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Environmental concerns related to high thallium levels in soils and thallium uptake by plants in southwest Guizhou, China

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Abstract

Thallium (Tl) contamination in soils poses a significant threat to human health due to the high toxicity of Tl and its ready assimilation by crops. This study is focused on high concentrations of Tl in soils in the Lanmuchang area of southwest Guizhou, China, which is related to natural processes of Tl-rich sulfide mineralization. Thallium contents range from 40 to 124 mg/kg in soils originating from the mining area, from 20 to 28 mg/kg in slope wash materials, from 14 to 62 mg/kg in alluvial deposits downstream, from 1.5 to 6.9 mg/kg in undisturbed natural soils and <0.2 to 0.5 mg/kg Tl in soils from the background area. These values indicate that both the erosion of natural soils from the Tl mineralized area and the mining activity are responsible for the distribution of high Tl concentrations in soils. Two other important toxic metals of interest, mercury and arsenic, also show high contents in soils, and are generally higher than Tl concentrations. Thallium concentration in plants exhibit species-dependent preferences. Thus, the enrichment of Tl in the edible parts of crop species decreases in the following order: green cabbage > carrot > chili > Chinese cabbage > rice > corn. The highest level of Tl in green cabbage is up to 500 mg/kg as dry wt., surpassing the values of Tl in the soils in which the green cabbages grow. In contrast, Hg and As are relatively less concentrated in local plants. The average daily uptake of Tl by the villagers of the Lanmuchang area through consumption of locally planted crops has been estimated to be 1.9 mg/person, which is 50 times the daily ingestion of individuals from the Tl-free background area. The daily ingestion of As and Hg from the study area are 0.03 and 0.01 mg, respectively. This 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, and poses a significant threat to the health of the local villagers. Arsenic may pose a lesser health hazard, but mercury has an insignificant health risk. This study illustrates a real environmental concern related to land use and human health in areas containing high contents of Tl in soils

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associated with the natural occurrence of Tl-rich sulfides and coals, with or without mining activities. Thallium contamination in soils should be a critical parameter for proper land use and health related environmental planning and regulations.

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Keywords: Thallium; Soil contamination; Uptake of toxic metals; Food chain; Environmental impact

1. Introduction

Thallium's high potential for toxicity is well demonstrated (Smith and Carson, 1977; Schoer, 1984; Mulkey and Oehme, 1993). Thallium is more toxic to mammals than cadmium, lead, copper or zinc, and it is known to have caused many accidental, occupational and therapeutic poisonings since its discovery in 1861 (Smith and Carson, 1977; Mulkey and Oehme, 1993). Although widely distributed in the natural environment, Tl is generally present in very low concentrations in soils. Concentrations of Tl in uncontaminated soils generally range from 0.01 to 3 mg/kg, but most soils contain Tl at concentrations of less than 1 mg/kg (Fergusson, 1990).

Thallium minerals and mineralization are rare in nature, thus Tl is often excluded from the list of metals to be analyzed despite its high toxicity. Thallium environmental impact related to the natural occurrence of Tl has received relatively little attention. The authors believe that a full understanding of the behavior of Tl in a local ecosystem is vitally important and critical for the identification, remediation and management of Tl-related health problems.

Natural anomalies of Tl related to several widely scattered gold–mercury–arsenic and coal deposits have been recognized in southwest Guizhou, China (Cunningham et al., 1988; Li and Peters, 1998). Especially noteworthy is the disseminated Tl mineralization with discrete Tl ore bodies, discovered in the study area (Chen, 1989a,b; Li, 1996). However, distributions of Tl in soils and its impacts around the aforementioned Tl related mineralized areas were not properly established.

The absence of detailed knowledge of the distribution and dispersion of Tl, through both natural processes and human activities (e.g. mining, farming) that have produced adverse impact on the

local ecosystem and human health, is a matter of concern. Recognition of this problem prompted a group of multidisciplinary-environmental studies pertaining to litho-geochemistry, soil geochemistry, hydrogeochemistry and biogeochemistry of Tl and its impact on human health (Xiao, 2001). This paper presents the results of an investigation into the natural occurrence of Tl in soils and its uptake by crops and other plants in the Lanmuchang Tl–Hg–As mineralized area, and outlines the impact of Tl dispersion on the local ecosystem.

2. Study area

The study area, in the southwest Guizhou Province in China, is centered on Lanmuchang, a small town with approximately 1000 inhabitants. The area presents a karstic topography, with a generally higher elevation in the northwest and lower in the southeast. A sinkhole dominates the lowest elevation in the south. The average altitude is 1400 m above sea level with a relative relief of 100–200 m.

The Lanmuchang Tl–Hg–As mineralized area is located within the southwest limb of the E–W-trending Huijiabao anticline. The local geology and mineralization of the Huijiabao Au–As–Hg–Tl metallogenic belt and the Lanmuchang Hg–Tl–As mineralized area were described by Xiao (2001) and Xiao et al. (in press). A brief description of the geological setting will suffice as a prelude to this article. The E–W-trending Huijiabao anticline corresponds to a metallogenic belt of gold, mercury, thallium, arsenic and coal, 18 km long and 5 km wide (Fig. 1). The Lanmuchang Hg–Tl–As deposit occurs in the middle portion of the belt. 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 (P₂l: limestone, argillite

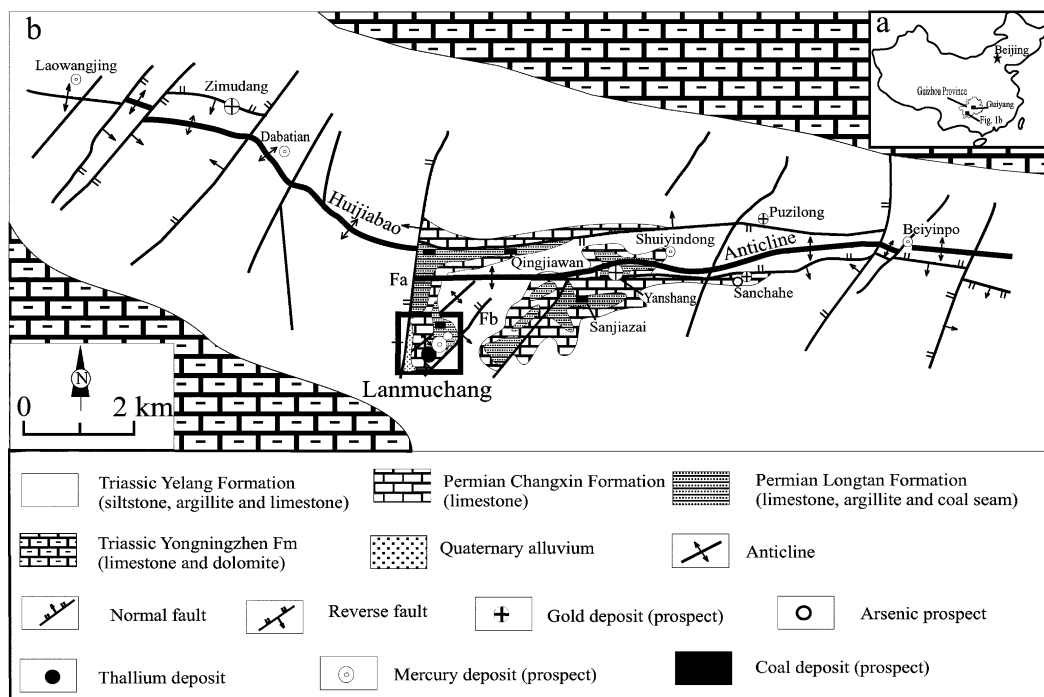


Fig. 1. Geological sketch map of the Huijiabao anticline metallogenic belt in southwest Guizhou, China (after Xiao et al., in press).

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). The limbs of the anticline have outcrops of the Yelang Formation and the Yongningzhen Formations (T_{1yn} : limestone and dolomite). Thallium mineralization in this metallogenic belt is associated with disseminated Tl mineralization, gold mineralization or coal mineralization (Chen, 1989b; Liu, 1997; Xiao, 2001). Thallium in the Lanmuchang Tl–Hg–As deposit, located in the formations P_{2l} and P_{2c} , is characterized by abundant Tl minerals, mainly lorandite ($TlAsS_2$), plus other identified Tl minerals such as christite ($TlHgAsS_3$), imhofite ($Tl_6CuAs_{16}S_{40}$), raguinite ($TlFeS_2$) and lanmuchangite ($TlAl(SO_4)_2 \cdot 12H_2O$) (Chen, 1989a; Li et al., 1989; Li, 1996; Chen et al., 2001). The sulfides such as cinnabar, realgar, orpiment, arsenopyrite and pyrite are also rich in Tl (Chen, 1989b; Li, 1996; Xiao, 2001). This deposit has a long mining history (~350 years) for mercury, and has been

worked exclusively for Tl since the 1990s. Thallium is also present in coals. Sporadic artisanal mining of the coal seams is 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.

The soil horizons in the Lanmuchang area are not well developed. These soils mainly originate from the weathering of outcrops and accumulate naturally on the slight to moderately steep slopes within the mineralized area. They are of limited areal extent. Much of the slope materials are proximal to the bedrock from which they are derived, and therefore, contain weathering products (e.g. mud, silt and some talus) that reflect the bedrock, and they may migrate downslope, contributing to arable soils.

The Lanmuchang area has been widely developed for agricultural and residential purposes, and related disturbances, for purposes of farming, surface grading and excavations for foundations and

septic systems, are very common. Some areas have been treated with 'fill', material variably composed of local soils, mining wastes and coal ashes, whereas the farming and residential areas are largely made up of reworked original surface materials including alluvial and colluvial deposits.

