High thallium content in rocks associated with Au–As–Hg–Tl and coal mineralization and its adverse environmental potential in SW Guizhou, China

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ABSTRACT: Very few investigations have dealt with the environmental impact of the highly toxic metal thallium (Tl), and its subsequent dispersion through natural processes and human activities such as mining and farming. This study is focused on high concentrations of Tl in rocks in SW Guizhou, China, that are related to several widely scattered disseminated gold–mercury–arsenic and coal deposits, and a primary Tl deposit within an Au–As–Hg–Tl metallogenic belt of the Huijiabao anticline. The Tl, Hg and As in the Lanmuchang Hg–Tl deposit area are associated with the abundant occurrence of sulfide minerals such as lorandite, realgar, orpiment and cinnabar. Concentrations of Tl range from 100 to 35 000 ppm in sulfide ores, and 39–490 ppm in host rocks. The enrichment of Au, Tl, Hg, As, and Sb in the Yanshang gold mineralized area reflects the occurrence of Au mineralization and its mineral assemblage of Tl–Hg–As–Sb sulfides. Thallium ranges from 0.22 to 16 ppm in Au ores and host rocks. Thallium in coals is enriched up to 46 ppm within the Au–As–Hg–Tl metallogenic belt, and is derived from the regional Au–As–Hg–Tl mineralization. Mercury and As show a similar distribution to Tl with high concentrations in sulfide ores, coals and host rocks.

Human populations living near and downstream of Tl deposits and Tl-bearing ore deposits are susceptible to Tl contamination because of its high toxicity and high uptake rate by crops. The dispersion of Tl, Hg and As associated with the primary mineralization of Au–As–Hg–Tl can be traced through physical erosion and chemical weathering, producing secondary dispersion into soils, groundwater and surface water and crops. Mining activities compound the natural processes, readily dispersing Tl into the surface environment. The Lanmuchang area illustrates Tl contamination related to a Tl-rich deposit due to both natural processes and the impact of mining. The Yanshang area demonstrates Tl contamination related to a Tl-bearing gold deposit, caused by natural processes in the absence of mining activity.

KEYWORDS: *thallium, environmental impacts, natural process, human activity, Guizhou, China,*

INTRODUCTION

Thallium (Tl) is a highly toxic metal (Smith & Carson 1977; Schoer 1984; Mulkey & Oehme 1993). Although widely distributed in the natural environment, Tl is generally present in low concentrations, exhibiting, for example, a mean crustal abundance of only 750 ppb (Taylor & McLennan 1985). Nevertheless, despite the characteristic low concentration of Tl, it is still more abundant than Ag (50 ppb), Cd (98 ppb) and Au (1.8 ppb) in the upper crust (Taylor & McLennan 1985). Unlike many metals, however, Tl does not occur in a native form and is rarely enriched in specific minerals. Thallium minerals are rare in nature and their deposits are so small as to have no commercial importance as a source of Tl. Thallium typically occurs in relatively high concentrations in sulfide deposits (Ikramuddin *et al.* 1986; Murao & Itoh 1992; Percival & Radtke 1993).

Previous studies in the literature considered Tl occurrence in rocks mainly as a pathfinder for gold exploration (Ikramuddin *et al.* 1983; 1986; Calderoni *et al.* 1985; Percival & Radtke 1993). High Tl concentrations have been reported from the following localities: Allchar (Yugoslavia), with Sb–As–Tl mineralization

*Deceased

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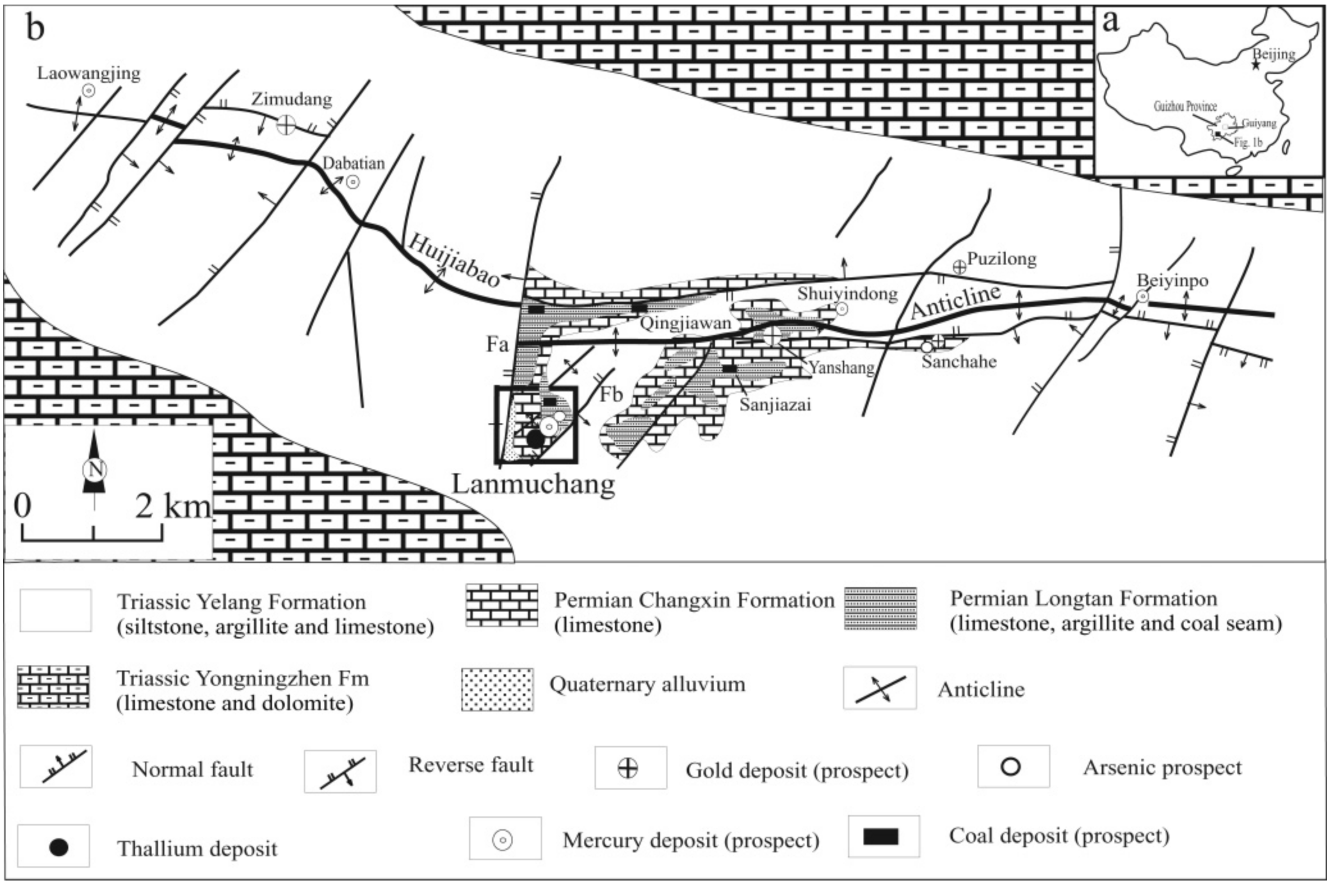

Fig. 1. Geological sketch map of Huijiabao anticline metallogenic belt in southwest Guizhou, China (modified after Wang *et al.* 1994).

