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Potential health risk in areas of high natural concentrations of thallium and importance of urine screening

Tangfu Xiao [a,b,c,*], Jayanta Guha [b], Cong-Qiang Liu [a], Baoshan Zheng [a], Graham Wilson [d], Zengping Ning [a,e], Libin He [a,e]

[a] *State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[b] *Sciences de la Terre, Université du Québec à Chicoutimi, Québec, Canada G7H 2B1*
[c] *State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China*
[d] *Turnstone Geological Services Limited, P.O. Box 130, Station "B", Toronto, Canada M5T 2T3*
[e] *Graduate University of Chinese Academy of Sciences, Beijing 100039, China*

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Abstract

There is a lack of information in the literature regarding Tl exposure from naturally occurring Tl enrichment. This paper draws attention to the potential health risk posed by high concentrations of naturally occurring Tl in the environment. The inhabitants of a rural area in SW Guizhou Province, China, reside within a natural Tl accumulated environment resulting from Tl-rich sulfide mineralization, and they face ongoing severe Tl exposure. High Tl concentrations were detected in urine of the local residents. Urinary Tl concentrations are as high as 2668 μg/L, with most subjects surpassing the accepted world urinary Tl concentration at <1 μg/L for "non-exposed" humans. The urinary Tl concentrations show significant differences among three communities ($n = 21$, $p = 0.001$), but no significant difference in either sex or age groups ($n = 21$, $p = 0.7806$). However, there is a positive statistical relationship between the extent of Tl exposure from Tl concentrations in soil and crops in the immediate environment and the concentrations of Tl detected in urine. A majority of the volunteer subjects from the communities have urinary Tl concentrations above 4.5–6 μg/L, implying early adverse health effects, and some of them have over 500 μg/L urinary Tl, considered to be at/about the level of clinical intoxication. This study has been able to identify that the elevated urinary Tl concentrations are mainly attributable to Tl accumulation in locally grown vegetables, which acquire Tl from the soil. This study also shows that Tl in urine of the local population represents a steady-state condition with long-term exposure, and that urinary Tl concentrations can be taken as a bio-marker of total dose based upon total daily dietary intake. This study demonstrates that natural sources of elevated Tl pose a potential health risk to the population, and that monitoring the urinary Tl concentration is a reliable and accurate way of bio-marking Tl exposure.

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1. Introduction

Thallium is one of the 13 priority metal pollutants (Keith and Telliard, 1979). The triad of

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[*] Corresponding author. Address: State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China. Fax: +86 851 5895318.
E-mail address: xiaotangfu@vip.gyig.ac.cn (T. Xiao).

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gastroenteritis, polyneuropathy and alopecia is regarded as the classic syndrome of Tl poisoning (Liu, 1983; Feldman and Levisohn, 1993; Tabandeh et al., 1994; WHO/IPCS, 1996). Since its discovery in 1861, it has been employed as a rodenticide and also for depilatory and homicidal purposes (Smith and Carson, 1977), but it is now mainly used in the industrial fields of semiconductor, superconductivity, optical glass and alloys. Thallium poisoning used to be largely attributed to industrial occupational hazards such as coal burning and smelting (Smith and Carson, 1977; Brockhaus et al., 1981; Wells, 2001), but less attention has been paid to evidence of naturally occurring enrichment of Tl, a potential cause of serious health effects.

Although, Tl is typically present at low concentrations, generally 0.7 mg/kg in the Earth's crust on average (Taylor and McLennan, 1985), 0.01–3 mg/kg in soil (Fergusson, 1990), 0.001–0.25 μg/L in water (Banks et al., 1995), and 0.03–0.3 mg/kg in food crops (Kabata-Pendias and Pendias, 1992), occurrence of Tl in ore deposits may result in high concentrations in the surface environment via natural weathering and/or mining activity. For example, the total amount of Tl contained in Zn resources is about 17×10^6 kg with 630×10^6 kg in the world coal resources (USGS, 2006a). World annual production of Tl in terms of byproduct metal recovered from smelting of Cu, Zn and Pb ores is about 15 tons in recent years (USGS, 2006b). Utilization of Tl-bearing sulfide minerals may release Tl into the surface environment.

In a rural area at Lanmuchang (LMC) in southwestern Guizhou Province, China, naturally occurring Tl in soil deriving from sulfide mineralization poses a potential health risk to the local population. Many of the local adult population have suffered from Tl poisoning in the past four decades. Symptoms related to thallotoxicosis, such as weakness, muscle and joint pain, disturbance of vision and hair loss, were detected in the 1960s and 1970s with 189 cases of Tl poisoning (Liu, 1983; Zhou and Liu, 1985).

The early investigations determined elevated Tl concentrations in drinking water (3.7–40 μg/L) (APASSGP and EGLIGCAS, 1974; Zhou and Liu, 1985), which was considered a major source of local chronic Tl poisoning in the 1960s and 1970s. In addition, the study of Zhou and Liu (1985) determined high Tl concentrations in cabbage grown in the local garden soil with low pH values (3.5–4.5), which presented the other source of Tl intoxication through consumption of Tl-rich cabbage. Zhou and Liu (1985) further pointed out that liming of local garden soils to raise pH to 7.5–9.0 resulted in no cases of thallotoxicosis in the subsequent 6 years of monitoring after 1977. The local community started to use Tl-free drinking water piped from outside the area in the 1990s (Xiao et al., 2003).