3. Sampling and analysis

Thirty-two soil samples were collected within the Lanmuchang Tl–Hg–As mineralized area and from an adjacent area chosen as a reference for the estimation of natural geochemical background levels (Fig. 2). The background area, with similar stratigraphy to the Lanmuchang mineralized area but lacking known sulfide mineralization (Guizhou Geological Bureau, 1990a,b), is located approximately 2–3 km horizontally removed from Lanmuchang to both west and east, with the same lithologies exposed as outcrops or in quarries (limestone, siltstone, sandstone, argillite of T_{1y}, P_{2c} and P_{2l}). The sampling patterns, whether sequential or random, correspond to the characteristics of soils associated with natural pedogenesis and with mining-related disturbance, and serve to delineate the variations of Tl and other trace metals in the study area and grouped as: soils in mining area (soils derived from mine wastes and arable soils in mining areas), alluvial deposits, slope wash materials, undisturbed natural soils and background soils. The sampling pattern also reflects the topographical characteristics (e.g. hill top, hill slopes and lowland areas) related to the Tl mineralization.

The soil samples were collected using a stainless steel shovel from natural sites and mining localities around the mineralized area so as to represent the natural soils and also the arable soils on which the locally consumed crops and wild plants are grown. At each sampling site, 3 sub-samples (0–20 cm depth) were taken over an area of 5 m² to form a final composite sample. In order to estimate the reproducibility of the sampling procedure, duplicate samples at every 10th site were taken at a distance of 5 m from the original sample location. All the soil samples were kept in polyethylene bags and air-dried in the laboratory pending final processing. The soils were processed for geochem-

ical 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.

Thirty-six crops and three wild plant samples were also collected in the study area, including 9 crop samples from the background area (Fig. 3). The edible parts of the crops (vegetables and cereals) were the focus of the investigation for toxic metals. The vegetables include Chinese cabbage, green cabbage, chili and carrot root, mainly collected during the harvest season. All the cereal samples (corn and rice) were collected in the harvest season. All the vegetables and cereals examined are the main crops planted in the study area. Some wild plants (fern leaf and edible wild herbs for livestock or human consumption) were also collected in the study area. The sampling sites for crops and wild plants generally correspond to the locations of soil samples since the soils on which the plants were growing were also collected. The vegetable and the wild herb samples were cleaned using de-ionized water in the field and air-dried in labeled paper bags. The samples of corn, rice, chili and fern leaf were kept in paper bags before shipment to the laboratory. All the plant samples except corn and rice were cut into small pieces (1–2 cm long) in the laboratory. The rice samples were treated to remove their outer sheaths. The rice, corn, cut vegetable and wild plant samples were then stored in labeled paper bags and placed in an electric drying cabinet heated to 25 °C until completely dry.

The analysis of major elements in soils was undertaken by fused-disk wavelength-dispersive X-ray Fluorescence at the Analytical Chemistry Laboratories of the Geological Survey of Canada (ACLGSC) in Ottawa (Bélanger, 2001, personal communication). Ferrous iron was determined using the Wilson Method (titrimetric). Total S was determined by combustion followed by infrared spectrometry using a LECO SC444-DR sulfur/carbon determinator. Soil pH values were measured by means of soil in CaCl₂ solution at the ACLGSC (Bélanger, 2001, personal communication). The cation exchange capacity (CEC) was determined by the Norwest Laboratories (Edmon-

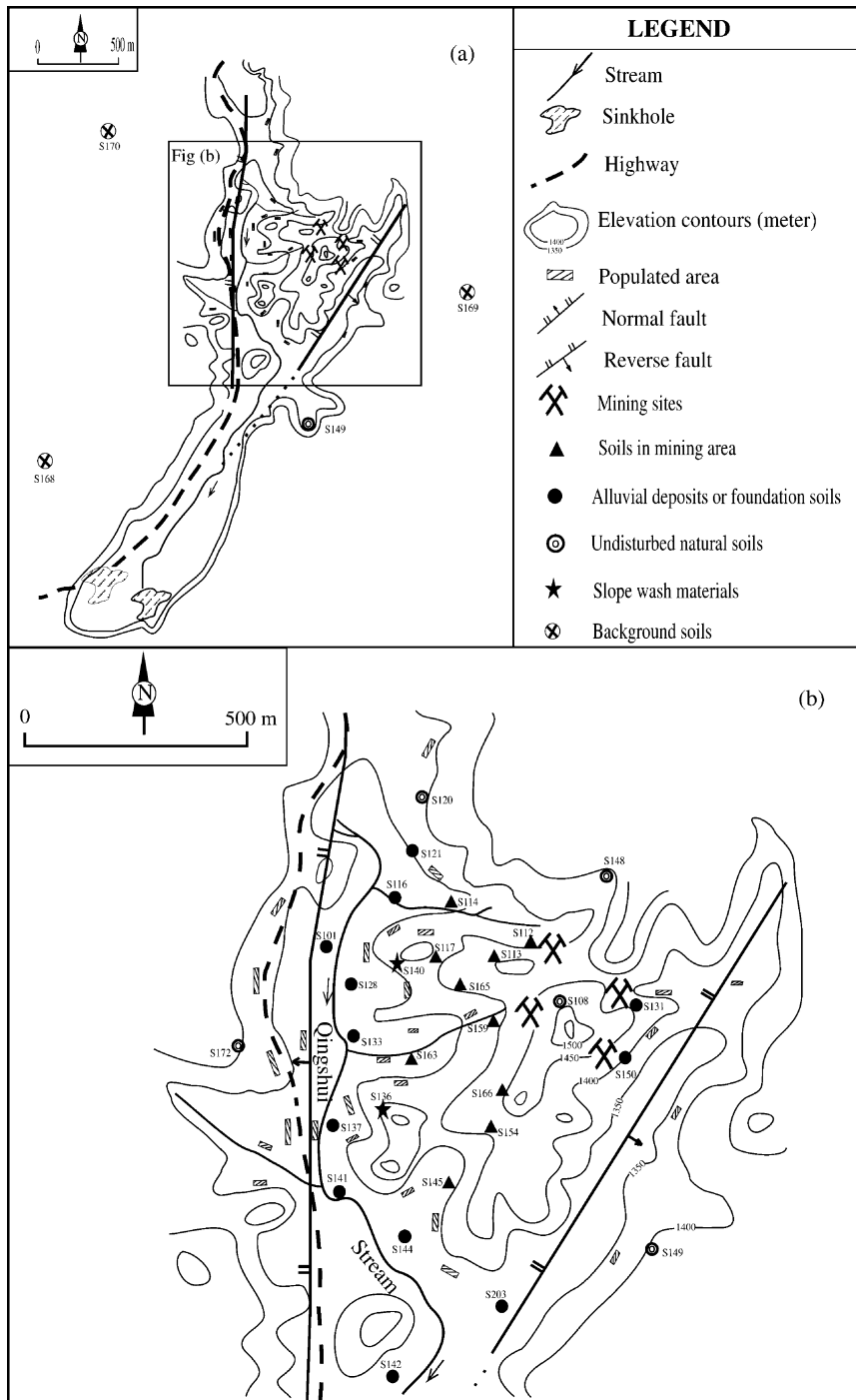
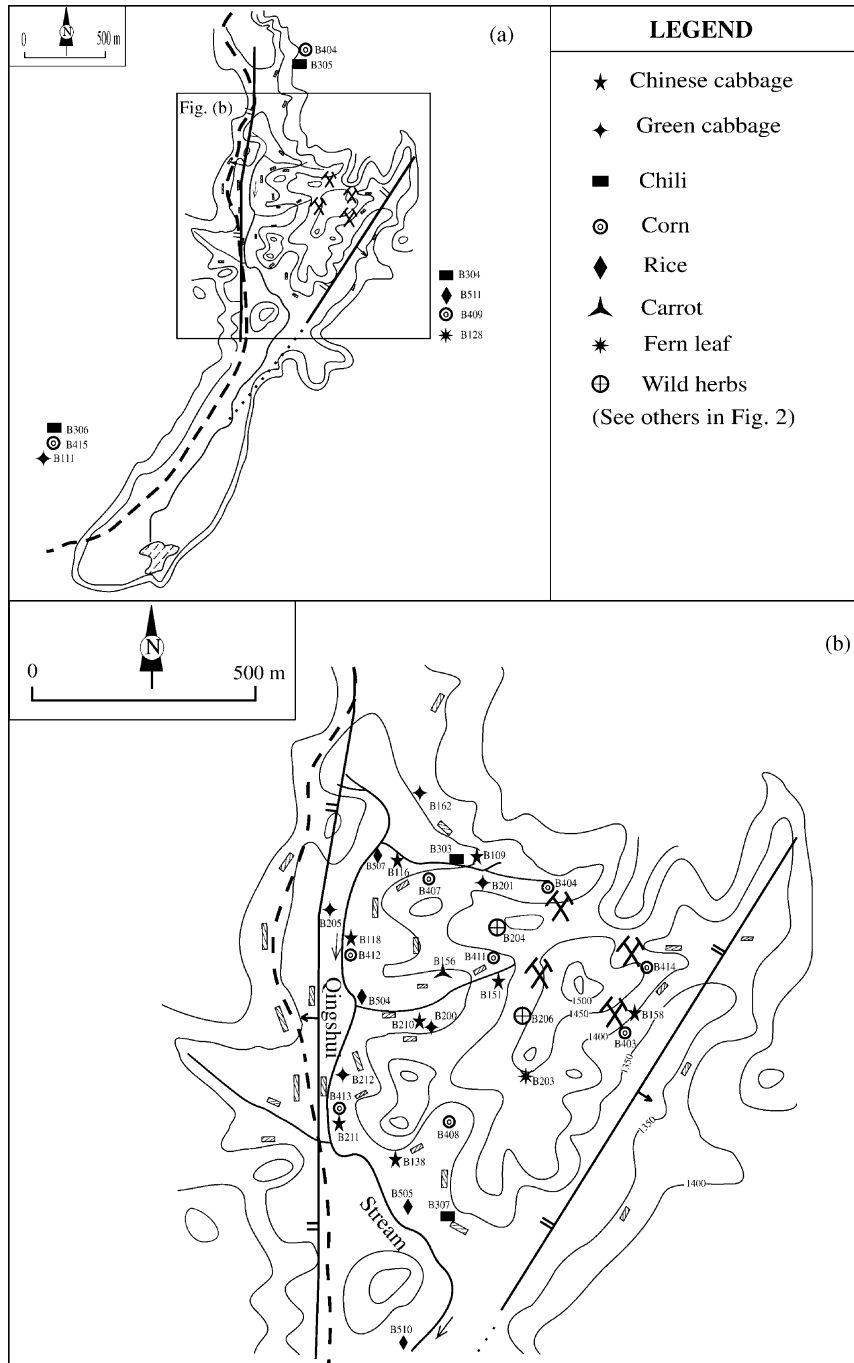