(Jankovic 1989; Percival & Radtke 1994), Lengenbach (Switzerland), with Pb–Zn–As–Ba–Tl mineralization (Hofmann & Knill 1996); and in some Japanese Kuroko-type deposits (Lu 1983; Murao & Itoh 1992). Thallium distribution in various rocks and minerals has been summarized by De Albuquerque & Shaw (1972). Unfortunately, there are few detailed case studies related to the natural occurrence of Tl.

Enrichments of Tl, Hg, As and Sb associated with Carlin-type gold deposits have been recognized in SW Guizhou, China. A maximum of 100 ppm Tl was determined in the gold ores of the Sanchahe gold deposit (Cunningham *et al.* 1988). A range of 14–20 ppm for Tl in the Zimudang gold deposit was reported by Wang *et al.* (1994), compared with 0.42–0.61 ppm Tl in host rocks of the ore (Li & Peters 1998). Natural anomalies of Tl related to several widely scattered Au–Hg–As and coal deposits have been documented (Cunningham *et al.* 1988; Li & Peters 1998; Xiao 2001). Especially noteworthy is disseminated Tl mineralization, with discrete Tl ore bodies, discovered in the study area (Chen 1989a, b; Li 1996).

The absence of detailed knowledge of the dispersion of Tl, through both natural processes and human activities (e.g. mining, farming) that have produced adverse impacts on the local ecosystem and human health, is a matter of concern (Xiao 2001). Recognition of this problem promoted a multidisciplinary environmental study encompassing lithogeochemistry, soil geochemistry, hydrogeochemistry and biogeochemistry of Tl and its impacts on human health in SW Guizhou, China (Xiao 2001). This paper presents the results of an investigation into the natural occurrence of Tl in the rocks and ores of the Au–As–Hg–Tl mineralized belt of the Huijiabao anticline, and outlines the potential impacts of primary dispersion of Tl on the local ecosystem. The Lanmuchang Hg–Tl deposit, Yanshang gold deposit, and nearby coal occurrences are the specific focal points of the current study.

GEOLOGICAL SETTING AND MINERALIZATION

The east–west trending Huijiabao anticline (18 km long and 5 km wide) hosts the Au–As–Hg–Tl metallogenetic belt in SW Guizhou (Fig. 1). The western part of the Huijiabao anticline hosts the gold deposits of Zimudang and Taiping Dong, and the mercury deposit of Dabatian; the middle part hosts the Lanmuchang Hg–Tl deposit, and the eastern part hosts the gold deposits of Yanshang and Sanchahe (Fig. 1). In addition, a number of mineralized prospects for As, Hg, Tl and Au as well as coal seams occur within this metallogenic belt, including the mercury prospect of Shuiyindong, the arsenic prospect of Sanchahe, and coal deposits at Lanmuchang and Sanjiazai (Fig. 1).

The study area is made up of sedimentary rocks of Permian and Triassic age, overlain by Quaternary alluvium (Fig. 1). 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). The limbs of the Huijiabao anticline have outcrops of the Yelang Formation (T_1y) and the Yongningzhen Formation (T_1yn: limestone and dolomite). The strata are horizontal to sub-horizontal (5–20°), and the stratigraphies of the two limbs are relatively symmetrical. Around the anticlinal axis are a number of secondary folds and faults, which give rise to favourable ore-forming structures (Fig. 1).

Thallium in the study area is associated with disseminated Tl mineralization (e.g. the Lanmuchang Hg–Tl deposit), disseminated gold mineralization (e.g. the Yanshang gold deposit and the Zimudang gold deposit), and/or coal mineralization (e.g. the Lanmuchang and Sanjiazai coal deposits). Hydrothermal alteration commonly occurs as decalcification, silicification, pyritization, baritization, argillization and kaolinization in both areas (Chen 1989b; Liu 1997; Xiao 2001). Furthermore, the supergene alteration is widespread throughout the entire Lanmuchang area, whereas it is sparse in the Yanshang area.

Thallium in the Lanmuchang Hg–Tl deposit, located in the Longtan and Changxing Formations (P_2l and P_2c, respectively) is characterized by abundant Tl minerals, mainly lorandite ($TlAsS_2$). This deposit has a long mining history (about 350 years) for mercury, and has been worked exclusively for Tl in the 1990s. The deposit is located in an area *c.* 1 km wide and 1.5 km long, confined by two faults: Fa (the Lanmuchang Fault) and Fb (the Huangnijiang Fault (Fig. 1). Lorandite occurs as individual aggregates or in association with realgar–orpiment, cinnabar, pyrite–marcasite, barite and quartz. Lorandite crystals typically reach sizes of 5–20 mm, exceptionally up to 4 cm. The crystals present needle-like, columnar and radiating forms. They occur as stockworks and bands. Several other Tl minerals were also identified in the Hg–Tl deposit, including christite ($TlHgAsS_3$), imhofite ($Tl_6CuAs_{16}S_{40}$) and raguinite ($TlFeS_2$) (Chen 1989a; Li 1996; Li *et al.* 1989).

Thallium also occurs in the Yanshang gold deposit that was explored during a drilling project by a Canadian company (Denstone Minerals Ltd) in the late 1990s. This unexploited deposit is characterized as a Carlin-type deposit (Yang, personal communication, 1998), and is hosted by the P_2l Formation. Contrary to the Carlin gold deposits in the United States where many Tl minerals were identified (Ikramuddin *et al.* 1986; Percival & Radtke 1993), no Tl minerals were reported from the Yanshang gold deposit.

