Groundwater-related thallium transfer processes and their impacts on the ecosystem: southwest Guizhou Province, China

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Abstract

The small karstic watershed of Lanmuchang, in a Hg–Tl mineralized area in SW Guizhou Province, China, exhibits an enrichment of toxic Tl in groundwater and related stream water. This affords an excellent demonstration of the natural processes of Tl dispersion, and the resultant impact on the local ecosystem. The distribution of Tl in the water system follows a decreasing concentration pattern from deep groundwater to stream water to shallow groundwater. Tl shows high levels (13–1100 µg/L) in deep groundwater within the Tl-mineralized area, decreasing with distance away from the mineralized area to background levels (0.005 µg/L). The distribution of Tl in the water system is constrained by Tl mineralization, water–rock interactions and hydrogeological conditions. Tl concentrations in waters generally correlate with concentrations of total dissolved solids, sulphate, Ca and pH values, suggesting the contribution of water-rock interactions to water geochemistry. Water–rock interactions are driven by weathering of Tl-bearing sulfides which decreases pH values in groundwater, and by dissolution of limestone enhanced by acid fluids. Tl in stream water in both the base-flow and flood-flow regimes shows higher concentrations than it does in shallow groundwater that serves as the stream's source (mainly springs, dug-well flows and karstic cave waters). Concentrations of Tl in stream water in the flood-flow regime are generally lower than in the base-flow regime due to dilution effects, but those in the waters of mid-stream are almost the same as in the base-flow regime, probably due to contribution from Tl-rich soil water seepage or from acid mine drainage (AMD). Unexpectedly, Tl concentrations in stream water in both regimes are remarkably higher (2–30 fold) downstream than up- and mid-stream. These pronounced increases of Tl concentration are likely caused by unidentified discharges of deep groundwater through fractured zones to the downstream trace. The groundwater-related Tl transfer processes affect the ecosystem through contamination of water supply and arable soil and ultimately the food chain with undoubted risks to human health. Therefore, the results of this study are important for environmental planning and regulations, and will also serve as baseline data for future research on Tl natural dispersion processes.
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1. Introduction

Thallium is one of the most toxic metals and causes chronic and acute poisoning (Zitko, 1975a; Schoer, 1984). It is more toxic to mammals than Hg, Cd, Pb, Cu or Zn, and it is known to have caused many accidental, occupational and therapeutic poisonings since its discovery in 1861 (Zitko, 1975a; Smith and Carson, 1977; Mulkey and Oehme, 1993).

Thallium is widely distributed in the natural environment, but it is generally present in very low concentration. The mean abundance of Tl in the earth's crust is 0.75 µg/g (Taylor and McLennan, 1985), 0.001–0.25 µg/

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L in groundwater (Banks et al., 1995), 0.001–0.036 μg/L in lake water (Cheam et al., 1995; Lin and Nriagu, 1999), and 0.012–0.016 μg/L in seawater (Flegal and Patterson, 1985). Thallium minerals are very rare in nature and their deposits are too small to have a commercial importance as a source of Tl. The metal occurs in relatively high concentrations in some sulfide deposits. For instance, Tl contents range from 100 to 1000 μg/g in realgar of the Lojane deposit in Yugoslavia (Jankovic, 1989) and from 4 to 1300 μg/g in galena and sphalerite of the Truskavets deposit in Ukraine (Voskresenskaya, 1969). Thus, Tl is often recovered as a minor by-product of Zn, Pb, Cu and Fe smelters and from H_2SO_4 plants (Zitko, 1975b; Schoer, 1984). Previous studies in the literature on the effects of Tl on aqueous systems are mainly related to sulfide mineralization and commercial recoveries (e.g. Magorrian et al., 1974; Zitko, 1975b; Schoer, 1984), but studies of Tl dispersion through aqueous systems associated with specific Tl mineralization are few. Compared to such elements as As, Hg, Cd, Pb and Zn, the occurrence and mobility of Tl in aqueous systems is much less studied, despite its high toxic potential.