Fig. 2. Location of sampling sites of soils.



ton, Alta., Canada) (Crichton, 2000, personal communication). The mineral compositions were also determined by X-ray diffraction (XRD) at the Institute of Geochemistry, Chinese Academy of Sciences, Guiyang.

The determination of trace metals in soils at Norwest Laboratories employed a microwave digestion method using concentrated nitric acid (HNO_3) in a closed vessel. The digested solution was analyzed by ICP-MS for Tl, As, Ba, Cd, Cr, Cu, Pb, Zn and Mo, and for Hg by the cold-vapor method (Tran, 2000, personal communication). The results represent the strong-acid-extractable concentrations of metals, i.e. the 'environmentally available' labile fraction of metals in soils.

All the plant samples were analyzed at the Activation Laboratories Ltd (Ancaster, Ont., Canada). The air-dried samples were ashed at 475 °C for 36 h. 0.25-g aliquots of ash were dissolved in 1 ml of concentrated HNO_3 and 1 ml of concentrated H_2O_2 at 90 °C for 2 h and then diluted to 10 ml with 18-M Ω water. The samples were further diluted to a final dilution of 1000:1. Samples were spiked with internal standards and analyzed by ICP-MS using a Perkin Elmer SCIEX ELAN 6000 for Tl, As, Ba, Cd, Cr, Cu, Pb, Zn and Mo, and Hg was determined by cold-vapor method based on the dry samples (Hoffman, 2001, personal communication). The ash yield factor, i.e. the ratio of ash wt. (AW) to dry wt. (DW) of plant samples, was also measured after ashing.

The analytical precision, determined by quality assurance/quality control procedures, using duplicates, blanks, internal standards and reference samples, was better than $\pm 10\%$.

4. Results

4.1. Major characteristics of soils

The results of major element determinations and some parameters relating to soil properties are listed in Table 1. The soils in the study area are characterized by low CEC, ranging from 8.6 to 28.3 meq/100 g. Seventy percentage of the pH values fall within the range of pH 3.3–6.0, and the other 30% of samples have higher pH values of from 6.4 to 7.3. The pH values show the soils

ranging from a normal, near-neutral, Ca-rich limestone-derived soil to acidic, sulfide-rich materials in the mineralized area. The comparably higher pH values (6.4–7.3) determined from both mining-affected and alluvially-deposited soils are probably due to the buffering of limestone as illustrated by higher contents of CaO in these soils (Table 1).

The major-element chemistry of the soils reflects the clay mineralogy in soils. In the soils of the mineralized area >70 wt.% of the major-element components are accounted for by the SiO_2 – Al_2O_3 – Fe_2O_3 assemblage, with minor quantities of TiO_2 and K_2O . Based on a comparison to the North American shale composition (Gromet et al., 1984) and the average composition of the upper crust (Condie, 1993), these soils are relatively ferruginous, with considerably lower levels of Na_2O , MgO and CaO . The XRD results for soil samples also show very similar mineralogical compositions in all soil types, characterized by the clay mineralogy of the parent materials. The mineralogy is mainly composed of quartz, kaolinite, illite and goethite.

These soils are highly concentrated in sulfur, ranging from 0.06 to 2.9 wt.%. The high sulfur contents are attributable to the abundance of sulfide minerals. The high loss-on-ignition (LOI) may also characterize the soils containing high sulfur, carbonate C (e.g. limestone particles in soils) and/or organic C (e.g. organic matter in top soils from farmland or organic components from the bedrock).

4.2. Distribution of trace elements in soils

The analytical data for selected trace elements are listed in Table 2. Based on comparison with typical shale (Turekian and Wedepohl, 1961; Gromet et al., 1984), average continental crust (Taylor and McLennan, 1985; Condie, 1993) and regional background values (this study), the elements Tl, Hg, As and Ba are enriched, whereas Cu, Pb, Zn, Cd, Co, Ni, Cr, Se and Mo show average crustal concentrations. This is consistent with the intensive mineralization of Tl, Hg and As, the presence of barite, and the lack of base-metal mineralization in the bedrock. The high concentrations of Tl, Hg and As indicate that these three specific toxic

Table 1

Compositions of major elements and characteristics of soils (unit in wt.% except where indicated)

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O _{3t} ^a	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S _t ^b	LOI ^c	CEC ^d	pH
Soils in mining areas														
S112	44.8	2	11.2	13	0.07	0.51	0.64	0.2	1.3	0.4	2.1	15.3	22.6	5.1
S113	49.2	2	12.2	12	0.13	0.64	3	0.1	1.5	0.39	0.76	15.6	21.2	7.2
S114	43.3	2.1	11.6	12.7	0.11	0.92	1	0.2	1.4	0.45	1.8	16.5	17.8	6.6
S117	53	3	14	10.2	0.1	0.93	0.66	0.1	1.6	0.36	0.58	13.5	19	6
S145	50.7	2.6	12.3	9.9	0.01	0.47	0.2	0.1	1.4	0.31	1.05	20.2	13.6	3.5
S154	46.1	2.5	13.2	14.1	0.09	0.53	1.3	0.1	1	0.64	0.57	18.2	20.4	7
S159	44.5	2.1	12.9	12.4	0.04	0.52	0.35	0.1	1.3	0.46	0.7	24.2	23.1	4
S163	54.3	2.2	12.4	10.7	0.08	0.67	0.37	0.1	1.4	0.54	0.29	16.6	17.6	4.5
S165	53.8	2.4	12.7	11.7	0.05	0.51	0.33	0.1	1.4	0.38	0.59	15.7	27.4	4.5
S166	54.7	2.2	12.1	12.8	0.04	0.55	0.28	0.1	1.5	0.37	0.82	13.2	15	4.5
Alluvial deposits														
S101	42.9	3.1	13.7	14.6	0.11	0.78	2.3	0.1	1	0.38	0.7	17.4	19.7	7
S116	49.6	2.9	14.9	11.4	0.11	0.99	0.81	0.1	1.6	0.44	0.38	15.3	18.3	6.6
S121	47.1	3	15	13	0.11	0.74	0.97	0.1	1.1	0.63	0.25	16.9	28.3	6.5
S128	48.9	3.4	14.6	12.5	0.13	0.95	0.44	0.1	1.2	0.53	0.26	15.4	20.7	4.6
S131	50.5	3.2	15.6	13.8	0.11	0.72	0.68	0.1	1	0.33	0.23	12.8	21	5.6
S133	47.7	2.5	13.1	14.7	0.06	0.55	0.43	0.1	1.2	0.59	0.73	17.9	23.3	4.3
S137	47	3.2	15.7	13.3	0.08	1.05	0.43	0.1	1.3	0.52	0.24	16.4	22.4	4.6
S141	43.2	1.7	14.3	10.7	0.12	0.59	0.68	0.1	1.4	0.56	0.43	24.9	25.8	4.4
S142	46.3	3.4	15.6	13.7	0.13	1.2	0.46	0.2	1.3	0.57	0.13	15.9	26.8	4.7
S144	44.8	2.6	15.1	12.6	0.13	0.83	1.3	0.1	1.4	0.58	0.31	18.6	24.7	6.7
S150	50.2	2.9	14.5	12.5	0.08	0.93	0.22	0.1	1.2	0.49	0.51	15.1	17.3	4
S203	44.3	2.9	15	15.6	0.12	1.1	2.1	0.1	1.2	0.46	0.34	16.5	17.4	7.3
Slope wash materials														
S136	45.1	3.3	15.9	13.8	0.13	1	0.57	0.1	1.2	0.51	0.23	17.3	22.7	5.2
S140	44.3	2.9	14.6	13	0.12	0.8	0.91	0.1	1.1	0.62	0.31	19.9	23.7	5.4
Undisturbed natural soils														
S108	75.4	2.9	10.8	2.4	0	0.16	0.07	0.1	0.29	0.39	0.39	nd ^e	3.3	4.2
S120	49.1	2.6	15.4	12.4	0.23	1	0.5	0.1	1.5	0.61	0.11	15.4	21.3	5.3
S148	44.3	4	18.8	15.8	0.18	0.59	0.06	0	0.74	0.41	0.06	12	12.2	3.9
S149	48.8	4.3	19.1	15.3	0.14	0.48	0.05	0	0.69	0.45	0.06	9.8	8.6	4
S172	50.1	2.2	14.7	3.9	0	0.56	1.6	0.1	2.1	0.13	1.3	21.8	12	3.3
Background soil														
S168	46.6	4.3	17.3	16.3	0.15	1.8	0.29	0.1	1.5	0.19	0.02	11	16.6	4.8
S169	37.6	5	22.6	21.2	0.25	0.93	0.06	nd	0.53	0.29	0.02	12.5	14.5	4.3
S170	43.7	3.9	20.1	16.9	0.23	1.2	0.06	0.1	1.4	0.23	0.03	12.1	20.6	4.1

^a Total Fe.^b Total sulfur.^c Loss of ignition.^d Cation exchangeable capacity (meq/100 g).^e Not detectable.

metals are enriched in the soils of the study area, in proportions which vary from one substrate to the next, such as soils derived from the mining wastes, slope-wash materials, alluvial deposits, undisturbed natural soils and background soils (Table 2; Fig. 4).