Tl is also present in coals. Over ten coal seams in the study area are hosted along a vertical section in the coal-bearing Longtan Formation. The coal seams stand out because of their black-grey-coloured outcrops. Sporadic artisanal mining of the coal seams is undertaken by local residents to augment their supplies of fuel for heating.

SAMPLING AND ANALYSIS

A total of 46 samples from the two deposits and coal seams were collected. Twenty-nine samples were collected from the Lanmuchang Hg–Tl deposit from surface outcrops, underground mine sites and exposed mine wastes. The sampling included secondary minerals in both underground and surface outcrops. A suite of nine rock samples was collected from drill cores at the Yanshang gold deposit. Two coal samples were collected from underground sites at the Sanjiazai area, and one sample was from the drill core at the Qingjiawan area (Fig. 1). Five background samples were collected from the area with similar rock units (mainly Formations P_2l, P_2c and T_1y) that are barren of metallic mineralization and associated alteration, including one coal sample from the underground site of Dayakou, 50 km south of the Lanmuchang area.

All rock samples were prepared for geochemical analysis by jaw-crushing to 1.5 cm, quartering and pulverizing in a ceramic disc grinder, followed by reduction to <100 mesh in a ceramic ball mill. The final product is a 20-g vial of representative powder suitable for acid dissolution or fusion.

The determination of major elements was undertaken by fused-disc wavelength dispersive X-ray fluorescence (XRF) at the Analytical Chemistry Laboratories of the Geological Survey of Canada (GSC) in Ottawa, Canada (Analytical Chemistry Laboratories 2003). However, for samples containing greater than 5% sulfur, because of problems in the production of a fused disc, major elements were determined by inductively coupled plasma–emission spectrometry (ICP-ES). For the ICP-ES method, analysis was carried out by fusing the sample with a mixed lithium metaborate–lithium tetraborate flux, dissolution of the fusion melt followed by analysis by ICP-ES. Ferrous iron was determined using the Wilson Method (titrimetric). Total sulfur was determined using combustion followed by infrared spectrometry using a LECO SC444-DR Sulphur/Carbon Determinator.

For the determination of trace elements (except for Hg, As and Au) at the GSC, the determinations were based on the total dissolution of the sample using nitric, perchloric and hydrofluoric acids followed by a lithium metaborate fusion of any residual material, and analysis by ICP-ES and inductively coupled plasma–mass spectrometry (ICP-MS). Arsenic and Au were determined by instrumental neutron activation analysis (INAA) whereas Hg was determined by cold vapour ICP-MS at Activation Laboratories Ltd in Ancaster, Ontario, Canada. The analytical precision, determined by QA/QC through the duplicates is better than 10% for major ions and trace metals.

RESULTS

The analytical results are listed in Table 1. Based on comparison with typical shale concentrations (Turekian & Wedepohl 1961; Gromet *et al.* 1984), and with the average composition of upper crust or bulk crust (Taylor & McLennan 1985; Condie 1993) and regional background values (this study), the elements Tl, Hg, As, Sb, Ba and Au are enriched, whereas Cu, Pb, Zn, Cd, Co, Ni, Cr, V and Mo show average crustal concentrations. The concentrations of the above elements indicate that Tl, Hg, As, Sb, Ba and Au are the main components of mineralization and the base metals are poorly represented in the mineralized belt of the Huijiabao anticline. In the Lanmuchang area, the element suite is represented by Tl, Hg, As, and Ba, whereas Au, Tl, As, Hg and Sb are the main elements in the Yanshang area.

Distribution of Tl and other metals in the Lanmuchang Hg–Tl deposit

Thallium enrichment is widespread in the Lanmuchang Hg–Tl mineralized area with high contents in various host rocks, ores and secondary minerals. Concentrations range from 100 to 35 000 ppm Tl in sulfide ores of Tl, Hg and As, with the highest concentrations present in Tl ores, mainly lorandite, ranging from 2.5% to 3.5%. In Tl–As ores or As ores (mainly realgar and orpiment), there is up to 1300–18 000 ppm Tl, and in Tl–Hg ores or Hg ores (mainly cinnabar) there is 100 to 490 ppm Tl. According to the distribution patterns, the sulfide assemblage of Tl–Hg–As in the Lanmuchang area is the carrier of Tl in the primary ores.

Thallium also shows high concentrations in the secondary minerals, ranging from 25 to 1100 ppm, with an average of 405 ppm. The secondary minerals occur mainly in the fault or fracture zones, due to either deep or surface weathering from leaching by briney water and rainwater (Chen 1989b). According to X-ray diffraction analysis, the secondary minerals are composed mainly of kaolinite, copiapite, epsomite, fibroferrite, pickeringite, zaherite and halotrichite (Xiao 2001).

Mine wastes on the surface contain from 32 to 2600 ppm Tl, attaining ore-grade concentrations, and the Tl minerals occur as fine particles.

Table 1. *Selected analytical results for trace and major elements in rocks from the Huijiabao Au–Hg–As–Tl metallogenic belt in SW Guizhou*