However, symptoms of chronic Tl intoxication including hair loss, muscle and joint pains and reduced vision still occurred amongst some of the population during the field investigation of 1998–2003. It was also found that the local garden soils still have low pH values from 3.2 to 4.5, and that the locally planted vegetables were still rich in Tl and were the main food crops consumed by the local communities (Xiao et al., 2004a). This implied that the local population was dangerously ignorant of Tl exposure in their living environment.

The presence of Tl in the locally produced food crops and the occurrence of symptoms of Tl intoxication led to the hypothesis that the local population is still subjected to high exposure of Tl and that their dietary habit may contribute to the adverse health effects. This study aims to address: (1) the concentrations of Tl in urine and its distribution pattern within the local communities, (2) factors controlling urinary Tl concentrations, and (3) the reliability of urine as a bio-marker for identifying chronic Tl exposure.

2. Methods

2.1. Study area

The study area is centered on LMC where naturally high Tl concentrations occur in soil. The source of Tl is associated with Tl–Hg–As sulfide mineralization centered around this area (Fig. 1). Details of the local geology and mineralization of the LMC Hg–Tl–As mineralized area were described by Xiao et al. (2003, 2004b). A brief description of the geological setting will suffice as a prelude to this paper. The study area is made up of sedimentary rocks of Permian and Triassic ages, overlain by Quaternary alluvium. The exposed rocks include the Longtan Formation (P_2l: limestone, argillite and coal seams), the Changxing Formation (P_2c: limestone), the Dalong Formation (P_2d: arkosic shale) and the Yelang Formation (T_1y: siltstone, argillite and limestone). Thallium occurs in the minerals lorandite ($TlAsS_2$), christite ($TlHgAsS_3$), imho-

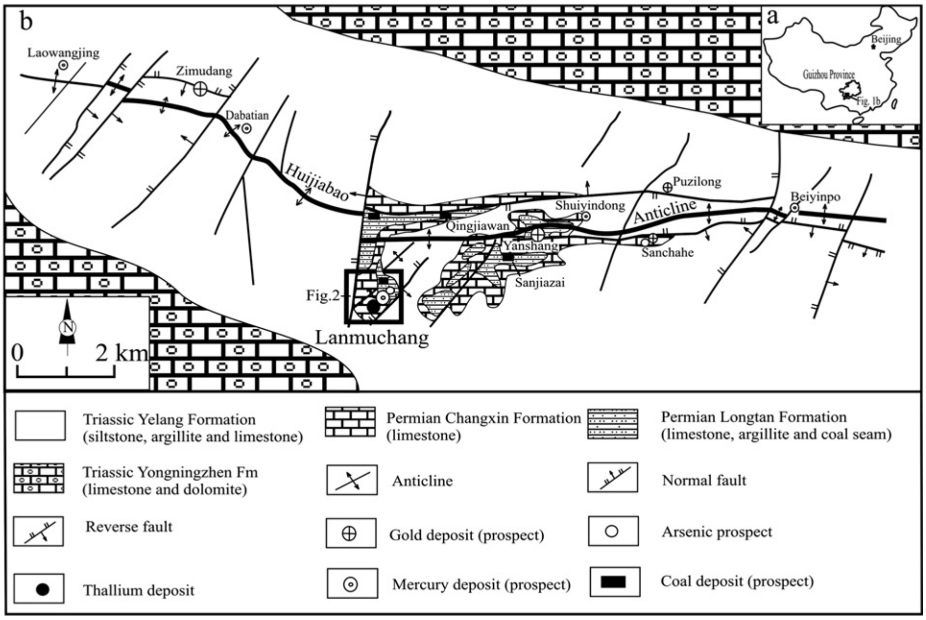

Fig. 1. Regional geological sketch map showing sulfide mineralization in the study area.

fite ($Tl_6CuAs_{16}S_{40}$), raguinite ($TlFeS_2$) and lanmuchangite ($TlAl(SO_4)_2 \cdot 12H_2O$) (Chen, 1989a; Li et al., 1989; Li, 1996; Chen et al., 2001). Other sulfide minerals such as cinnabar, realgar, orpiment, arsenopyrite and pyrite are also rich in Tl (Chen, 1989b; Li, 1996; Xiao et al., 2004b). This area has a long mining history (about 350 a) for Hg and coal, and was worked for Tl in the 1990s. Thallium is also present in coals. Sporadic artisanal mining of the coal seams has been undertaken by local residents to augment their supply of coal for heating. The Tl mineralization outcrops are located in the hills where it is susceptible to weathering and dispersion by natural processes (Fig. 2).