Thallium occurs at high concentrations in soils derived from mine wastes, ranging from 40 to 124 mg/kg. In slope wash materials, concentrations of Tl range from 20 to 28 mg/kg. In alluvial deposits along the Qingshui Stream downwards the Tl mineralized area, Tl content ranges from 14 to 62

Table 2
Concentrations of selected trace elements in soils (mg/kg)

Samples	Tl	Hg	As	Ba	Cd	Cr	Cu	Pb	Zn	Mo
Soils in mining area										
S112	78	243	298	2030	0.5	23	70	95	44	5.3
S113	63	264	326	1720	0.6	23	74	28	68	4.4
S114	69	421	212	2890	0.5	27	63	40	65	3.8
S117	43	505	319	1600	0.5	39	67	17	58	3.7
S145	81	410	504	1380	0.6	21	40	10	17	4.2
S154	63	207	185	1960	0.6	52	84	38	110	6.2
S159	124	243	201	1420	0.4	24	86	95	37	5.9
S163	40	130	157	1040	0.4	33	64	26	98	5.2
S165	47	192	202	920	0.4	25	71	20	82	4.8
S166	62	186	301	1530	0.5	26	59	21	62	6.1
Alluvial deposits										
S101	46	950	257	2500	0.5	61	65	23	250	5.8
S116	35	353	194	2390	0.5	39	82	29	83	3.2
S121	14	72	115	1020	0.4	67	119	34	104	3.4
S128	31	135	140	1760	0.4	69	83	40	86	1.8
S131	40	116	158	1410	0.3	66	85	25	55	4
S133	31	659	424	1400	0.56	40	76	28	29	8.6
S137	27	72	106	1400	0.31	72	106	20	82	1.6
S141	23	375	54	1580	0.38	28	56	17	79	3.7
S142	16	62	70	936	0.35	89	92	19	105	0.85
S144	29	136	179	1590	0.44	37	90	18	113	2.8
S150	62	374	338	1970	0.52	38	90	15	72	3.6
S203	39	109	146	2010	0.5	75	89	23	191	1.6
Slope wash materials										
S136	28	82	96	1540	0.4	79	93	23	107	1.2
S140	20	64	109	1880	0.52	61	80	21	115	2.5
Undisturbed natural soils										
S108	2.9	19	59	3360	0.1	15	18	9	3	1.3
S120	6.9	28	89	651	0.49	39	93	21	115	1.9
S148	4.2	13	37	60	0.27	95	132	13	74	1.6
S149	4.5	10	47	47	0.26	108	150	12	83	1.6
S172	1.5	0.8	50	48	0.09	5.5	24	19	31	9.7
Background soils										
S168	0.33	0.87	4.7	105	0.17	154	98	13	105	<0.05
S169	<0.2	0.26	4.4	54	0.22	137	113	11	62	<0.05
S170	0.5	0.5	7.5	32	0.16	105	73	18	56	0.14

mg/kg, with a median of 31 mg/kg. Comparatively, the undisturbed natural soils within and around the mining area show lower concentrations of Tl, ranging from 1.5 to 6.9 mg/kg. Soils from the background area have very low Tl contents ranging from <0.2 to 0.5 mg/kg.

Mercury in soils derived from the mine wastes and alluvial deposits along the stream occurs over a wide range of concentrations from 62 to 950 mg/kg. In the undisturbed natural soils within and

around the mineralized area, Hg occurs at much lower levels of 0.8–28 mg/kg. In the slope-wash materials, Hg concentration ranges from 64 to 82 mg/kg. The background level of Hg is low, down to 0.5 mg/kg.

Arsenic nearly shows the same distribution pattern as Hg in soils. Concentrations of As range from 54 to 586 mg/kg in soils derived from the mine wastes and alluvial deposits. In the undisturbed natural soils within and around the miner-

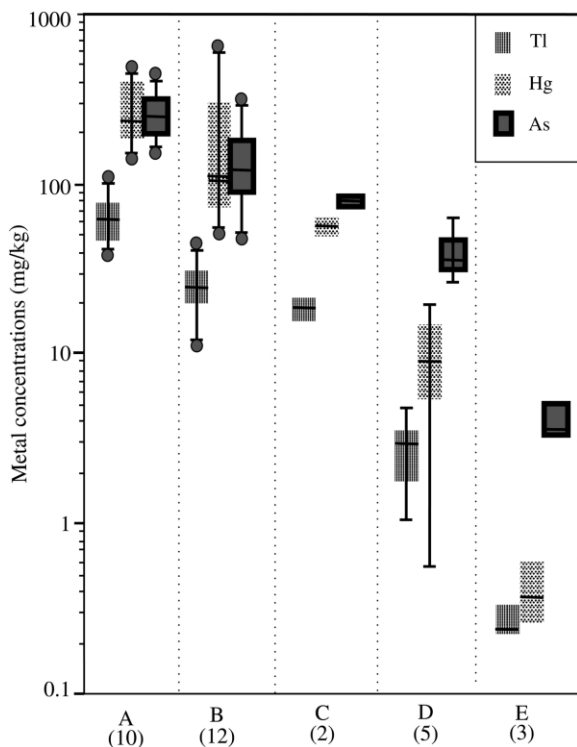


Fig. 4. Box plots for the concentration distribution of Tl, Hg and As in soils. A, soils in mining area; B, alluvial deposit soils; C, slope wash materials; D, undisturbed natural soils; E, background soils; figures in the bracket refer to number of samples.

alized area, arsenic occurs at slightly lower levels of 37–89 mg/kg. In the slope-wash materials, arsenic concentrations are 96–109 mg/kg. The background level of As is low, down to 5.5 mg/kg.

Correlations between Tl, Hg and As concentrations and pH or measured CEC values in the soils were not found using data (Tables 1 and 2) obtained in this study.

4.3. Distribution of major and trace elements in crops and wild plants

The analytical data for major and trace elements in various crops and wild plants are listed in Tables 3 and 4. Note that the data, based on DW for the

determined composition (except for Hg) are converted from the laboratory analyzed data based on AW, by multiplying the laboratory report data to the ash yield factor (wt.%). Mercury was determined directly on dry samples by cold-vapor ICP-MS, and the results are based on DW.

The major-elements Na, Mg, Ca, Fe, Mn, Al and Si are more enriched in green cabbage, Chinese cabbage and carrot than in chili, corn and rice, where concentrations are higher by 3 orders of magnitude (Table 3). Wild herbs and fern leaves are also rich in the above-mentioned major elements. Among the major elements, Ca and Mg show the highest concentrations in crops and wild plants. Corn shows the lowest concentrations, particularly for Na, Al, Mn and Si.

The trace elements Tl, As, Hg, Zn, Mo, Cd, Ba and Pb generally show higher concentrations in green cabbage, Chinese cabbage and carrot than in chili, corn and rice, except for Cu which exhibits almost the same concentrations in all the plant samples (Table 4).

Thallium, Hg, As and Fe show higher-than-average abundances relative to land plants and edible plants worldwide (Tables 4 and 5), whereas the other metals Ba, Cd, Cr, Cu, Pb, Zn and Mo show a similar range of concentrations as in the world land and edible plants and show no potential risk to human health. However, the higher concentrations of Tl, Hg and As in crops have highly adverse health impacts, and their distributions in crops and wild plants are described below.

Thallium shows the highest concentration in green cabbage, ranging from 120 to 495 mg/kg with an average of 338 mg/kg, whereas only 0.4 mg/kg has been detected in cabbage from the background area. However, Tl shows lower concentrations (15–32 mg/kg) in the early growing stage of the green cabbage. This implies that Tl accumulation in vegetation increases with time throughout the growth process. The widely-planted Chinese cabbage contains 0.87–5.4 mg/kg Tl, with an average of 2.5 mg/kg, whereas Tl concentration in samples from the background area was 0.31 mg/kg. Thallium concentration in chili ranged from 0.8 to 5.3 mg/kg, and 0.27 mg/kg Tl from the background area. Shelled rice con-

Table 3
Concentrations of major elements in various crops and wild plants (DW, mg/kg)

Sample		Na	Mg	Ca	Fe	Mn	Al	Si
Green cabbage (N=5)	Range	1374–9836	2856–5443	28 765–66 690	215–546	40–226	64–289	125–277
	Mean	3766	3990	50 847	373	88	109	177
Chinese cabbage (N=8)	Range	1438–10 030	2223–25 709	11 834–379 011	161–488	26–565	77–316	46–305
	Mean	7090	3081	34 670	325	53	145	199
Chili (N=3)	Range	30–53	1534–2896	613–1572	146–213	18–51	20–57	25–42
	Mean	37	1608	683	160	21	38	41
Corn (N=8)	Range	2–7	868–1270	41–89	15–33	5–9	2–24	2–7
	Mean	2	1111	58	21	7	2	3
Rice (N=4)	Range	7–24	1118–1266	106–129	13–22	16–29	8–19	8–10
	Mean	8	1188	113.5	16	25	8	9
Carrot root (N=1)	Range	612	4261	38 785	660	1060	505	569
	Mean	612	4261	38 785	660	1060	505	569
Fern leaf (N=1)	Range	270	3950	21 138	3398	343	1513	278
	Mean	270	3950	21 138	3398	343	1513	278
Wild herbs (N=2)	Range	13–189	1703–3709	532–16 121	532–4124	321–4124	812–2825	161–233
	Mean	101	2706	9487	2328	454	1818	196

Concentrations of K were not detectable due to over the instrument working range. *N*=number of samples (not including the background samples).

tained 1–5.2 mg/kg Tl, with an average of 2.4 mg/kg, and 0.27 mg/kg Tl from the background area. Thallium in granular corns showed lower concentration, ranging from 0.78 to 3.1 mg/kg and averaging 1.4 mg/kg, and only 0.07 mg/kg Tl on average from the background area. One sample of carrot root contained 22 mg/kg of Tl, although it is not a crop commonly planted in the Lanmuchang area. Some wild herbs (for livestock forage or human consumption) also showed high concentrations for Tl, with an average of 36 mg/kg. Fern, widely growing on mountainsides in the Lanmuchang mineralized area, showed a concentration of 15 mg/kg Tl.