Sample no.	Rocks/ores	Tl	Hg	As[a]	Ba	Cd	Cr	Sb	Cu	Pb	Zn	Mo	Rb	Cs	Sr	Au[a] (ppb)	Al_2O_3 (%)	Fe_2O_{3t}[b] (%)	MnO (%)	CaO (%)	K_2O (%)	S_t[c] (%)
Lanmuchang area																						
Outcrops																						
98R-107	Argillite	53	400	15.1	360	nd	78	0.7	nd	15	6	1.3	25	1.5	4700	nd	9.4	0.9	nd	0.07	0.48	2.07
98R-146	Siltstone	330	130	240	1700	nd	90	0.5	21	11	7	0.6	14	4.4	2200	2	7	1.8	nd	0.05	0.25	1.29
98R-169	Argillite	71	120	311	1600	nd	110	0.7	23	9	11	2.2	25	2.3	810	4	14.8	2.2	nd	0.04	0.47	0.73
98R-199	Siltstone	25	21	16.3	390	0.3	73	5.0	nd	7	56	0.9	31	1.7	1800	nd	10.4	0.6	nd	0.04	0.84	0.32
99R-205	Limestone	8.3	0.14	2.8	nd	nd	23	nd[d]	nd	nd	58	0.3	0.25	0.03	980	nd	nd	0.3	0.07	54.89	0.01	0.07
98R-332	Clay stone	6	9	50	7000	nd	89	0.6	29	5	7	0.5	7.6	3.1	770	nd	4.6	5.8	nd	0.66	0.13	0.30
Secondary minerals																						
98R-126	Halotrichite	25	39	331	242	0.9	80	4.2	86	2	84	6.4	2.6	0.76	231	nd	5.90	15.40	0.03	0.16	0.10	11.3
98R-139	Kalinite	89	30	416	354	0.3	127	0.4	64	11	141	1.1	60	5.8	1668	nd	11.80	9.37	nd	0.15	1.33	7.24
98R-198	Jarosite	1100	370	217000	1880	nd	38	1.5	28	2	8	3.4	8.8	1.4	248	nd	1.20	3.48	nd	0.12	0.21	19.5
Host rocks																						
98R-103	Argillite	200	65	786	1060	0.5	98	0.7	101	14	164	1.2	76	6.0	2405	15	13.6	10	nd	0.13	1.68	8.28
98R-108	Argillite	210	34	185	1970	0.4	113	0.5	89	11	74	0.9	74	5.9	1108	nd	13.1	7.55	nd	0.1	1.42	5.9
98R-109	Siltstone	47	na[e]	na	140	nd	89	0.3	28	4	50	1.3	11	2.9	500	na	6.5	1.5	nd	0.04	0.23	1.39
98R-117	Argillite	490	68	755	445	0.6	126	0.7	69	11	205	4.6	70	4.6	2637	3	13.8	14.5	nd	0.10	1.62	11.8
99R-118	Argillite	48	na	na	860	0.4	72	12	18	2	17	2.6	4.6	1.2	950	na	2.7	1.2	nd	0.36	0.1	1.77
98R-174	Siltstone	39	na	na	6420	nd	94	18	126	7	39	1.2	69	6.8	2124	na	15.3	8.62	nd	0.09	1.32	6.64
Ores																						
98R-113	As ore	1300	280	442000	4420	nd	27	2.0	18	nd	16	nd	2.6	0.7	164	nd	0.6	1.47	nd	0.11	nd	25.6
98R-119	Tl ore	35000	120	11500	5460	0.4	88	0.7	113	4	234	0.5	18	3.6	611	nd	7.8	13.2	nd	0.1	0.37	12.1
98R-181	Hg ore	490	12000	735	2810	nd	61	4.4	nd	26	nd	1.0	46	4.8	659	48	12	1.75	nd	0.08	0.87	2.59
98R-173	Coal	12	1.88	15.4	2970	0.5	nd	1.3	28	6	40	13	6.8	1.4	nd	nd	2.1	3.49	0.01	3.83	0.27	3.02
98R-190	Tl-As ore	4400	120	3600	2240	nd	112	1.3	96	8	156	0.9	37	3.4	622	74	11.7	12	nd	0.09	0.87	10.2
98R-192	Tl ore	31000	95	11300	6490	nd	102	0.8	91	10	156	5.0	42	4	2884	36	13.7	11.6	nd	0.1	0.99	11.1
98R-193	Tl ore	25000	na	na	21300	nd	111	3.2	112	9	150	1.4	38	5	1340	na	8.2	16.2	nd	0.13	0.97	15.2
98R-196	Tl-Hg ore	100	94000	996	1970	nd	28	12.0	20	46	36	5.7	0.86	0.49	1030	nd	6.1	7.28	nd	0.35	0.05	11
98R-208	Coal	46	3.9	183	1260	0.6	18	1.3	36	4	227	6.8	4.5	1.5	22	nd	10.8	0.88	nd	0.68	0.16	1.98
98R-334	Tl-As ore	18000	1500	79800	8950	0.6	75	1.5	133	12	107	28	27	3.2	2054	nd	14.8	9.7	0.01	0.2	1.5	8.03
98R-333	Tl-Hg ore	130	na	na	383	nd	105	10.0	139	12	104	1.9	53	14	1870	na	5.6	8.56	0.01	0.15	0.6	13
Mine wastes																						
99S-111	Argillite	32	63.7	56.4	5700	nd	103	1.4	33	14	19	2.6	97	9.9	1000	na	14.3	3.6	nd	0.01	1.73	3.27
99S-162	Argillite	136	188	261	3800	0.2	117	14	56	22	42	7.4	53	7	650	na	11.7	9.4	0.01	1.42	1.5	2.56
99R-206	Fault gouge	2600	87	1290	1520	nd	106	0.6	63	9	125	0.9	47	3.4	2570	53	12.3	5.59	nd	0.09	1.11	3.59
Yanshang area																						
98R-281	Au ore	3.6	17	5000	360	0.3	173	43	147	11	163	4.8	130	17	330	4050	16.4	12.1	0.24	0.08	3.68	nd
98R-299	Siltstone	16	27	350	6200	1.5	54	247	17	4	83	35	2.8	2.6	110	237	1.1	4.1	nd	3.36	0.08	3.5
98R-300	Pyrited siltstone	2.5	7	1280	424	nd	155	23	108	14	180	1.3	70	11	167	239	13.9	19.4	0.04	1.81	3.33	14.9
98R-301	Au ore	1.1	na	na	88	nd	50	7.3	40	6	56	0.9	17	1.7	660	na	3.2	12.2	0.55	20.34	0.71	2.19
98R-302	Au ore	1.6	4	2910	25	nd	21	11	27	2	53	0.4	0.52	0.08	310	43500	0.1	6.6	0.25	24.54	0.03	3.23
98R-304	Au ore	0.22	nd	373	nd	nd	28	1.3	11	nd	53	nd	0.44	0.14	320	6230	0.1	2.6	0.18	22.01	0.02	0.36
98R-305	Argillite	3.1	16	1230	244	nd	95	27	201	21	101	2.7	49	6.6	137	414	9.5	26.6	0.07	3.52	2.27	20.3
98R-306	Coal	0.3	na	na	34	0.4	nd	nd	56	8	42	36	12	3.3	nd	na	2.4	4.59	0.04	6.87	0.43	3.33
98R-308	Coal	1.2	nd	56	203	1.7	9	0.7	63	5	51	14	14	7.2	17	nd	3.7	14	0.02	1.16	0.49	11.8