LMC is a small town with approximately 1000 residents, where pockets of poverty persist. The local population is permanent and year-round residents inhabit villages A, B and C, within the small watershed of the Qingshui Stream (Fig. 2). Their daily staples are composed of rice, corn and vegetables. Rice is mainly commercially supplied from market, but corn and vegetables are locally produced. Volunteers for the study group were recruited mainly from villages A, B and C, plus a small number of subjects from control areas, i.e. the background area and the provincial capital city of Guiyang (Fig. 2). The volunteers were selected randomly from the LMC exposed area and non-exposed control areas, but in general the selection covers all parts of the three villages of LMC. An exception to this was a particularly poor family, whose members showed evident symptoms of Tl intoxication and all of them were involved with the volunteer group.

2.2. Sampling and analysis

Four urine samples (three samples from Village A and one sample from Village B) were collected in December 2002 for a preliminary urinary Tl screening, and a follow-up suite of 21 morning urine samples ($n = 8$ at Village A, $n = 7$ at Village B, $n = 6$ at Village C) were collected from the three communities in May 2003. In May 2003, three samples from an area devoid of the presence of Tl mineralization were taken as background samples and four samples were collected from the capital city of Guiyang. The sampling sites are shown in Fig. 2.

During field sampling, a detailed questionnaire was employed to collect data on age, sex, dietary and behavioral habits of each participant. The volunteers were also adequately informed of the aims, methods and anticipated benefits of the study. Informed consent was obtained from all study participants prior to the collection of urine samples.

The urine samples were sealed in pre-cleaned 60 mL Nalgene® bottles. A field duplicate was collected at every 6th site. The specimens were stored in coolers at −20 °C in both the field and the laboratory, and were analyzed within two-weeks of

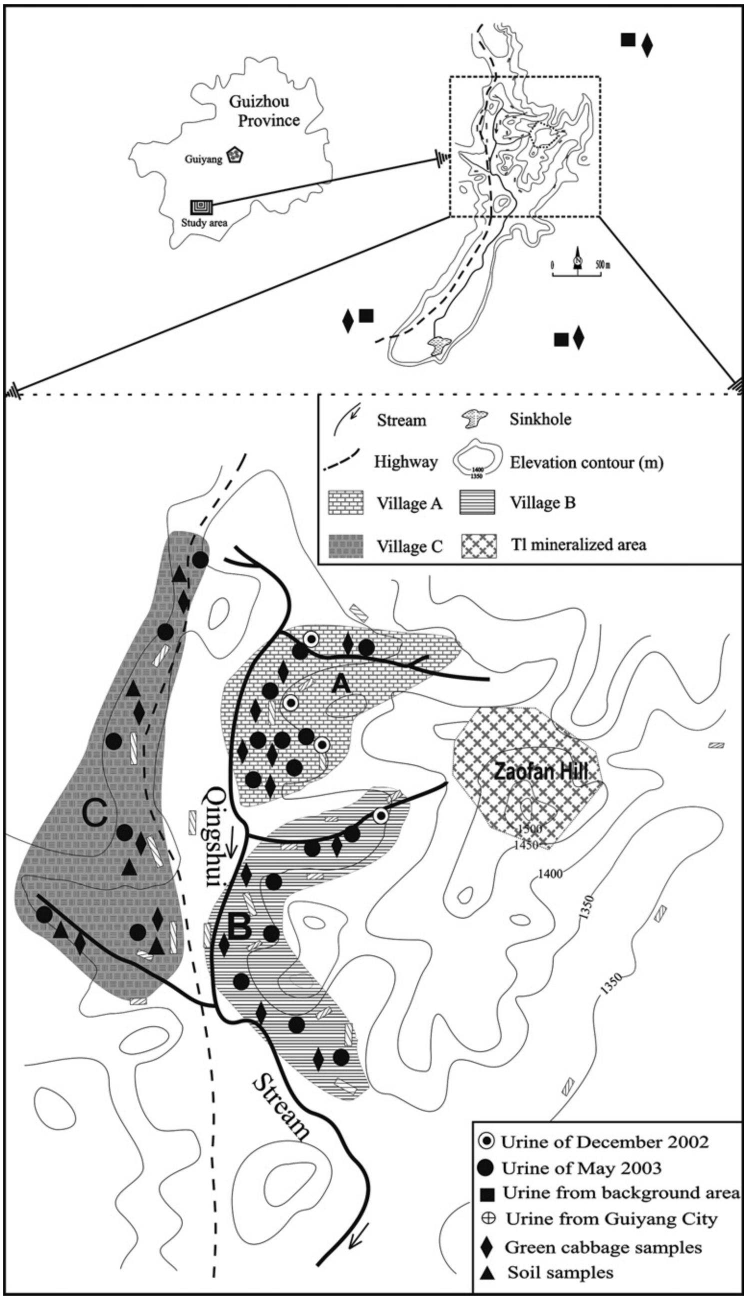

Fig. 2. Map showing the study area and sampling sites of urine and environmental subjects.

collection. A 1 mL urine sample was diluted quantitatively (1:9 v/v) to 10 mL with Millipore superpure water, and the 10 mL diluted solution was further spiked with internal standard (0.2 ml Rh solution) and analyzed for Tl by inductively coupled plasma-mass spectrometry (ICP-MS) using a Finnigan MAT instrument at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang. The detection limit for Tl is 0.05 μg/L in urine samples.