Mercury showed slightly higher concentrations in green cabbage, Chinese cabbage and carrot, generally ranging from 0.4 to 0.7 mg/kg on average, but occurred at very low levels in chili and corn, generally being 0.02 mg/kg. Mercury showed very low concentrations in corn, a concentration value below the detection limit (0.005 mg/kg). However, there were high contents of Hg in wild herbs, with up to 4.2–13 mg/kg, which is

nearly tenfold higher than in crops. In fern, Hg showed concentration of 0.45 mg/kg. Concentrations of Hg in crops from the background area were as low as 0.01–0.3 mg/kg.

Arsenic in crops were found at slightly higher levels than Hg, but lower than Tl. Arsenic contents in green cabbage, Chinese cabbage and carrot were much higher than in corn and rice, generally ranging from 0.7 to 1.3 mg/kg. In corn and rice, As contents were down to 0.02–0.18 mg/kg. Arsenic in carrot was up to 1.3 mg/kg. The average contents of As in crops from the background area were low, generally below 0.02–0.3 mg/kg. Arsenic showed high concentrations in wild herbs (up to 13 mg/kg) and in fern leaves (2.3 mg/kg).

5. Discussion

5.1. Sources of Tl in soils and factors controlling its dispersion pattern

The in situ undisturbed natural soils and the slope wash materials are the main components of

Table 4
Concentrations of selected trace elements in crops and wild plants (DW, mg/kg except where indicated)

Sample	Tl	As	Hg	Ba	Cd	Cr	Cu	Pb	Zn	Mo	Ash yield (%) ^a
Chinese cabbage											
B109	0.99	0.78	0.45	110	0.37	0.33	6.9	2.3	48	2.1	26
B116	0.87	0.71	0.53	40	0.18	0.53	5.5	2.5	44	1.8	25
B118	1.1	0.87	0.26	99	0.43	0.69	6	2.1	56	2.1	26
B138	1.2	0.96	0.3	49	0.31	3.67	5.5	12	49	3.8	25
B151	5.4	1.3	0.7	55	0.25	0.80	5.6	1.4	92	0.5	26
B158	3.8	0.91	0.67	75	0.15	0.54	9.6	1.3	37	0.3	23
B210	5.3	0.73	0.15	24	0.15	0.55	3.5	1	30	0.6	24
B211	1.3	0.17	0.09	31	0.18	0.29	5.6	0.4	44	0.2	16
B128 ^b	0.31	0.37	0.3	37	0.63	0.95	6.5	2.2	39	0.9	16
Green cabbage											
B162 ^c	15	0.7	0.38	90	0.35	0.74	7.9	2.1	57	0.6	23
B200	120	0.89	0.72	82	0.35	0.40	3.1	0.7	92	0.9	24
B201	400	0.84	0.71	62	0.17	0.36	2.9	0.7	33	1.4	25
B205	495	0.38	0.45	46	0.28	0.31	2.7	0.5	32	1.2	23
B212 ^c	32	0.98	1.3	56	0.38	0.71	3.8	1	46	1.3	21
B111 ^b	0.4	0.32	0.33	52	0.1	0.64	3.5	0.7	34	1.1	16
Chili											
B303	2.9	0.29	0.04	4	0.04	0.13	7.1	0.2	14	0.1	9.4
B305	0.8	0.15	0.01	1.5	0.11	0.16	7.9	0.3	24	0	6.7
B307	5.3	0.24	0.01	1.4	0.05	0.09	8.6	0.2	20	0.7	13
B304 ^b	0.35	0.24	0.02	1.7	0.1	0.19	7.6	0.2	16	0.1	12
B306 ^b	0.19	0.14	0.01	0.8	0.05	0.14	6.5	0.2	11	0.2	11
Corn											
B403	1.3	0.02	Nd ^d	0.45	0.01	0.01	2.3	0.06	20	0.03	1.5
B404	0.78	0.02	nd	0.2	0.02	0.05	1.4	0.04	17	0.3	1.3
B407	1.6	0.02	nd	0.1	0.01	0.01	1.3	0.03	19	0.1	1.4
B408	3.1	0.02	nd	0.8	0.01	0.01	3.1	0.03	19	0.2	1.5
B411	1.1	0.03	nd	0.5	0.03	0.02	1.8	0.04	17	nd	1.1
B412	0.78	0.02	nd	0.2	0.02	0.01	1.4	0.04	23	0.2	1.4
B413	1.4	0.02	nd	0.1	0.16	0.06	1.3	0.11	21	0.5	1.3
B414	1.4	0.01	nd	0	0.01	0.01	1.4	0.03	18	0	1.3
B409 ^b	0.09	0.03	nd	0.1	0.06	0.12	0.9	0.04	17	0.4	1.6
B415 ^b	0.05	0.02	nd	0.3	0.09	0.02	1.3	0.1	26	0.1	1.4
Rice											
B504	2.3	0.1	0.02	2	0.02	0.02	0.8	0.06	24	0.2	1.6
B505	1	0.16	0.03	0.6	0.03	0.03	0.4	0.03	17	0.3	1.7
B507	5.2	0.18	0.02	0.6	0.03	0.09	0.2	0.04	17	0.2	1.5
B510	1.1	0.14	0.04	0.8	0.02	0.03	1.6	0.05	18	0.2	1.5
B511 ^b	0.27	0.06	0.01	0.4	0.01	0.01	1.1	0.04	20	0.2	1.5
Carrot root											
B156	22	1.3	0.55	60	0.85	1.0	5100	1.9	100	0.6	24
Fern leaf											
B206	15	2.3	0.45	19	0.23	0.48	3.1	7.3	22	0.2	6.6
Wild herbs											
B203	47	17	13	63	0.61	1.88	18	2	55	0.6	14
B204	25	8.8	4.2	35	0.45	1.71	16	2.6	81	0.8	11

^aAW divided by DW of samples (%); ^bBackground sample; ^cSamples at early growing stage; ^dNot detectable.

Table 5
Average levels of trace elements in plants (DW, mg/kg)

Metals	Land plants	Edible plants
Tl	0.008–1.0	0.03–0.3
Hg	0.005–0.02	0.013–0.17
As	0.02–7	0.01–1.5
Cd	0.1–2.4	0.05–2.0
Cu	1.8–16.2	1.1–8.8
Zn	12–47	10–44
Mo	0.33–2.3	0.07–1.75
Ni	0.13–2.6	1.2–3.6
Ba	142–198	2–160
Fe	18–1000	25–130
Mn	17–334	1.3–113
Al	25–3410	2.6–135
Si	3000–12 000	–

Sources: Bowen (1979) and Kabata-Pendias and Pendias (1992).

original soils in the Lanmuchang area as described above. Concentrations of Tl, Hg and As in these soils may represent their geochemical baselines in the Lanmuchang Tl–Hg–As mineralized environment.

The average concentration of Tl in the undisturbed natural soils within the mineralized area is approximately 4 mg/kg. The slope materials con-

tain 20–28 mg/kg Tl with an average of 24 mg/kg. These Tl contents in the original soils probably indicate the pre-anthropogenic background in the study area, and thus can represent the baseline concentrations for Tl before mining (Table 6). The concentration of Tl in natural soils from the background area ranges from <0.2 to 0.5 mg/kg. The baseline values for mercury and arsenic are also listed in Table 6.