Table 1. *continued*

Sample no.	Rocks/ores	Tl	Hg	As[a]	Ba	Cd	Cr	Sb	Cu	Pb	Zn	Mo	Rb	Cs	Sr	Au[a] (ppb)	Al_2O_3 (%)	Fe_2O_{3t}[b] (%)	MnO (%)	CaO (%)	K_2O (%)	S_t[c] (%)
Sanjiazai area																						
98R-156	Coal	8.4	10	226	nd	0.5	nd	22	17	5	19	16	3.4	1.6	nd	nd	0.9	13.5	0.01	0.36	0.16	11
98R-210	Coal	5.7	na	na	nd	10.0	nd	13	27	8	27	7.1	3.5	1.5	nd	na	1	12.6	0.01	1.22	0.14	10.2
Qingjiawan area																						
98R-307	Coal	0.31	nd	12.2	86	2.0	14	0.5	86	9	45	16	21	11	12	nd	4.2	7.37	0.01	1.1	0.79	5.61
Background area																						
98R-152	Coal	0.16	nd	14.9	111	0.4	nd	nd	64	7	84	2.3	13	0.73	nd	nd	3.1	22	0.23	2.07	0.43	18.4
98R-180	Limestone	nd	na	na	nd	nd	11	0.5	nd	nd	58	nd	2.4	0.16	462	na	0.3	0.41	0.03	50.9	0.05	0.04
98R-184	Siltstone	0.06	na	na	190	nd	194	1.9	32	5	81	0.2	26	5.5	640	na	6.6	6.8	0.06	28.17	1.12	0.02
98R-185	Limestone	nd	0.06	2.6	nd	nd	nd	nd	nd	nd	58	nd	1.6	0.02	1122	nd	0.3	0.32	0.02	52.5	0.13	0.08
98R-186	Clay stone	0.2	na	na	190	nd	281	nd	92	13	137	0.6	52	1.9	87	na	14.2	10.7	0.45	0.52	1.65	nd
NASC[f]					636		125	2.1					125	5.16	142							
Upper Crust[g]					626		112			18			87		269							
Continent crust[h]		0.45			425	0.2	100	0.2	55	13	70	1.5	90		375							
Shale[i]		1.40			580	0.3	90	1.5	45	20	95	2.6	140	5	300							
Carbonate[j]		0.0x			10	0.0	11	0.2	4	9	20	0.4	3		610							

[a]Units in ppm except where indicated
[b]As and Au are determined by INAA, and the other trace elements by ICP-MS
[c]Fe_2O_{3t} as total Fe
[d]S_t as total sulfur
[e]Not detected (nd)
[f]Not analysed (na)
[g]Gromet *et al.* (1984)
[h]Condie (1993)
[i]Taylor (1964)
[j]Turekian & Wedepohl (1961)

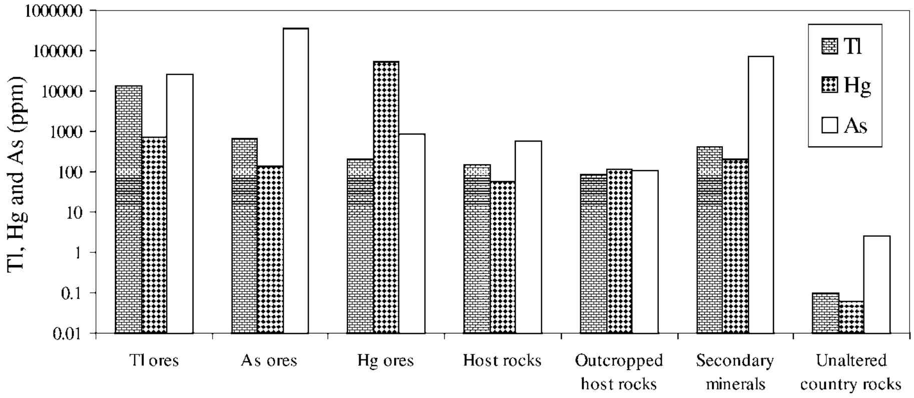

Fig. 2. Average concentration distribution of Tl, Hg and As in various rocks/ores in the Lanmuchang area.

The concentrations of Tl in the altered host rocks range from 39 to 490 ppm, with an average concentration of 152 ppm. In outcrop samples (mainly siltstone, claystone and limestone), concentrations of 6 to 330 ppm Tl are recorded, of which the highest value is related to the occurrence of secondary minerals in fractures (Xiao 2001). Unaltered country rocks from the background area yielded average levels of 0.1 ppm.

From the above results it is apparent that the dispersion of Tl decreases from: thallium ore > arsenic ore > secondary mineral > mercury ore > unexposed altered host rocks > outcropped altered host rocks > unaltered country rocks (Fig. 2).

Mercury and As both show similar distributions to Tl in host rocks and ores (Fig. 2). They have high concentrations in sulfide ores and the secondary minerals. The highest values are up to ore-grade, with 9.4% Hg and 44.2% As. In altered host rocks, these two elements are both enriched, whereas they are quite low in the unaltered country rocks from the background area. Barium is highly enriched in both altered host rocks and sulfide ores of Tl–Hg–As relative to the unaltered country rocks. The high Ba can be explained by the presence of barite in the Tl–Hg–As mineralization in the Lanmuchang area (Xiao 2001).

Distribution of Tl and other metals in the Yanshang gold deposit

The geochemistry of rocks/ores in the Yanshang area is characterized by enrichment of Tl, Hg, As and Sb in sulfide minerals associated with the gold mineralization. Concentrations of Au range from 237 ppb to 43 500 ppb, representing values higher than the commercially targeted gold ore-grade 3–10 g/t in this area (Liu 1997; Ran 1999). The gold ore bodies are at a depth of 300–400 m from surface (Liu 1997), and they have yet to be mined.

Thallium is present in the country rocks at levels of 0.22 to 16 ppm, with an average of 4 ppm, and the highest value of 16 ppm (sample 98R-299) is from the host-rock containing 237 ppb Au. Because of the limited access to the drill-core samples for this study, the above Tl values must serve to represent the primary gold ore zone obtained from selected drill-holes.

Thallium seems to have good correlations with Fe and S in rocks and ores in the Yanshang area (Fig. 3). Because Tl sulfide minerals have not been identified from these Carlin-type gold deposits in SW Guizhou, Tl is thought to be enriched in the pyrite-rich host rocks and gold ores. Thallium also correlates well with K and Rb in the rocks/ores (Fig. 4). The correlation probably reflects the abundance of argillite and siltstone in which Tl may substitute for K and Rb. Note that there is an outlier sample (98R-299) that does not follow the trends of the other samples in Figures 3 and 4. The sample with the highest value of Tl (16 ppm) also contains the highest contents of Ba (6200 ppm) and Sb (247 ppm). This is probably due to the mineralization of barite and stibnite associated with the gold mineralization.

