other plant species. Environ Pollut 1997b;97:161–8.

Vanek A, Komarek M, Chrastny V, Becka D, Mihaljevic M, Sebek O, et al. Thallium uptake by white mustard (*Sinapis alba* L.) grown on moderately contaminated soils—agro-environmental implications. J Hazard Mater 2010a;182:303–8.

Vanek A, Chrastny V, Komarek M, Galuskova I, Drahota P, Grygar T, et al. Thallium dynamics in contrasting light sandy soils—soil vulnerability assessment to anthropogenic contamination. J Hazard Mater 2010b;173:717–23.

Wenzel WW. Rhizosphere processes and management in plant-assisted bioremediation (phytoremediation) of soils. Plant Soil 2009;321:385–408.

WHO/IPCS (World Health Organization/International Program on Chemical Safety). Thallium. Environmental health criteria, 182. Geneva: World Health Organization; 1996.

Xiao TF, Boyle D, Guha J, Rouleau A, Hong YT, Zheng BS. Groundwater-related thallium transfer processes and their impacts on the ecosystem: southwest Guizhou Province, China. Appl Geochem 2003;18:675–91.

Xiao TF, Guha J, Boyle D, Liu CQ, Chen JA. Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China. Sci Total Environ 2004a;318:223–44.

Xiao TF, Guha J, Boyle D. High thallium content in rocks associated with Au–As–Hg–Tl and coal mineralization and its adverse environmental potential in SW Guizhou, China. Geochem Explor Environ Anal 2004b;4:243–52.

Xiao TF, Guha J, Boyle D, Liu CQ, Zheng BS, Wilson G, et al. Naturally occurring thallium: a hidden geoenvironmental health hazard? Environ Int 2004c;30:501–7.

Xiao TF, Guha J, Liu CQ, Zheng BS, Wilson G, Ning ZP, et al. Potential health risk in areas of high natural concentrations of thallium and importance of urine screening. Appl Geochem 2007;22:919–29.

Xiao TF, Yang F, Li SH, Zheng BS, Ning ZP. Thallium pollution in China: a geo-environmental perspective. Sci Total Environ 2012;421:51–8.

Yang CX, Chen YH, Peng P, Li C, Chang XY, Xie CS. Distribution of natural and anthropogenic thallium in the soils in an industrial pyrite slag disposing area. Sci Total Environ 2005;341:159–72.

Zhou DX, Liu DN. Chronic thallium poisoning in a rural area of guizhou province, China. J Environ Health 1985;48:14–8.

Zitko V. Toxicity and pollution potential of thallium. Sci Total Environ 1975;4:185–92.