Environmental exposure of thallium and potential health risk in an area of high natural concentrations of thallium: southwest Guizhou, China

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Abstract

Little is known in the literature about thallium (Tl) exposure from naturally occurring Tl contamination. 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 of southwest Guizhou Province, China, reside within a natural Tl accumulated environment resulting from the Tl-rich sulfide mineralization, and they face a severe Tl exposure in their daily lives. The daily intake 1.9 mg Tl from the consumed food crops was estimated for a local adult inhabitant of Lanmuchang. High Tl concentrations were detected in urines of the local residents. Measured urinary Tl levels are as high as 2.51-2,668 μg/L, surpassing the accepted world urine Tl level <1 mg/L for "non-exposed" humans. However, there is a positive relationship between the extent of Tl exposure from Tl in soil and crops in the immediate environment and the levels of Tl detected in urine. This study has been able to identify that the elevated urinary Tl levels are mainly attributable to Tl accumulation in locally grown vegetables acquiring Tl from natural sources in the local soils. This study indicates clearly that natural sources of high concentrations of Tl poses a potential health risk to the population, and that monitoring the urinary Tl level is a reliable and accurate way of bio-marking Tl exposure.
Keywords: Thallium, environmental exposure, public health, soil, crop, Guizhou, China.

1 Introduction

The environmental aspects of heavy metals (e.g. Cd, Hg, As, Cr, Pb, Zn, Co, Ni, etc.) have been widely documented during the past few decades. However, thallium (Tl), one of the extremely toxic metals, has often been neglected in public health studies or regulations, although its high toxicity was recognized soon after its discovery in 1861.

Thallium's role as a toxic health threat, which mainly affects the central nervous system, causes visual disorders (with failing eyesight or total blindness), hair loss and even death, has been investigated extensively [1-2], However, no previous comprehensive study has provided evidence of environmental exposure of natural contamination processes of Tl that may have serious consequences for public health.

This paper presents a case study from southwestern Guizhou Province, China, where the local population endures a high environmental exposure to soil contamination with Tl and suffers from a potential public health.

2 Materials and methods

2.1 Study area

The study area, centered on Lanmuchang, a small town with approximately 1000 inhabitants, was chosen for a pilot study for Tl's potential health impact on the local inhabitants during both natural process and man-made disturbance.

The source of naturally occurring Tl is associated with sulfide mineralization, and the main ore minerals are lorandite ($TlAsS_2$), realgar (AsS), orpiment (As_2S_3), cinnabar (HgS) and pyrite (FeS_2). The concentrations of Tl in the sulfide ores range from 100-3 5000 mg/kg, and 2-2 600 mg/kg in the mine wastes [3].

A detailed description of the local geology has been recently reported and published [3,4-5]. Therefore, only a brief summary is provided here. The Lanmuchang Hg-Tl-As deposit area is underlain by Permo-Triassic sediments and overlain by Quaternary alluvium. The exposed rocks include limestone, argillite and coal seams. Thallium enrichment is associated with the sulfide minerals of Tl-As-Hg. Thallium mineralization outcrops in the hills, where it is susceptible to weathering and dispersion by natural processes.

The local population is permanent and year-round residents inhabiting in Lanmuchang within the small watershed of the Qingshui Stream over the year (Figure. 1). Their daily staples are composed of locally planted rice, corn and vegetables. Many of the local adult population 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 [6].

However, symptoms of chronic Tl intoxication including hair loss, muscle and joint pains and reduced vision still occurred amongst some of the population during our filed investigation of 1998-2003. The locally planted vegetables are the main food crops consumed by the local communities. Our earlier analyses carried out over 1998-1999 demonstrated quite high levels of Tl but lower arsenic and mercury levels in the locally grown food crops, particularly in green cabbage [5]. The drinking-water problem was resolved by piping Tl-free groundwater (<0.005 μg/L) from outside the study area in the early 1990s for service to most of the families, and the local domestic well water still serving to the left families who cannot afford to the pipe water contains much lower Tl levels (0.12-0.38 μg/L) [4].