Mercury, As and Sb are also enriched in the host rocks and gold ores in the Yanshang area, with abundances of 4–27 ppm Hg, 350–5000 ppm As, and 1.3–247 ppm Sb, especially in cinnabar, arsenopyrite, arsenic-bearing pyrite or marcasite, and stibnite, respectively. The occurrence of needle-like arsenopyrite from the sampled drill-cores contributes to the high contents of arsenic. Cinnabar in the sulfide minerals is the main source of Hg in rocks. Stibnite was also identified from the cores.

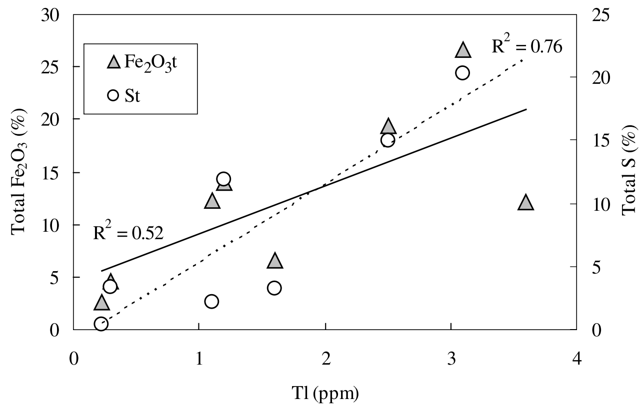

Fig. 3. Plot of total Fe_2O_3 and total S versus Tl contents in rocks/ores of the Yanshang gold mineralized area.

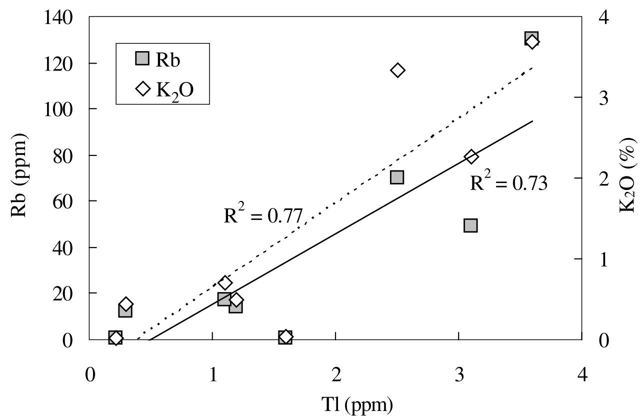

Fig. 4. Plot of K_2O and Rb versus Tl contents in rocks of the Yanshang gold mineralized area.

Table 2. *Abundance distribution of ore-forming elements in the ore-host strata of Tl deposits (prospects) in southwestern Guizhou (Chen* et al. *1996)*

Strata	Sample number	Tl (ppm)	Hg (ppm)	As (ppm)	Sb (ppm)	Au (ppb)
T_1y	70	8.52	14.4	26.9	2.54	8.28
P_2c+P_2d	39	4.9	0.81	43.3	3.05	8.18
P_2l	31	1.38	4.11	172.9	2.49	72.9
Upper crust[a]		0.75	0.4[b]	1.5	0.2	1.8

[a]Taylor & McLennan (1985)
[b]Turekian & Wedepohl (1961)

Distribution of Tl and other metals in coals

Coals contain 12 to 46 ppm Tl in the Lanmuchang area, 0.30–1.2 ppm Tl in the Yanshang area, and 5.7–8.4 ppm Tl in the Sanjiazai are. One coal sample from the Qingjiawan area contains 0.31 ppm of Tl, and another sample from the background area exhibits a lower value of 0.16 ppm.

Mercury and As in coals from the Lanmuchang area range from 1.9 to 4 ppm and 15 to183 ppm, respectively. Mercury in coals from the Yanshang area was not determined, but As contents range from 56 to 226 ppm.

Thallium contents in coals are generally low (Swaine 1990). However, Tl in coals from this study clearly shows much higher concentrations than those in coals elsewhere in China (Feng *et al.* 1999; Zhuang *et al.* 1999) and worldwide (Swaine 1990). The concentration of Tl in coals in northern China generally ranges from 0.15 to 0.88 ppm (Zhuang *et al.* 1999), and 0.10 to 0.73 ppm in western and central Guizhou Province, respectively (Feng *et al.* 1999). Thallium in coals worldwide was estimated to be <0.2–1 ppm by Swaine (1990). The enrichment of Tl in coals in the study area is likely attributable to the regional mineralization of Au–As–Hg–Tl. Coals affected by the Lanmuchang Hg–Tl mineralization show the highest contents of Tl, whereas coals from the background area barren of metallic mineralization contain very low Tl (Table 1).

DISCUSSION

Sources of Tl in rocks/ores and factors controlling its dispersion pattern

Compared to their abundances in the upper crust (Table 2), Tl, Hg, As, Sb and Au are the most enriched ore-forming elements in the rock units of Permian to Triassic age in the study area, as evident from the study of trace element geochemistry of various strata (Chen *et al.* 1996), regional mineral resources exploration (Guizhou Geological Bureau 1990) and stream sediment mapping (Yang 1999).

The disseminated Tl ore bodies in the Lanmuchang mineralized area (Chen 1989b; Xiao 2001), which are relatively rare worldwide, are evidently the source of Tl contributing to high concentrations of Tl in rocks and ores. The appreciable amounts of Tl occur mainly in lorandite, Tl-bearing sulfides realgar, orpiment, cinnabar, pyrite or marcasite (Li 1996). In the Yanshang area, the mineralizing process related to the Carlin-type gold mineralization generally rich in Hg, As, Sb and Tl (Li & Peters 1998), contributed to high Tl contents in the sulfides or coals, in spite of the fact that visible Tl minerals were not identified.

The distribution of Tl in various rocks and ores in the study area highlights abnormally high contents of Tl due to natural mineralizing processes. Thallium with high concentrations in rocks and ores can be dispersed into the surface environment through physical erosion and chemical weathering, thus giving rise to secondary dispersion into soils, groundwater and surface water in the surrounding or downstream areas.

Because of hydrothermal alteration and the presence of sulfide minerals, primary ore zones are generally more easily eroded than unaltered rocks (Li & Peters 1998). Decalcification, a common mode of alteration in the mineralized areas under study, causes host rocks to be porous and permeable. Brittle siliceous rocks (chert, quartz, arenite, etc.) are also commonly fractured and become permeable. They, in turn, facilitate flow of shallow groundwater to great depths. Karst conduits or caves, that also facilitate groundwater flow, are common in the karstic southwestern area of Guizhou (Xiao 2001; Xiao *et al.* 2003). These metal-rich host rocks thus release Tl into groundwater by meteoric water flow through fault or fracture zones (Xiao *et al.* 2003). The migrating groundwater can disperse Tl to deeper groundwater circulation or discharge Tl to surface waters (Xiao *et al.* 2003). The rainwater leaching through the surface fractures also dissolves some Tl from the rocks and forms secondary minerals in the fractures or rock surface by evaporation during the dry season (Xiao 2001; Xiao *et al.* 2003). The dual interaction of leaching and evaporation leads to more Tl-bearing sulfates releasing Tl into the ambient ecosystem over time. The abundance of rainfall and a warm, humid climate in SW Guizhou facilitates this cycle.