The baseline concentrations of Tl, Hg and As in the Lanmuchang area are over both the Chinese and Canadian environmental quality guidelines, and also higher than those in natural soils of many countries (Table 6). The high geochemical baselines confirm that soils of the Lanmuchang mineralized area are highly enriched in Tl, Hg and As. The source of the concentrated metals in soils is almost certainly linked to the natural sulfide mineralization of Tl, Hg and As in sedimentary rocks, including coal seams in the study area (Xiao et al., in press). For instance, concentrations of Tl range from 100 to 35 000 mg/kg in sulfide ores, 39 to 490 mg/kg in host rocks and 12 to 46 mg/kg in coals (Xiao et al., in press). Mercury and arsenic show similar distributions to Tl, with high concentrations in the sulfide ores, the host rocks

Table 6
Baseline values of Tl, As and Hg in various natural soils

Soils	Tl (mg/kg)	Hg (mg/kg)	As (mg/kg)
Undisturbed natural soils within and around the mineralized area ($N=5$)	2.9–6.9 ($M=4$)	0.8–28 ($M=14$)	37–89 ($M=50$)
Slope wash materials within the mineralized area ($N=2$)	20–28 ($M=24$)	64–82 ($M=73$)	96–109 ($M=102$)
Natural soil from the background area ($N=3$)	<0.2–0.5 ($M=0.3$)	0.26–0.87 ($M=0.5$)	4.4–7.5 ($M=5$)
Chinese guidelines for agricultural land use ¹		1.5	30
Canadian guidelines for agricultural land use ²	1	6.6	12
Natural soils in China ³	0.29–1.2 ($M=0.58$)		
Arable soils in France ⁴	0.13–1.5 ($M=0.29$)		
Natural soils in the Great Britain ^{5,6}	0.03–0.99	0.01–0.09 ($M=0.03$)	4–95 ($M=16$)
Natural soils in Canada ^{6,7}	0.25–0.71	0.01–0.07 ($M=0.06$)	1.3–17 ($M=4.8$)
Natural soils in the world ^{5,8}	0.01–3 ($M=0.2$)		

N =number of samples; M , median value. Source: 1, Xia (1996); 2, CCME (1999); 3, Qi et al. (1992); 4, Tremel et al. (1997); 5, Fergusson (1990); 6, Kabata-Pendias and Pendias (1992); 7, Mermut et al. (1996); 8, Bowen (1979).

and the coals (Xiao et al., in press). The natural processes of chemical and physical weathering of the highly altered outcrops or near surface bedrock can lead to the transfer of large amounts of Tl, Hg and As to the soils (Xiao et al., in press), producing high concentrations of the toxic trace elements. The mobile fraction data for Tl (extracted by strong HNO_3) and the major-element distribution in soils (Tables 1 and 2) indicate that Tl may exist as thallium sulfate, hydrous Fe–Al–Mn oxides, thallium sulfide or adsorbed on clays (Xiao, 2001), although their host soils have similar mineralogical compositions. Furthermore, enzyme leaching, which involves extraction of metals trapped in the amorphous form of Mn and/or Fe oxides that occurs in coatings on mineral grains in stream sediments (Xiao, 2001) also showed that the Fe/Mn hydroxide coatings on sediment particles are the carriers of the mobile fraction of Tl and other metals, and this fact is likely also true for the soils of the study area.

Human activity is another factor contributing to the concentrated toxic metals in the arable soils. The high concentrations of Tl, Hg and As in the arable soils downslope and downstream from the mining area and along the Qingshui Stream are generally in excess of baseline values (Tables 2 and 6), implying more input of these metals to the soils than the contribution from natural processes. The higher concentration of Tl in the arable soils along the Qingshui Stream and its branches is probably caused by the mining operations, which over the years released Tl-bearing mine wastes to the farm lands downstream. Note that the arable soils formed largely by alluvial deposition at sites S121 and S142 have lower concentrations of Tl than those in the slope wash materials (Table 2). This may be caused by the migration of more alluvial deposits from slightly away from the center of the Tl mineralization (Fig. 2). The mining, occurring on the hill slopes, has brought large amounts of mine wastes containing metal-rich clastic sediments to the surface. The toxic metals Tl, Hg and As and their host minerals are enriched in the fine particles of these wastes, which can migrate through runoff and fluvial transport to the farm lands below. Mine wastes found on the downward slope surface were also reworked by

local farmers for use in farming. These farming soils often contain mine debris, important evidence of disturbance related to human activity. Another possible source of Tl contamination in soils is from the domestic utilization of coal by local villagers. Local coals are enriched in Tl, with levels of up to 12–46 mg/kg (Xiao et al., in press), and are often crushed and mixed with mud from the mine wastes to make small coal balls for easy storage and combustion. The ash of such fuel is often used as an additive to arable soils, or is used to pave village roads. This explains the presence of layers of black coal ash, mixed with other mine debris, identified in arable soils during the field study.

The spatial variation of Tl concentrations in various soils of the Lanmuchang area is illustrated in Fig. 5. The spatial variation pattern implies that Tl distribution in soils was originally constrained by the sulfide mineralization of parent material, but the redistribution was controlled by natural fluvial/colluvial processes and human activities. The natural process involves the Tl–Hg–As-rich weathering products migrating downslope to be deposited in the arable soils and thus producing a toxic metal-rich environment. The human disturbance involves the addition of mine wastes and the coal ash, enhancing the concentrations of toxic metals in soils. These two processes explain the high enrichment of Tl, Hg and As in arable soils at locations below the mineralized area.

5.2. Favorable and species-dependant uptake for Tl in various crops

Thallium, together with Hg and As, shows a distinct dispersion pattern in the edible parts of those vegetables and cereals which are commonly cultivated in the study area of Lanmuchang. Thallium is more enriched in crops than its counterparts Hg and As, and As is slightly richer in crops than Hg (Fig. 6). This distribution tendency is quite different from that in soils, where the general tendency of concentration distribution is that $\text{Hg} > \text{As} > \text{Tl}$ (Fig. 4). Thus, Tl seems to be taken up preferentially by crops and other plants.

The favorable uptake of Tl into the plants is likely due to the close geochemical affinity

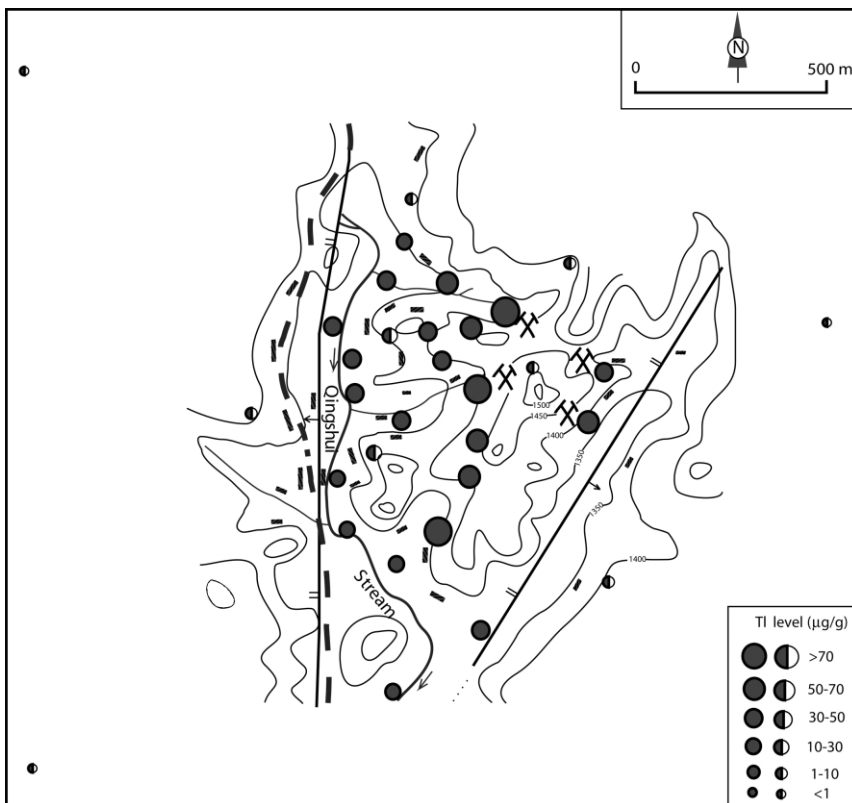


Fig. 5. Spatial dispersions of Tl concentrations in various soils in the Lanmuchang area. Mining soil and alluvial deposited soil sites are indicated by filled circles. Natural soils, slope washed material and background soil sites are indicated by partially filled circles. (Other legends are as in Fig. 2).

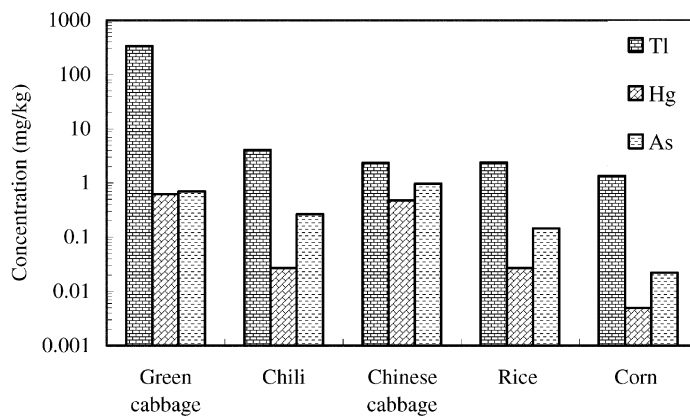


Fig. 6. Concentration distribution of Tl, Hg and As in crops.

between thallium and potassium. These two elements have similar ionic radii of Tl^+ (1.59 Å) and K^+ (1.51 Å) (Shannon, 1976). Because of the very similar ionic radii, Tl can readily substitute for K in plants during biochemical processes. The substitution of Tl for K in plants has been described by many researchers (e.g. Siegel and Siegel, 1976; Schoer, 1984; Tremel et al., 1997; Leblanc et al., 1999). In biochemical processes, Tl occurs as a singly-charged, weakly-hydrated cation (Tl^+) with ionic radius similar to K^+ , and is expected to interfere competitively with K-dependent biological reactions (Siegel and Siegel, 1976). Thallium has the ability to yield complexes with sulfur-containing and phosphorus-containing ligands, leading to a substitution with K at its specific adsorption sites. The Na^+/K^+ -ATPase² plays the main role in uptake of Tl^+ (Edwards et al., 1995). The concentration values for K in all plant samples were beyond the analytical instrument working ranges and were not quantified in this study, but K, as one of the major constituents in vegetation, is certainly available for substitution by Tl. However, the specific factors, which render particular plant species effective hosts for Tl–K substitution, are still unclear.