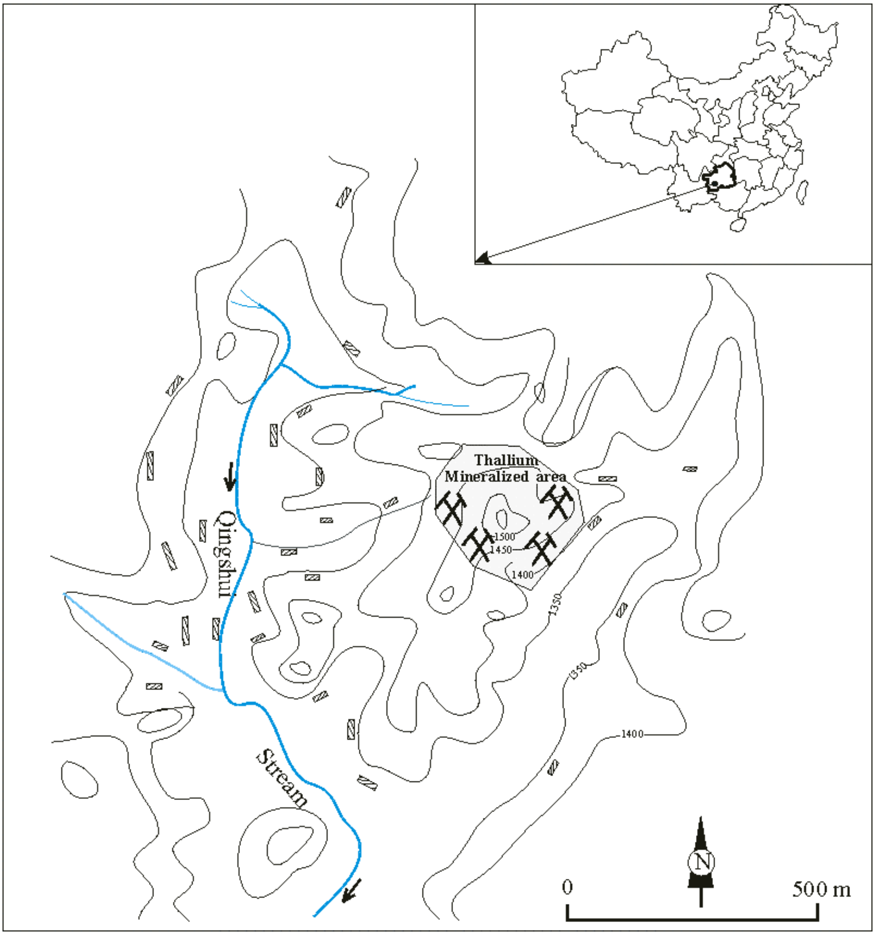

Figure 1: Thallium mineralized area in Lanmuchang, southwest Guizhou, China.

2.2 Sampling and analysis

A suite of 21 morning spot urine samples were collected from the Lanmuchang community for a preliminary urinary Tl screening in May 2003, and three samples from an area devoid of the presence of Tl mineralization were taken as background samples. During the field sampling, the volunteers were adequately informed of the aims, methods and anticipated benefits of the study. Informed consent was obtained from all the study participants prior to the collection of urine samples.

The urine samples were 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 0.005 μg/L in urine samples. The analytical precision, determined by quality assurance/quality control procedures, using duplicates, reagent blanks, internal standards was better than ±10%.

3 Results and discussion

3.1 Environmental exposure of Tl in the Lanmuchang area

There are three pathways of Tl exposure to the local population, and they are water exposure, soil exposure and food crops exposure (Table 1). Through these three exposure pathways, Tl may enter the food chain and cause heath risk on the public health.

Table 1: Concentrations of Tl in various sampling media from LMC area.