In the sampling period of May 2003, 23 green cabbage samples ($n = 6$ at Village A; $n = 5$ at Village B; $n = 5$ at Village C; $n = 4$ in background area; and $n = 3$ in Guiyang City), and five soil samples from Village C were also collected for the purpose of comparison (Fig. 2). The determination for Tl in crop and soil samples was also undertaken by ICP-MS, and the method is detailed elsewhere (Xiao et al., 2004a). The detection limit for Tl is 0.05 mg/kg. The analytical precision, determined by quality assurance/quality control procedures, using duplicates, reagent blanks, and internal standards, was better than ±10%.

2.3. Statistical analysis

The software package Analyse-it® (version 1.71, Analyse-it Software Ltd., Leeds, United Kingdom) for Windows was used for descriptive statistics, statistical tests and correlation analysis for testing the stated hypotheses that: (i) the LMC communities are significantly different from the control locations with respect to urinary Tl and that (ii) urinary Tl concentrations are principally correlated to concentrations of Tl in soil and crops. The data was evaluated using non-parametric equations because of the small sample size and non-normal distribution of the data. Mann–Whitney tests were used for two-way comparisons and the Kruskal–Wallis test was used for analyses involving more than two groups. To test the alternate hypothesis that villages A, B, C and control locations were significantly different, the Mann–Whitney and Kruskal–Wallis tests were used for Tl in urine, soil and crop.

3. Results

The analytical results for Tl in urine samples from the preliminary test of December 2002 are listed in Table 1. High Tl concentrations, from 39.55 to 277.6 μg/L in three urine samples from Village A and 78.9 μg/L Tl in one sample from Village B, were recorded. This led to follow-up sampling extending from villages A and B to village C to control locations for a larger number ($n = 28$) of urinary Tl determinations, and the analytical results are reported in Table 2.

Table 1
Thallium concentrations in urine samples of December 2002

Samples	Sex	Age	Tl (μg/L)
Village A			
UR03	Male	58	277.6
UR04	Male	6	39.55
UR05	Female	9	195.9 (184.7)
Village B			
UR06	Male	28	78.9 (70.0)

Figures in bracket refer to concentrations of duplicate samples.

The results in Tables 1 and 2 show that Tl occurs at high concentrations in urine of the local inhabitants of LMC, ranging from 2.50 to 2668 μg/L ($n = 25$) with a mean value of 521.9 μg/L (95% CI = 203.3–840.5). The determined urinary Tl concentrations varied markedly from village to village.

In village A, located along the upstream course of the Qingshui Stream and downhill from the Tl mineralized area, Tl concentrations in urine samples range from 640.8 to 2668 μg/L (mean = 1432 μg/L, 95% CI = 767.6–2097) (Table 2). In village B, located in the mid-course area of the Qingshui Stream, Tl concentrations in urine samples range from 37.0 to 207.7 μg/L (mean = 131.9 μg/L, 95% CI = 69.2–194.6) (Table 2). In village C, located to the west of the Qingshui Stream and thus furthest removed from the Tl-mineralized area, Tl

Table 2
Thallium concentrations in urine samples of May 2003

Samples	Sex	Age	Tl (μg/L)
Village A			
UR15	Female	9	756.1
UR16	Male	58	2668
UR23	Male	40	1621 (1633)
UR24	Male	8	640.8
UR25	Male	6	2252
UR30	Female	40	1931
UR31	Female	46	936.7
UR32	Female	29	651.4 (649.2)
Village B			
UR11	Male	71	174.5
UR14	Male	48	47.6
UR20	Male	66	37.0
UR26	Male	28	207.7
UR27	Female	27	139.8
UR28	Male	8	123.6
UR29	Female	67	193.2
Village C			
UR12	Male	28	2.50
UR13	Female	69	12.1
UR17	Male	10	27.7 (25.4)
UR18	Male	8	10.8
UR19	Male	21	17.0
UR21	Female	31	4.1
Background area			
UR33	Male	51	1.05
UR34	Female	42	1.50
UR35	Female	36	1.70 (1.60)
Guiyang City			
UR07	Male	33	0.96 (0.93)
UR08	Female	46	0.728
UR09	Male	2	0.528
UR10	Female	26	0.387

Figures in bracket refer to concentrations of duplicate samples.

concentrations in urine samples are 2.50–27.7 μg/L (mean = 12.38 μg/L, 95% CI = 2.71–22.05) (Table 2). The Kruskal–Wallis test suggests statistical difference of urinary Tl concentrations between the villages ($p = 0.0001$) (Table 3).

The urinary Tl concentrations from the three villages are 1–4 orders of magnitude higher than the values from the control locations (Table 2). In the background area with no recognized Tl mineralization, urinary Tl concentration range between 1.05 and 1.70 μg/L (mean = 1.40 μg/L), whereas urinary Tl ranging from 0.387 to 0.96 μg/L (mean = 0.651 μg/L) was recorded from Guiyang City. The Mann–Whitney test suggests significant difference in urinary Tl concentration of the LMC area ($n = 21$) versus the background area ($n = 3$) ($p = 0.003$) and Guiyang City ($n = 4$) ($p = 0.0009$) (Table 3).