The enrichment of Tl in crops is also characterized as species-dependant (Fig. 6). Thallium is more enriched in green cabbage than in other crops, generally 2 orders of magnitude higher (Table 2). The enrichment of Tl at a lower level of concentration can be seen in carrot root, chili, shelled rice and Chinese cabbage and finally in corn. The marked genotypical differences of vegetation for uptake of Tl have not been clearly demonstrated in previous studies by other researchers. However, this study shows that the amounts of major elements Ca and Mg in plants seem to be one of the factors contributing to the different degree of uptake of Tl. The higher accumulation of Tl in crops generally corresponds to elevated concentrations of Ca and Mg, although the plots

for Chinese cabbage do not provide a good example (Table 3, Fig. 7a and b). If the samples of Chinese cabbage were excluded from the plots, the correlations of Mg vs. Tl and Ca vs. Tl would be markedly elevated (Fig. 7c and d). However, the mechanism whereby the high concentrations of Ca and Mg trigger uptake of Tl by plants is still not clear. There may be other factors that favor the high uptake of Tl by certain crops and this warrants further study.

The enrichment of Tl in crops and other plants is closely related to the concentrations of Tl in soils. High concentrations of Tl in the plants growing in the Tl-rich soils in the study area support the idea that toxic metals are being transferred from soil to crops through the roots of the plants. In contrast, crops growing in uncontaminated soils in the background area show low concentrations of Tl. For instance, the concentrations of Tl in both green cabbage and Chinese cabbage correlate with the contents of Tl in the soils on which these crops are growing (Fig. 8). Therefore, the high concentrations of Tl in plants directly reflect its immediate source in the contaminated soils.

The enrichment factor for Tl (ratio of Tl concentration in crops to its concentration in soils on which the crops are growing) for green cabbage is over 1, with maximum factor of 11 (Fig. 8a), but it is under 1 for the Chinese cabbage (Fig. 8b). Corn, chili and rice show similar factors as the Chinese cabbage, generally below 1. This also clearly illustrates that green cabbage has the highest uptake for Tl from the Tl-contaminated soils. This study also points strongly to the conclusion that efficient bioaccumulators of Tl like green cabbage should not be planted in areas of Tl-rich soils such as Lanmuchang.

Thallium concentrations also differ depending on the period of growth for the same species of crops. For example, young green cabbage contains much lower Tl concentration than harvested cabbage. Green cabbage labeled B162 and B212 collected at its early growth stage contained 15–32 mg/kg of Tl, whereas the harvested cabbages contained 120–495 mg/kg of Tl (Table 4). The data show that Tl concentrations in harvested green cabbage were 10 times higher than in the younger

² ATPase (adenosine triphosphatase): refers to an enzyme in skeletal muscles that provides energy to the muscles. The Na^+/K^+ -ATPase refers to a certain pump within the cell membrane that actively transfers Na^+ from the inside and K^+ from outside of the cell, and is catalyzed by the enzyme ATPase.

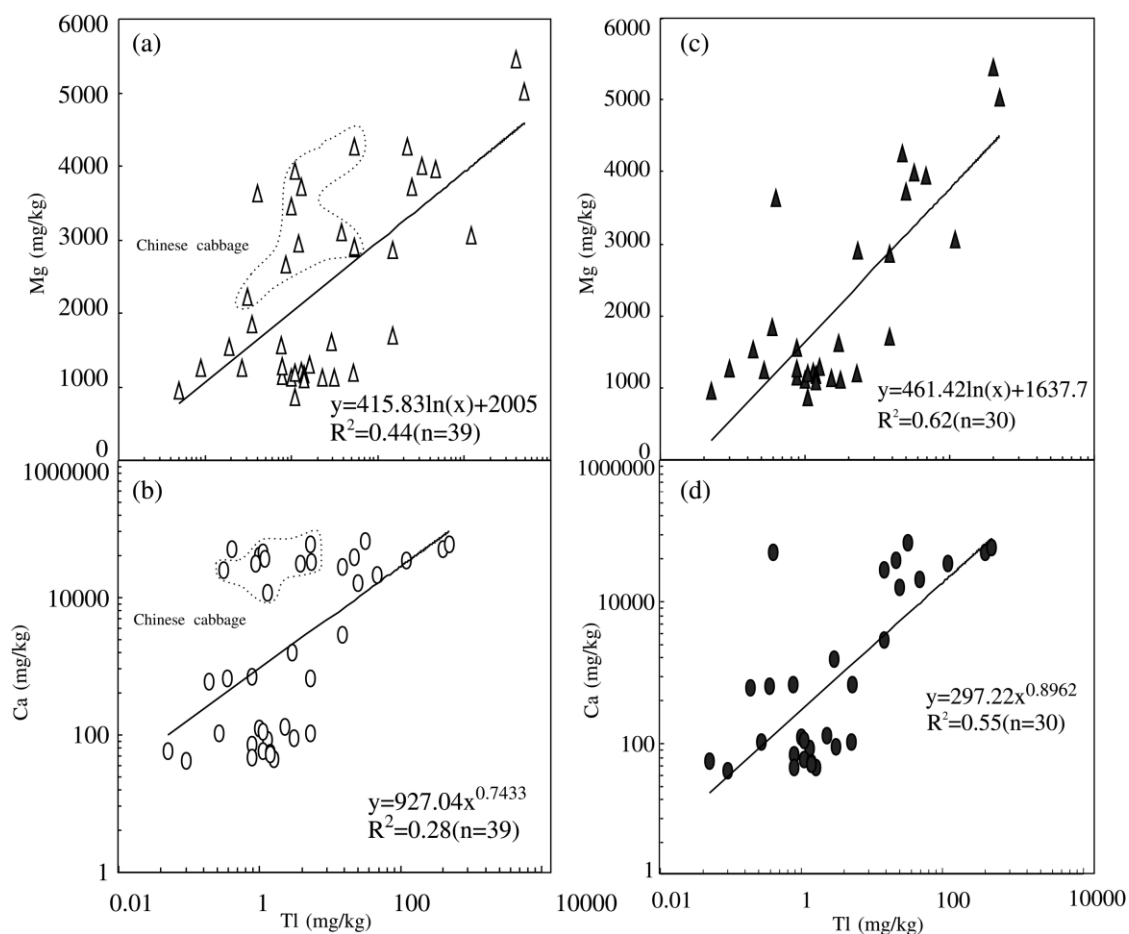


Fig. 7. Plots of Ca and Mg vs. Tl in plant samples: plots in (a) and (b) for all the samples, and plots in (c) and (d) for all the samples except for Chinese cabbage.

growths, suggesting that the accumulation of Tl in plants increases with time.

5.3. Evaluation of environmental impacts of Tl, Hg and As in crops

The minimum lethal dose (LD_{LO}) of soluble thallium salts has been estimated to be 0.7–1.1 g or 10–15 mg/kg for a 70-kg adult (Moeschlin, 1980). The LD_{LO} s are 1–4 g or 14–57 mg/kg for inorganic mercury and 0.042 g or 0.6 mg/kg for inorganic arsenic, respectively (RAIS, 2002). The oral reference dose (RfD) for Tl is 0.056 mg/day or 0.0008 mg/kg/day for a 70-kg adult, whereas

0.021 mg/day or 0.0003 mg/kg/day for both Hg and As (RAIS, 2002). The RfD represents an estimate of a daily oral exposure to the human population that is likely to be without an appreciable risk of deleterious effects during a lifetime. Studies of Tl exposure to humans in a wide variety of geographic locations have indicated less than 2 μg as the average daily intake of Tl from environmental sources (Sabbioni et al., 1984). The largest source of arsenic exposure for most people is from food and is approximately 25–50 $\mu\text{g}/\text{day}$ (RAIS, 2002).

The local villagers in the Lanmuchang Tl–Hg–As mineralized area consume the crops growing

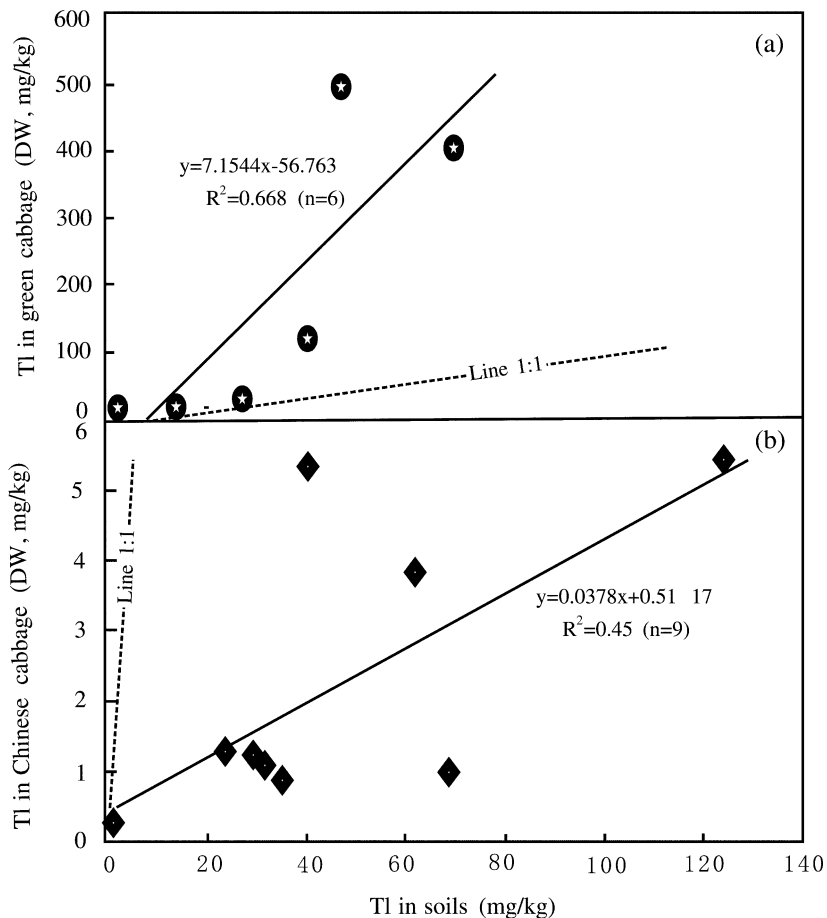


Fig. 8. Concentrations of Tl in (a) green cabbages and (b) Chinese cabbages vs. Tl concentrations in soils.