Sampling media		Sample Numbers	Tl concentrations	
			Range	Median
Waters (μg/L)	Well water	5	0.01-0.38	0.2
	Stream water	12	0.09-31	1.8
	Background groundwater	2	<0.005	<0.005
Soils (mg/kg)	Soils in mine area	10	40-124	63
	Alluvial deposited soils	12	14-62	31
	Background area	3	<0.2-0.5	0.3
Crops (mg/kg, DW)	Green cabbage	6	15-495	120
	Carrot	1	22	22
	Chili	3	0.8-5.3	2.9
	Rice	4	1-5.2	1.7
	Chinese cabbage	9	0.87-5.4	1.3
	Corn	8	0.78-3.1	1.3
	Background area	7	0.05-0.35	0.27
Urine (μg/L)	Urine	21	2.51-2668 (95% CI = 217.8-968.5)	174.5
	Background area	3	1.05-1.69	1.47

Thallium levels in the supplied drinking water by the Tl-free piped groundwater (<0.005 μg/L) and the well waters (0.01-0.38 μg/L) are both below the US EPA international limits (2 μg/L) (Tables 1 and 2), and seem to show no potential risk on the local public health. Thallium in stream water (0.09-31 μg/L) shows higher concentrations than those found in shallow groundwater (0.005-0.75 μg/L), which serves as the stream's source (mainly springs, dug-well flows and karstic cave waters). The stream water is the only source for domestic use and irrigation in the Lanmuchang area. The local villagers use the Tl-rich stream water for daily washing (e.g. washing clothes or vegetables), making it possible for Tl to enter the human body through the skin or through the vegetables consumed, but detailed information about this risk is unclear. The Tl-rich stream water can also cause Tl contamination in soils through irrigation. Tl-contaminated soils, in turn, contaminate vegetables or cereals by uptake of Tl, providing a Tl source to the food chain [5]. This also implies that natural Tl in the aqueous system can multiply its effect through soil and agricultural contamination, and finally reach the food chain.

Table 2: Environmental safe limits for thallium exposure.

	Tl	Sources
Drinking water	2 μg/L	[7]
Irrigating water	1 μg/L	[8]
Arable soils	1 mg/kg	[9]
World land plants	0.008-1.0 mg/kg (DW)	[10]
World edible plants	0.03-0.3 mg/kg (DW)	[10]
World average daily intake	2 μg/day	[11]
Oral reference dose	0.056 mg/day	[12]

Thallium levels in soils of the Lanmuchang area range from 40 to 124 mg/kg in soils from the mine area, 14 to 62 mg/kg in alluvial deposits along the stream banks, and <0.2-0.5 mg/kg in soils from the background area devoid of sulfide mineralization (Table 1). These values demonstrate that the erosion of natural soils from the Tl-mineralized area, and local past mining activities, are both responsible for the dispersion of high Tl values in soils [5]. All the contaminated soils were applied for cropping due to limited farming lands in the local community area, and Tl in these soils may transfer to crops.

Thallium concentrations in crops are species-dependent [5]. The enrichment of Tl in the edible parts of crop species decreases in the following order regarding to median values: green cabbage > carrot > chili > rice > Chinese cabbage ≅ corn (Table 1). The highest level of Tl in green cabbage is up to 500 mg/kg (DW), surpassing the values of Tl (14-124 mg/kg) in the soils in which the green cabbages grow. The enrichment factor (i.e. the ratio of metal concentration (DW) in crops to that in soils) for Tl in green cabbage is up to 1-10, indicating that green cabbage is a high crop accumulator for Tl. The local crops of the study area contain much higher Tl content than those from the background area. In the background area, seven crops samples of green cabbage (2), carrot (1), chilli (1), rice (1), Chinese cabbage (1) and corn (1) contain Tl 0.05-0.35 mg/kg, and the higher Tl levels were also found in the two analyzed green cabbage samples.