The natural dispersion pattern of Tl originating from rocks is accentuated by human disturbance. The human impacts consist of mining activity that produces rock exposures, mine wastes and acid mine drainage, and farming activity (Xiao 2001). The Tl-rich mine wastes exposed on the surface are a direct source of Tl contamination. Leaching or weathering of these mine wastes easily disperses Tl into the ambient and downhill soils and groundwater and surface water. These anthropogenic factors overlap the natural processes of Tl dispersion as discussed above and compound the contribution of Tl in the ecosystem. The dispersion of Tl, Hg and As in the Lanmuchang area from the primary rocks/ores to the surrounding and downstream soils, sediments, groundwater and surface water and crops is an excellent case indicating the contribution of both natural processes and mining and farming activities (Xiao 2001; Xiao *et al.* 2003, 2004). However, the Yanshang area constitutes a case of Tl dispersion through natural processes only, without disturbance from mining, which can be used as environmental baseline.

Potentials of adverse environmental impacts of Tl dispersion from primary source

Thallium, Hg and As are elements with a high potential for adversely affecting the environment and hence require particular attention (Fergusson 1990). High contents of Tl, Hg and As associated with the Au–As–Hg–Tl–coal mineralization of the Huijiabao metallogenic belt is a concern for environmentally sound socio-economic development. The importance and significance of the high environmental threat of Tl is characterized by its high toxicity (Smith & Carson 1977; Schoer 1984; Mulkey & Oehme 1993), low safe limits for drinking water and

Table 3. *Environmental quality guidelines for Tl, Hg and As*

Elements	Countries	Arable soils (mg/kg)	Drinking water (μg/l)
Tl	Canada[a]	1	
	US-EPA[b]		2
Hg	Canada[a]	6.6	1
	China[c]	0.3-1.0	1
	US-EPA[b]		2
As	Canada[a]	12	25
	US-EPA[b]		10
	China[c]	20-40	50

[a]CCME (1999)
[b]USEPA (2003)
[c]China-EPA (2003)

agricultural soils (Table 3) and its high accumulation in certain crops (Table 4). The residents in SW Guizhou rely heavily on limited and interactive local resources such as farmland, local crops, groundwater, coal (for energy) or mining (for their subsistence). The residents are closely tied to the surrounding Tl-high environment and the endemic diseases related to Tl contamination can affect the population directly. For instance, chronic Tl poisoning, discerned in the Lanmuchang area in the 1960s and 1970s, is an obvious endemic case related to the mining for Hg ore cinnabar (Liu 1983; Zhou & Liu 1985). Thallium poisoning, which has affected a large portion of the population and caused symptoms such as hair loss, body aches, reduced vision and blindness, is deemed to be largely due to high concentrations of Tl in vegetables and in drinking water related to pollution caused by mining activity (Liu 1983; Zhou & Liu 1985; Zhang *et al.* 1997). However, in the above-mentioned studies, there were no attempts to establish an interactive link between ores, rocks, water and soils leading to the contamination of the food chain.

Xiao *et al.* (1999, 2003) have shown that surface and groundwater associated within the Huijiabao Au–As–Hg–Tl metallogenic belt contain elevated concentrations of one or more of the elements Tl, Hg and As, and cause downstream dispersion of these metals. For instance, the groundwater-related Tl transfer processes from the Lanmuchang Hg–Tl mineralized area produced a wide dispersion downstream from the source, and poses a health risk to the local ecosystem. The distribution of Tl in the Lanmuchang aqueous system corresponds to the groundwater transfer processes, and shows specific patterns (Xiao *et al.* 2003). First, there are high levels (13.4–1102 μg/l Tl) in deep mine groundwater within the Tl mineralized area, with a decreasing trend away from this area to the background level (0.005 μg/l). Secondly, a stream supplied by discharge of groundwater from the mineralized and surrounding areas, indicates higher Tl levels downstream (3.1–33 μg/l) than upstream (0.76–0.99 μg/l) and mid-stream (1.4–2.1 μg/l) portions. The source of Tl in the stream water is from the groundwater transport of Tl from the leaching of Tl-rich sulfides or rocks, and possible Tl-rich soil water seepage. The markedly high levels of Tl in downstream reaches are probably caused by unidentified discharge of deep groundwater through fracture zones at the south margin of the Tl mineralized area (Xiao *et al.* 2003). The well waters supplying drinking water showed much lower levels of Tl (0.12–0.38 μg/l) (Xiao *et al.* 2003) compared to concentrations of 17–40 μg/l Tl detected by Zhou & Liu (1985). It can be argued that the groundwater recharging the wells is restricted to a very localized aquifer having depleted its Tl content over the years, that is, the oxidation process of Tl-bearing sulfides or host rocks actually tends to deplete the bonded Tl over time, and thus release less Tl into the groundwater recharging to the wells with time (Xiao *et al.* 2003).

Distribution of Tl, Hg and As in soils is mainly from the natural sources of weathering products and slope wash materials (Xiao *et al.* 2004). It involves Tl (Hg, As)-rich weathering products migrating downslope to deposit in the arable soils or valley alluvium and thus producing a toxic metal redistribution and enrichment. Distributions of Tl, Hg and As in various soils in both the Lanmuchang and the Yanshang areas are shown in Table 5. Thallium contents in both areas are higher than the world average level of 0.2 ppm (Bowen 1979), soil levels of 0.29–1.17 ppm in China (Qi *et al.* 1992), Canadian soil values, 0.25–0.71 ppm (Mermut *et al.* 1996), and the safe limit (1 ppm) in soils (CCME 1999).