Samples from the preliminary test (UR03, UR04, UR05 and UR06) collected in December 2002 show comparably lower concentrations than the values from the same volunteers in the investigation of May 2003 (UR16, UR25, UR15 and UR26, respectively), being generally 3- to 50-fold lower. However, the Mann–Whitney test suggests no statistically significant difference between the two different sampling periods ($p = 0.0571$) (Table 3).

The Mann–Whitney test suggests no statistically significant difference of urinary Tl concentrations in male ($n = 13$) and female groups ($n = 8$) from the LMC area ($p = 0.6452$) (Table 3). The Spearman correlation coefficient for urinary Tl concentration versus age is near zero, also indicating no correlation between urinary Tl concentration and age ($p = 0.9353$) (Table 3). This is not unexpected because all the local population consumes the locally produced vegetables rich in Tl, and also implies that a limited number of samples may identify the population at risk and provide a reasonable estimate of exposure to Tl.

Concentrations of Tl in the environmental samples (soils and green cabbages), taken from the local community area and the control locations, are compared in Table 4. Thallium is present at elevated concentrations in all soil samples from LMC ($n = 17$, mean = 25.9 mg/kg, 95% CI = 16.4–35.4), whereas Tl in soil samples from the background locations are below 1 mg/kg. The Kruskal–Wallis test suggests statistically significant differences in soil Tl concentrations among the three villages within LMC ($n = 17$, $p = 0.0036$), and the Mann–Whitney test also suggests significant differences in soil Tl concentrations between the LMC and the background locations ($p = 0.0035$) (Table 3). In green cabbage samples grown on the local garden soils, Tl concentrations range from several mg/kg to several hundred mg/kg ($n = 16$, mean = 101.7 mg/kg, 95% CI = 34.0–169.4), which are far above the values (<1 mg/kg) from the control locations (Table 4). The Kruskal–Wallis test indicates significant differences in Tl concentrations in green cabbage among the three villages within LMC ($n = 16$, $p = 0.0022$) (Table 3). The Mann–Whitney test also suggests statistically significant differences in Tl concentrations in green cabbage between the LMC ($n = 16$) and the background locations ($n = 4$) ($p = 0.0012$) and Guiyang City ($n = 3$) ($p = 0.0036$) (Table 3).

With respect to mean values of Tl in the environmental samples, the Spearman correlation coefficient is statistically significant ($r = 0.850$ and $p < 0.0001$) (Table 3) for crop Tl versus soil Tl from

Table 3
Statistical tests to evaluate the distribution of urinary Tl concentrations and their relationships with environmental subjects

Test	*p*-Value (*r*-value)
Kruskal–Wallis: Villages A ($n = 8$), B ($n = 7$) and C ($n = 6$)	0.0001
Mann–Whitney: LMC ($n = 21$) and background area ($n = 3$)	0.003
Mann–Whitney: LMC ($n = 21$) and Guiyang city ($n = 4$)	0.0009
Mann–Whitney: Urine samples from four volunteers in 2002 and 2003	0.0571
Mann–Whitney: LMC male ($n = 13$) and LMC female ($n = 8$)	0.6452
Kruskal–Wallis: Soils at villages A ($n = 7$), B ($n = 5$) and C ($n = 5$) of LMC	0.0036
Mann–Whitney: Soils at LMC ($n = 17$) and the background area ($n = 3$)	0.0035
Kruskal–Wallis: Crops at villages A ($n = 6$), B ($n = 5$) and C ($n = 5$) of LMC	0.0022
Mann–Whitney: Crops at LMC ($n = 16$) and the background area ($n = 4$)	0.0012
Mann–Whitney: Crops at LMC ($n = 16$) and Guiyang city ($n = 3$)	0.0036
Spearman correlation test: urinary Tl and age ($n = 21$) at LMC	0.9353
Spearman correlation test: crop Tl and soil Tl	<0.0001 (0.850)
Spearman correlation test: Urinary Tl and soil Tl	<0.0001 (0.952)
Spearman correlation test: Urinary Tl and crop Tl	<0.0001 (0.990)

Table 4
Comparison of Tl concentrations in soils and green cabbage of LMC and control locations (mg/kg)

Environmental samples	*n*	Mean	95% CI of mean	Median
Soil				
Total soil population from LMC	17	25.9	16.4–35.4	28.0
Soil in Village A of LMC*	7	39.3	24.8–53.8	35.0
Soil in Village B of LMC*	5	29.4	21.5–37.3	28.0
Soil in Village C of LMC**	5	3.6	0.89–6.2	2.7
Soil in background area*	3	0.31	−0.189–0.809	0.33
*Crops***				
Total crop population from LMC	16	101.7	34.0–169.4	32.05
Green cabbage in village A of LMC	6	224.4	85.9–362.9	207.5
Green cabbage in village B of LMC	5	46.6	−4.61–97.77	32.0
Green cabbage in village C of LMC	5	9.59	3.04–16.1	7.3
Green cabbage in background area	4	0.585	0.336–0.829	0.585
Green cabbage in Guiyang market	3	0.513	0.413–0.614	0.520

* Xiao et al., 2004a.
** From this study.