3.2 Public health risk implications of environmental exposure to Tl

The high concentrations of naturally-occurring Tl in the Lanmuchang area show that Tl disperses into waters, soils and ultimately crops at levels which are above the health guidelines set by many countries (Tables 1, 2). The local villagers in the Lanmuchang Tl mineralized area consume the crops growing in the Tl-contaminated soils during the entire year. The average daily intake of Tl by these villagers through consumption of locally-planted crops has been estimated at 1.9 mg per person [5]. The calculated average human ingestion rate of Tl (given a mean adult body weight of 70 kg) is up to 27 μg/kg/day in Lanmuchang, 50 times the ingestion rate of the metal (0.04 mg/day) in people of the Tl-free background area. This high ingestion rate of Tl is 1,000 times higher than the world average daily intake (2 μg/day) as indicated by Sabbioni et al. (1984) [11], and also far above the element's 'oral reference dose' of 0.056 mg/day [12]. This clearly indicates that Tl in the contaminated soils related to the natural Tl mineralization is being readily transferred to the human body through the food chain. It represents significant threat to the public health of the local villagers.

Thallium occurs at quite high levels in urine of the local inhabitants of Lanmuchang, generally ranging from 2.51 to 2668 μg/L (Mean = 593.1 μg/L; 95% CI = 217.8-968.5), which are several orders of magnitude higher than the accepted maximum urinary Tl level of <1 μg/L for "non-exposed" humans in the world [13,14], and imply that the public health of the local communities was severely impacted by the high exposure to Tl from their living environment. The local Tl urinary levels vary among various local community areas. The higher Tl levels (131.9-2668 μg/L) were determined from the community areas downhill the Tl mineralized zone and east bank of the Qingshui Stream (Fig. 1), and lower levels (2.51-27.73 μg/L) were found from the community areas located at the west bank area with higher topography and away from the mineralized area. The local population of LMC is static, residing permanently and hardly travelling outside the area. As a result, their urinary Tl values can represent steady-state conditions with long-term exposure, and their urinary excretion values can be taken as an indicator of total dose in terms of absorption following total daily dietary intake.

The urinary Tl levels are also 1-4 orders of magnitude higher than values from the background area (1.05-1.69μg/L, median = 1.47 μg/L). The Mann-Whitney test suggests significant difference of soil Tl levels between the LMC and the background locations (p = 0.0035) (Table 3). The Mann-Whitney test also suggests significant difference of Tl levels in crops between the LMC and the background locations (p = 0.0012) (Table 3). With respect to mean values of Tl in the environmental samples, the Spearman correlation coefficient (Table 3) is statistically significant (r = 0.850 and p < 0.0001) for crop Tl versus soil Tl from the LMC area, suggesting that Tl uptake by crops is positively affected by Tl contamination in soils on which the crops grow. The Spearman correlation test also provides statistically significant coefficients between Tl in environmental samples and urinary Tl (p < 0.0001) (Table 3). With respect to Tl mean values, the coefficients are r = 0.790 for the group of soil Tl versus urinary Tl, and r = 0.994 for the group of crop Tl versus urinary Tl (Table 3). The Spearman correlation coefficient for urinary Tl levels versus ages (from 8 to 71 years old) from both the LMC and control volunteers is near zero, indicating no correlation between urinary Tl level and age (p = 0.9353) (Table 3). This indicates that Tl intake through contaminated food crops is age-independent, and it may have the same health impact on children as on adults.

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

Test	*p*-value (r value)
Mann-Whitney: Urine at LMC and background area	0.003
Mann-Whitney: Soils at LMC and the background area	0.0035
Mann-Whitney: Crops at LMC and the background area	0.0012
Spearman correlation test: crop Tl and soil Tl	<0.0001 (0.850)
Spearman correlation test: Urinary Tl and soil Tl	<0.0001 (0.790)
Spearman correlation test: Urinary Tl and crop Tl	<0.0001 (0.994)
Spearman correlation test: urinary Tl and age at LMC	0.9353

4 Conclusions

Environmental exposure to Tl, particularly through soil contamination and crop uptake, may pose high potential health risk on humans due to both natural processes and human activities. The higher dietary intake for Tl from Tl-rich crops is mirrored by higher urinary Tl levels. The urinary Tl levels correlate with the extent of exposure, in terms of contaminated arable soils with and dietary differences for digestion of Tl. Monitoring the urinary Tl level is a reliable and accurate way of bio-marking chronic Tl exposure in areas of high levels of naturally occurring Tl.

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