in the metal-contaminated soils during the entire year. Chinese cabbage, green cabbage and chili are often freshly consumed, whereas corn and rice are consumed after air-drying. It is possible that some Tl would be leached from the cooked crops and dissolved in the broth, but the broth is invariably consumed by the local inhabitants. The yield of metals in vegetables from fresh to dried samples was determined by dividing the DW by the fresh wt. (Table 7). Thus, by using the values of dry yield, consumption amounts of fresh vegetables and dry cereals, the contents of metals from each crop type consumed by the local villagers can be quantitatively estimated by using the following equation:

$$\text{Daily consumption} = \sum_{i=1}^m C_i R_i M_i + \sum_{j=1}^n C_j M_j$$

where i , vegetable; j , cereal; C_i , C_j are concentration of metal based on DW (mg/kg); R_i , dry yield (DW/fresh wt., %); M_i , daily consumption of fresh vegetables (kg); M_j , daily consumption of dry cereals (kg).

For this study, the daily amounts of crops harvested from the farmland with Tl–Hg–As contamination and consumed by an adult are estimated in Table 7. The estimates show that the daily ingestion of Tl (1.9 mg) through foods within the Lanmuchang study area is high compared to areas barren of Tl mineralization (the background area,

Table 7
Estimation of daily ingestion of Tl, Hg and As from crops in the Lanmuchang area

Crops	Metals	DW (mg/kg)		Fresh wt. yield (%)	Consumption amounts (kg/day)	Total ingestion of metals (mg/day)	
		LMC	BK			LMC	BK
Chinese cabbage	Tl	2.5	0.31	2.5	0.2	0.013	0.0015
	Hg	0.31	0.3			0.002	0.0015
	As	0.8	0.37			0.004	0.0019
Green cabbage	Tl	212	0.4	6.7	0.1	1.42	0.003
	Hg	0.7	0.33			0.005	0.002
	As	0.8	0.32			0.005	0.002
Chili	Tl	3	0.27	5.3	0.05	0.008	0.0007
	Hg	0.02	0.01			0.00005	0.00003
	As	0.02	0.09			0.0006	0.0005
Corn	Tl	1.4	0.07		0.1	0.14	0.007
	Hg					0.002	0.002
	As	0.020	0.02				
Rice	Tl	2.4	0.27		0.1	0.24	0.27
	Hg	0.03	0.01			0.003	0.001
	As	0.15	0.06			0.0015	0.006
Total	Tl					1.9	0.04
	Hg					0.01	0.005
	As					0.03	0.012

LMC, Lanmuchang area; BK, background area.

0.04 mg, see Table 7). The calculated ingestion rate of Tl in the human body (body wt. of an adult is considered as 70 kg) is up to 27 $\mu\text{g}/\text{kg}/\text{day}$ on average from the Lanmuchang area, which is 50 times the concentration from the background area (Table 7). However, the daily ingestion for Hg and As are 0.01 and 0.03 mg, respectively, which are lower than for Tl (Table 7). The estimated amounts ingested in the background area are 0.005 mg for Hg and 0.012 mg for As (Table 7), which are also lower than for Tl. This clearly indicates that Tl in the contaminated soils is being readily transferred to the human body through the food chain, whereas the ingestion of Hg and As from the food chain are much lower compared to Tl. Therefore, the villagers within the Lanmuchang area ingest Tl (1.9 mg/day) from local food

sources which is a rate 1000 times higher than the world average daily intake (2 $\mu\text{g}/\text{day}$) as indicated by Sabbioni et al. (1984). This high ingestion rate for Tl is also far above the element's oral RfD of 0.056 mg/day. The ingestion of arsenic (0.03 mg/day) from the local food chain is slightly above its oral RfD of 0.021 mg/day, but the ingestion of Hg (0.01 mg/day) is lower than its oral RfD of 0.021 mg/day. This clearly indicates that Tl poses a significant health risk to the local villagers, and arsenic from the food chain may have some additional health risk. However, ingestion of mercury (0.01 mg) from the local food chain is lower than its oral RfD, indicating no potential of health risk to the local villagers at this time.

The other two pathways for toxic metals to enter the local food chain may come from the drinking

water and the consumption of domestically raised animals. However, the threat posed by toxic metals in the drinking water supply has been reduced by piping uncontaminated groundwater from outside the study area since the early 1990s. Current low concentrations of Tl, Hg and As in the local drinking water are within safe limits (Xiao et al., 2003). Although appreciable amounts of Tl in the locally consumed poultry, for example chickens were measured (APASSGP and EGLIGCAS, 1974) ranging from 5.2 to 26 mg/kg (DW), the local domestic birds and animals are usually raised in small numbers (5–10 chickens and 1–2 pigs commonly raised by each family). Therefore, the principal remaining risk to the local villagers is now the consumption of locally-harvested crops. However, the Tl concentrations in livestock and their consumption need to be monitored.

The large quantities of ingested Tl certainly has adverse effects on human health in the local area of Lanmuchang. Previous epidemiological studies showed high Tl levels in the villagers' urine, ranging from 600 to 3000 $\mu\text{g}/\text{l}$ during the 1970s (Zhou and Liu, 1985) and 78–2660 $\mu\text{g}/\text{l}$ in the 1990s (Zhang et al., 1999). Within the past three decades, high Tl levels in urine of local villagers have been nearly constant. This probably reflects the continuous ingestion of Tl over the years from the local food chain. Mercury concentration in urine of local villagers ranges from 0.03 to 3.3 $\mu\text{g}/\text{l}$ and arsenic ranges from 0.1 to 6.7 $\mu\text{g}/\text{l}$ (Zhang et al., 1999). Compared to the background area, slightly higher concentrations of As relative to Hg in urine of the local inhabitants is consistent with the fact that slightly higher amounts of As (0.03 mg/day) are ingested from the locally produced foods by the villagers as compared to Hg (0.01 mg/day) (Table 7). However, all the values for Hg and As in urine are 2–4 orders lower than the Tl values. It has been reported that the elimination of Tl, Hg and As for humans is mainly through the urine (ATSDR, 1989). Based on oral dosing tests, arsenic has a high elimination rate of approximately 3 days, whereas 3–8 days are required for Tl (Zitko, 1975) and 40 days for Hg (Goyer, 1991). However, the local inhabitants mostly rely on locally produced foods, and therefore, have a long-term exposure to Tl, Hg and As.

Despite the possible different absorption rates for Tl, Hg and As by humans, the different levels of Tl, Hg and As determined in the urine may still reflect a lower ingestion of Hg and As than Tl through the consumption of local foods. Therefore, Tl is the main metal that triggers the chronic poisoning crisis. Arsenic may have some potential to exacerbate this poisoning, and Hg is not a serious threat in the Lanmuchang area at this time.

6. Conclusions

This study of the high Tl levels in soils and its uptake by plants in the Lanmuchang area highlights previously little-known facts regarding soil contamination and other environmental impacts of highly toxic Tl.

The Lanmuchang area presents a specific geo-environmental context showing high enrichment of Tl, Hg and As in soils related to mineralization of Tl–Hg–As sulfides, through both natural processes and human activities. The baseline values for Tl, Hg and As in soils are higher than their quality guidelines, showing contribution from the natural processes of erosion and/or weathering of primary sulfide mineralization. Mining activity, domestic coal use and small-scale farming activities are all responsible for augmenting Tl, Hg and As levels in the arable soils of the study area.

Thallium shows much higher levels in certain crops than Hg and As. The high accumulation of Tl in crops is due likely to the substitution of Tl for K as these two ions have similar ionic radii. This study also shows marked genotypical differences of the crops for uptake of Tl. Thallium has the highest accumulation in green cabbage, and the lowest in corn. The amounts of Ca and Mg in crops seem to be one of the factors contributing to the species-dependent degree for uptake of Tl. Due to high uptake of Tl by crops, Tl is the main metal triggering chronic poisoning of human health. Arsenic may have some potential to augment the poisoning, while mercury is an unlikely contributor to the chronic poisoning in the Lanmuchang area. The pathway of Tl entering the food chain is mainly through the consumption of the local harvested vegetables and other crops grown in the Tl-rich contaminated soils.

This study documents the reality of Tl poisoning engendered by soil contamination and Tl uptake by crops in a Tl-bearing sulfide-mineralized area. It is important to note that Tl contamination may occur in the absence of mining activity, although mining may speed the transfer of toxic elements from bedrock to the food chain. The results also contribute to our knowledge base of environmental hazards related to naturally occurring Tl and its dispersion. This information is vital for planning and monitoring land use as well as for safeguarding the health of the population. A case in point is the planting of green cabbage, which in the specific environmental context depicted by the study area should be banned in order to safeguard the health of the population.

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