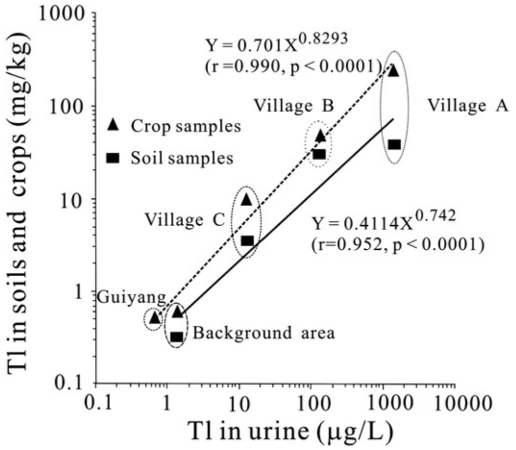

Fig. 3. Plot of Tl concentrations in soil and crop vs. Tl in urine.

the four groups (the three villages and the background area), suggesting that Tl uptake by crops is positively affected by Tl concentrations in soil on which the crops grow.

The Spearman correlation test also indicates statistically significant correlations between Tl in environmental samples and urinary Tl ($p < 0.0001$) (Table 3). With respect to mean Tl values, the coefficients are $r = 0.952$ for soil Tl versus urinary Tl, and $r = 0.990$ for crop Tl vs. urinary Tl (Table 3, Fig. 3).

4. Discussion

The LMC area presents a specific geo-environmental context with naturally high concentrations of Tl in soil related to the natural bedrock mineralization of Tl-bearing sulfides. The authors' earlier work has demonstrated that Tl release from Tl-rich rocks/ores during weathering is a natural, long-term process, modified in recent centuries by human activities, particularly mining and farming (Xiao et al., 2004b,a). High concentration of Tl in soil tends to facilitate high uptake for Tl by the locally grown vegetables. Consumption of the Tl-rich vegetables consequently results in elevated Tl concentrations in urine of the local population.

4.1. Pathways of high thallium into the human body

The study area is a rural region lacking current industrial activity, although some sporadic mining for Hg and coal occurred in the past. Because Tl is generally removed from the body via urine (ATSDR, 1992; WHO/IPCS, 1996), the high concentrations of Tl in human urine in the study area must be ascribed to high accumulation of Tl through the food chain.

Consumption of the locally produced crops is the major pathway to cause high Tl in urine. The local population of LMC has in general a vegetable-based diet (due to their inability to buy meat because of poverty) and commonly consumes vegetables (mainly green cabbage and Chinese cabbage) grown in the local Tl-enriched vegetable-garden soils throughout the entire year. The previous study has shown that the enrichment of Tl in the edible parts of crop species decreases in the following order with respect to mean values: green cabbage (212 mg/kg) > chili (3 mg/kg) > Chinese cabbage (2.5 mg/kg) > rice (2.4 mg/kg) ≅ corn (2.4 mg/kg), indicating high accumulation of Tl in green cabbage (Xiao et al., 2004a). The bio-concentration factor of Tl in green cabbage (dry weight) in relation to its concentration in dry soil is up to 10 (Xiao et al., 2004a). The reason for the preferential uptake of Tl into crops is unclear but is possibly due to the similar ionic and hydrated radii of Tl^+ (1.59 Å) and K^+ (1.51 Å) (Shannon, 1976). Green cabbage is the commonly cultivated vegetable due to its high yield and the harvest season is in the period from February to May. Therefore, the local villagers consume more green cabbage in this period of the year. In the period between October and January, the local villagers mainly consume the Chinese cabbage containing less Tl than the green cabbage. This explains the lower Tl concentrations in urine samples collected in December 2002 compared to higher concentrations detected in urine screened in May 2003 from the same volunteers.

The average daily dietary intake of Tl by the adult villagers from village A through ingestion of locally planted crops has been estimated at 1.9 mg per person, as compared to 0.01 mg for Hg and 0.03 mg for As (Xiao et al., 2004a). The calculated ingestion rate of Tl in the body (body weight of an adult is considered to be 70 kg on average) of the local population is up to 27 μg/kg/day on average, which is around 1000 times higher than the world average daily intake (2 μg/day) as indicated by Sabbioni et al. (1984). This high ingestion of Tl is also far above the 'oral reference dose' of 0.056 mg/day Tl (RAIS, 2003). This higher daily dietary intake for Tl is also markedly different than the 3.8 μg/day Tl for an average adult from vegetables in the USA (USEPA, 1980). The above findings strongly support the hypothesis that Tl in the soils of LMC related to the natural Tl mineralization is being readily transferred to the human body through the ingestion of locally produced food crops.