Thallium also shows a distinct distribution pattern in the edible parts of vegetables and cereals grown in the Lanmuchang area whereas all the crop plants from the background area (without the effect of mineralization and alteration) contain much lower Tl contents, generally down to 0.5 ppm. (Table 4; Xiao 2001; Xiao *et al.* 2004). Enrichment of Tl is species-dependent, that is, the highest enrichment of Tl is in green cabbage with 338 ppm (dry weight) on average. Thallium in chilli averages up to 4.1 ppm. In shelled rice and Chinese cabbage, Tl contents average 2.4 ppm and 2.2 ppm, respectively. Finally, Tl in corn has an average of 1.5 ppm. In crops, Tl is more enriched than its counterparts Hg and As (e.g. 338 ppm Tl, 0.63 ppm Hg, and 0.7 ppm As in green cabbage), showing its

Table 4. *Distribution of thallium in various crops*

Plants	Locality	Tl (ppm)[a]	Reference
Carrot	Non-contaminated area, Germany	0.02-0.25	Schoer (1984)
Green cabbage	Near a cement factory, Germany	45	Allus *et al.* (1987)
Cereal grain	Near a cement factory, Germany	9.5	Allus *et al.* (1987)
Edible plants	Worldwide	0.02-0.125	Smith & Carson (1977)
Mushroom	Europe	<0.25-5.5	Sager (1998)
Mushroom	Japan	0.001-0.34	Sager (1998)
Green cabbage	Lanmuchang, Guizhou	338	Xiao (2001)
Chinese cabbage	Lanmuchang, Guizhou	2.2	Xiao (2001)
Chinese cabbage	Yanshang, Guizhou	0.79	Xiao (2001)
Chili	Lanmuchang, Guizhou	4.1	Xiao (2001)
Rice	Lanmuchang, Guizhou	2.4	Xiao (2001)
Corn	Lanmuchang, Guizhou	1.5	Xiao (2001)
Fresh fruits and vegetables	Germany	0.1 (FW)[b]	Sager (1998)

[a]All concentrations are DW except where indicated (DW, dry weight; FW, fresh weight)
[b]Regulated tolerance level

Table 5. *Distributions of Tl, Hg and As in various soils in both Lanmuchang and Yanshang areas*

Area	Soil[a]	Tl (mg/kg) Range	Average	Hg (mg/kg) Range	Average	As (mg/kg) Range	Average
Lanmuchang	Soils in mine area (16)	53-282	120	122-505	249	153-504	247
	Alluvial deposits (16)	21-100	54	40.2-950	258.8	54.4-586	212.4
	Undisturbed soils (7)	2.2-29	10.8	0.8 -61.8	21.3	37.1-89.1	58.6
Yanshang	Undisturbed soils (6)	0.94-1.4	1.1	3.07-22	6.8	42.4-408	244

[a]Number in the parentheses refers to sample numbers

preferential uptake in green cabbage (Xiao *et al.* 2004). This is most likely caused by the substitution of Tl for K in crops (Xiao 2001; Xiao *et al.* 2004). The substitution is due to the fact that Tl and K have similar ionic radii – 1.59 Å for Tl^+ and 1.51 Å for K^+ (Shannon 1976).

The Yanshang gold-mineralized area has not yet been mined. Soils show concentrations of 1.1 ppm for Tl, 244 ppm for As, and 6.8 ppm for Hg (Table 5). These values are all above their safe limits for agricultural land use regulated by Canada (Table 3, Table 5). Concentrations of toxic metals in waters are all under the drinking water limits, that is, 0.2 μg/l for Tl, 1.5 μg/l for As and 0.51 μg/l for Hg (T. Xiao, unpublished data). Although levels of Tl, Hg and As in crops are not as high as those in the Lanmuchang area (0.79 ppm for Tl, 0.54 ppm for As and 0.04 ppm for Hg based on dry weight in Chinese cabbage: T. Xiao, unpublished data), a level of 0.79 ppm Tl is still higher than the values 0.02–0.125 ppm for edible plants (Smith & Carson 1977) and 0.04–0.125 ppm Tl for world value for cabbage (Ferguson 1990). The high concentrations of Tl in soils and crops in the Yanshang area indicate a natural contribution of Tl–Hg–As associated with the Yanshang Carlin-type gold mineralization. Therefore, levels of Tl, Hg, As and other trace elements in the Yanshang ecosystem are useful baseline markers for future environmental monitoring and assessment. Mining for primary Au ore rich in Tl, Hg and As has significant potential for adverse environmental impacts unless the above facts are taken into account during the planning stages.

Coals in the Au–As–Hg–Tl metallogenic belt are also an important host for the toxic elements Tl, Hg and As entering into the surface environment during the natural formation processes and subsequent mining operation and their domestic use (Xiao 2001). Leaching or weathering of coal mine wastes can also supply these metals into the surface environment (Feng *et al.* 1999; Zhuang *et al.* 2000). In addition, coal combustion produces amounts of ash that may still contain amounts of Tl, and this ash is commonly used for paving village roads or used as a farming land additive, producing an additional Tl dispersion process (Xiao 2001).

CONCLUSIONS

The current study of Tl contents in rocks and the high potential of environmental impact associated with the Au–As–Hg–Tl mineralization have brought to light previously little-known facts regarding adverse environmental impacts of Tl.

The Huijiabao metallogenic belt in SW Guizhou is a specific geological environment containing high enrichments of Tl, Hg and As related to disseminated sulfide mineralization and the widely distributed Carlin-type gold mineralization. The sulfide mineralization is mainly characterized by abundant occurrences of lorandite, cinnabar, realgar, orpiment, and pyrite or arsenopyrite. Enrichment of Tl in coals is mainly related to the regional Au–As–Hg–Tl mineralization. Mercury and As both show similar distribution patterns to Tl in the rocks and ores.

Naturally occurring Tl associated with sulfide and Carlin-type gold mineralization has great potential of adverse environmental impacts on the ecosystems because of the high toxicity of Tl and its high uptake by certain crops. Thallium in rocks and ores associated with Tl deposits in the Lanmuchang area provides an excellent case of Tl contamination due to both natural processes and impacts of mining and subsequent land use. The Tl contents of the groundwater, soil and crops show that Tl is being transferred from rocks and ores of mineralized areas. This dispersion is absent in background areas devoid of alteration and mineralization. Moreover, the presence of Tl in rocks associated with a Carlin-type gold deposit in the Yanshang area demonstrates a good case of Tl contamination due to natural processes without mining activity.

This study underlines the fact that Tl deposits and Tl-bearing mineral deposits, with or without mining activities, are potential health hazards and need to be considered in a geo-environmental context prone to Tl dispersion. The results also contribute to our knowledge base of environmental hazards related to naturally occurring Tl and its dispersion, vital for planning and monitoring land use as well as safeguarding the health of the population.

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