In addition to food crops, other potential pathways for Tl to enter the human body include the drinking water, consumption of domestic birds and animals, air inhalation from cooking and heating, and inadvertent soil ingestion. However, the threat from the drinking water supply has been reduced since the early 1990s by piping groundwater from outside the study area and by low Tl concentrations (0.12–0.38 μg/L) in the well water still serving some of the population (Xiao et al., 2003).

Although appreciable amounts of Tl can be found in domestic poultry and animals, for example, Tl in chickens range from 7.2 to 10.3 mg/kg (fresh weight), eggs from 3 to 12.7 mg/kg (fresh weight) and pork from 0.1 to 0.38 mg/kg (fresh weight) (Feng et al., 2001), the local domestic birds and animals are typically raised in small numbers (5–10 chickens and 1–2 pigs per family), and meat consumption is something extravagant for most of the local families. Only small quantity of non-locally produced meat is sporadically consumed (on average 500 g per week for a family of four). Thus, contribution of Tl to the food chain through meat consumption can be neglected.

Coal is often used for cooking and heating in the communities, but it is imported from areas 50 km south of LMC and has low Tl concentrations (0.16–0.31 mg/kg) (Xiao, unpublished data). Although higher Tl concentrations (12–46 mg/kg) occur in local coals of LMC (Xiao et al., 2004a), the coal production by past sporadic mining was quite small and the mines were banned in the early 1990s. Thus, Tl contribution through air inhalation from coal-based cooking and heating can also be discounted.

Finally, the inadvertent ingestion of Tl-bearing soils in the local environment should not be overlooked due to local living habits. As mentioned above, the local population has a long-term exposure to the Tl-enriched soil, thus the Tl-rich soils may be inadvertently ingested by so-called hand-to-mouth behavior, particularly for children who tend to ingest more soil than adults. Any outdoor manual farming activity is also likely to increase soil ingestion, for example, the local villagers often do not wash their hands properly prior to meals. Although, it has also been shown that soil ingestion is a health concern for children (Lambert and Lane, 2004), this study did not quantitatively assess inadvertent soil ingestion. However, it is possible that a small amount of Tl intake can occur through inadvertent soil ingestion whereas Tl intake from the drinking water, domestic birds and animals, and air inhalation from cooking and heating plays insignificant roles.

4.2. Potential adverse health effect of thallium exposure on the local population

The large quantity of Tl ingested via the locally-grown vegetables has the potential to produce adverse effects on human health in the study area. Previous epidemiological studies have shown high Tl concentrations in the villagers' urine, ranging from 600 to 3000 μg/L during the 1970s (Zhou and Liu, 1985), remaining high (mean = 825.4 μg/L, 95% CI = 339.8–1311 from villages A and B) today as shown in this study. These results indicate consistently high concentration of Tl in urine over the last three decades.

According to the report of the Word Health Organization (WHO), Tl has a short biological half-life, measured at about 10 days (WHO/IPCS, 1996). Therefore, the consistently high urinary Tl concentrations imply a long-term exposure to dietary Tl intake, since the local inhabitants with vegetable-biased diet rely mostly on locally produced food crops. This contrasts with low urinary Tl concentrations (0.387–0.960 μg/L) detected amongst citizens of Guiyang (Table 2) from a non-exposed area. The local population of LMC is static, permanent residents who rarely travel outside the area. As a result, urinary Tl concentrations of LMC residents represent steady-state conditions with long-term exposure, and urinary concentration can be taken as an indicator of total dose in terms of ingestion following total daily dietary intake.

The report from the WHO suggests that an approximately 15-fold increase in urinary Tl concentration above the mean non-exposed concentration of 0.3–0.4 μg/L may be related to early adverse health effects, and that exposures resulting in urinary Tl concentrations below 5 μg/L are unlikely to cause adverse health effects (WHO/IPCS, 1996). In the range of 5–500 μg/L the magnitude of risk and the severity of adverse effects are uncertain, whereas exposures over 500 μg/L Tl have been associated with clinical Tl poisoning (WHO/IPCS, 1996). In accordance with the above international health guidelines, all the urine samples from both villages A and B and two-thirds of the samples from Village C in this study have urinary Tl concentrations above 4.5–6 μg/L, indicating that the majority of the local population might suffer from the early adverse health effects. Furthermore, all subjects from Village A have urinary Tl concentrations over 500 μg/L, which can be considered approaching clinical intoxication. A health risk of this magnitude for the inhabitants of Village A is most likely related to consumption of vegetables with higher Tl concentration, which is attributable to the higher influx of Tl through alluvial deposition, along the stream bank, from washed materials derived from Tl-rich sulfide ores and rocks. On the other hand, vegetables in Village B are grown in areas away from the stream banks, and the garden soil has lower Tl concentrations. Thus, comparatively higher Tl concentrations in soil tend to cause higher Tl in vegetables and finally a higher intake of Tl by villagers.

Although, a symptom-based Tl exposure limit is still not available from the WHO (WHO/IPCS, 1996), the relationship of exposure-response is well illustrated by the case history of a very poor family in Village A. This family was severely affected by Tl poisoning in the 1960s and 1970s, with body-aches, hair loss, reduced vision and even total blindness. Compared to other families, this family consumes more vegetables, planted in its own Tl-enriched vegetable-garden within Village A to supplement their alternate daily staples due to poverty. Urinary Tl concentrations of the family members are still extremely high, from 640.8 to 2668 μg/L (Table 2). It is important to note that the two under-10-year-old children of this family also show high urinary Tl concentrations (640.8 and 2252 μg/L). This is of concern, suggesting that the onset of Tl loading occurs early in childhood. The pathway of Tl exposure to children is mainly from crop consumption but inadvertent soil ingestion should not be neglected.

The adverse effects of Tl on the exposed local population were also evidenced by high concentrations of Tl in nails and hair by Zhang et al. (1999). Thallium concentrations in hair range from 1.12 to 5.59 mg/kg, and from 2.97 to 32.24 mg/kg Tl in nails. These values are far above 0.4 mg/kg Tl in hair and 0.8 mg/kg in nail from the non-exposed background area (Zhang et al., 1999). However, testing the urinary Tl concentration of the population is a comparatively quicker way of identifying Tl exposure from the environment than testing Tl concentrations in hair and nails.

The natural source of the high Tl concentration in the study area and the existing adverse health effects make it a critical area for further epidemiological studies of the local population to determine whether there is an increased risk of pathological effects and to assess objectively the various symptoms related to Tl intoxication, coupled with a detailed dietary study.

4.3. Environmental implication beyond the study area

Although, Tl ore deposits are rare in nature, the occurrence of Tl in a number of hydrothermal ore deposits and alteration zones is well established and the presence of Tl has been used as a tracer for geochemical exploration (Ikramuddin et al., 1983). For example, hydrothermal precipitates in the Rotokawa geothermal system of New Zealand have Tl concentrations as high as 5000 mg/kg (Krupp and Seward, 1987). The Allchar Sb–As–Tl deposit in the former Yugoslavia also has high Tl concentrations in ores (Percival and Radtke, 1994), as does the Lengenbach Pb–Zn–As–Ba–Tl deposit in Switzerland (Hofmann and Knill, 1996). Some Chinese Fe sulfide deposits (e.g. Yunfu deposit in Guangdong), Hg deposits (e.g.Yilan deposit in Guangxi), Sb–Au deposits (e.g. Getang deposit in Guizhou) (not far from LMC), Au deposits (e.g. Dongbeizai deposit in Sichuan), Cu deposits (e.g. Chenmenshan deposit in Anhui), Pb–Zn deposits (e.g. Lanping deposit in Yunnan) and As–Tl deposist (e.g. Nanhua deposit in Yunnan) also show high Tl concentrations (Chen et al., 2001).

From this pilot study in the LMC area, with high baseline values of Tl in the surface environment, it is clear that Tl can be dispersed beyond a mineralized zone, and its abundances in soil and crops can rise above permissible levels and result in adverse health effects. Thallium is associated with hydrothermal mineralization in many mineralized areas of the world, in quantities similar to LMC and concentrated within rocks susceptible to weathering. Soils developed in situ on such rocks would have a higher background of Tl concentration and could enrich food crops, if the area is used for farming. Because Tl is rapidly and readily absorbed and its removal is mainly renal, concentrations of Tl in urine may be considered a relatively reliable indicator of exposure. Thus, testing the urinary Tl concentration of the population inhabiting those areas is a quick way of detecting Tl exposure because Tl poisoning symptoms may take years to manifest themselves in an unambiguous manner.

5. Conclusions

This study documents a real health risk to humans arising from naturally occurring Tl concentration through the food chain. A majority of the volunteer subjects from the study area of LMC have urinary Tl concentrations above 4.5–6 μg/L, implying early adverse health effects, and some of them have over 500 μg/L urinary Tl, considered to be in the level of clinical intoxication. The elevated urinary Tl concentrations are mainly attributable to Tl uptake by the locally grown vegetables from soil enriched by natural dispersion of Tl occurring in the local environment. The higher dietary intake for Tl is mirrored by higher urinary Tl concentration. The urinary Tl concentrations correlate with the extent of exposure, in terms of geographical, dietary and behavioral differences. The already affected health of the local population and its correlation with the Tl enrichment in the surrounding environment warrants detailed epidemiological studies.

Thallium is associated with hydrothermal mineralization in many mineralized areas of the world, in quantities similar to LMC and concentrated within rocks susceptible to weathering. Soils developed in situ on such rocks would have a higher background of Tl concentration and could be incorporated into the food crops, if used for farming. Since Tl is rapidly and well absorbed and its removal is mainly renal, concentrations of Tl in urine may be considered a relatively reliable indicator of exposure. Thus, testing the urinary Tl concentration of the population inhabiting those Tl-concentrated areas is a quick way of detecting Tl exposure because Tl poisoning symptoms may take years to manifest themselves in an unambiguous manner. The high concentrations of Tl in urine sound an alarm, calling for an in-depth study of the geo-environmental factors promoting the dispersion and enrichment by Tl before the health risk attains epidemic proportions.

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