A rural area in SW Guizhou Province, China, known to have high Tl accumulation in rocks and ores, has been targeted for study. The Hg–Tl mineralized area of Lanmuchang in Xingren County constitutes the study area. It has one of the world's highest-known enrichments of Tl due to the presence of the high Tl-bearing mineral lorandite ($TlAsS_2$) (Chen, 1989a,b). In the 1960s–1970s, Lanmuchang, with a population of approximately 1000 people, was affected by endemic Tl poisoning (APASSGP and EGLIGCAS, 1974; Liu, 1983; Zhou and Liu, 1985). The poisoning, which affected a large portion of the population and caused symptoms such as hair loss, body-aches, reduced vision and blindness, was thought largely to be due to Tl contamination in drinking water and vegetables (Zhou and Liu, 1985), although the other toxic elements As, Hg, Sb, etc. were not considered in the studies. Even though piped water from outside the study area has provided adequate drinking water since the early 1990s, a portion of the villagers (around 40% of the population) still rely on cheaper dug-wells or springs close to the mineralized area, and all rely on the natural water sources for agricultural and domestic uses.

Previous research on Tl has focused on rocks and minerals (Chen, 1989a,b; Chen et al., 1996; Li, 1996), and some environmental studies have considered the Tl poisoning issues (Zhou and Liu, 1985; Zhang et al., 1997), but the study of hydrogeology and groundwater-related metal transfer has been limited, and the extent of hydrogeochemical transfer processes, both natural and irrigational, and their impacts on the local ecosystem, is not known. Groundwater, flowing out of springs or karstic caves, is the only available natural source of water for irrigation and portable water to the Lanmuchang village. It affects surface waters by discharging to the Qingshui Stream, which runs through the centre of Lanmuchang area. As a result, this unique context makes studies of Tl transfer processes very significant. The importance of such a hydrogeochemical study can be further highlighted by the fact that the only source of Tl is from natural occurrences and localized vestiges of past mining, and without other anthropogenic sources like smelting or industrial processes found in most Tl related studies worldwide (e.g. Schoer, 1984)

The aim of this study, which is a part of a group of multidisciplinary-environmental studies pertaining to lithogeochemistry, soil geochemistry, hydrogeochemistry and biogeochemistry of Tl and its impacts on human health, is to determine the occurrence of Tl in the aqueous system, to understand groundwater-related Tl transfer processes and dispersion, and their impacts on the local ecosystem.

2. Land features and climate

The study area is part of a karst terrain attaining an elevation of 1200–1600 m above sea level (a.s.l.). The regional karstic topography is characterized by peaks, depressions, valleys, karstic caves, karstic underground rivers and sinkholes (Guizhou Hydrogeological Survey, 1985). The hills in the study area are almost bare, with sparse grasses, ferns and other woody shrubs. Soils are thinly developed and till cover is thin, generally ranging from 10 to 50 cm in thickness, and some of the farmlands are poorly productive. Severe erosion of soil has occurred owing to poor vegetation coverage.

The sub-tropical continental monsoon climate is warm and humid with annual precipitation of 1300–1500 mm, with maximum precipitation in July and August. The annual average temperature is around 14 °C, with the highest temperatures of 35 °C occurring in July and August.

3. Geology and hydrogeology

3.1. Geology

The Lanmuchang Hg–Tl mineralized area is located within the SW limb of the E–W-trending Huijiabao anticline (Fig. 1). This anticline corresponds to a metallogenic belt of Au, Hg, Tl, As and coal, 18-km long and 5-km wide. The occurrence of Hg–Tl ore-bodies is directly controlled by NE-trending faults, of which the Lanmuchang normal fault and the Huangnijiang reverse fault are the two main faults (Fig. 2). The regional rock units are from Permian to Triassic in age. The outcropping rocks in the study area include lithologies from
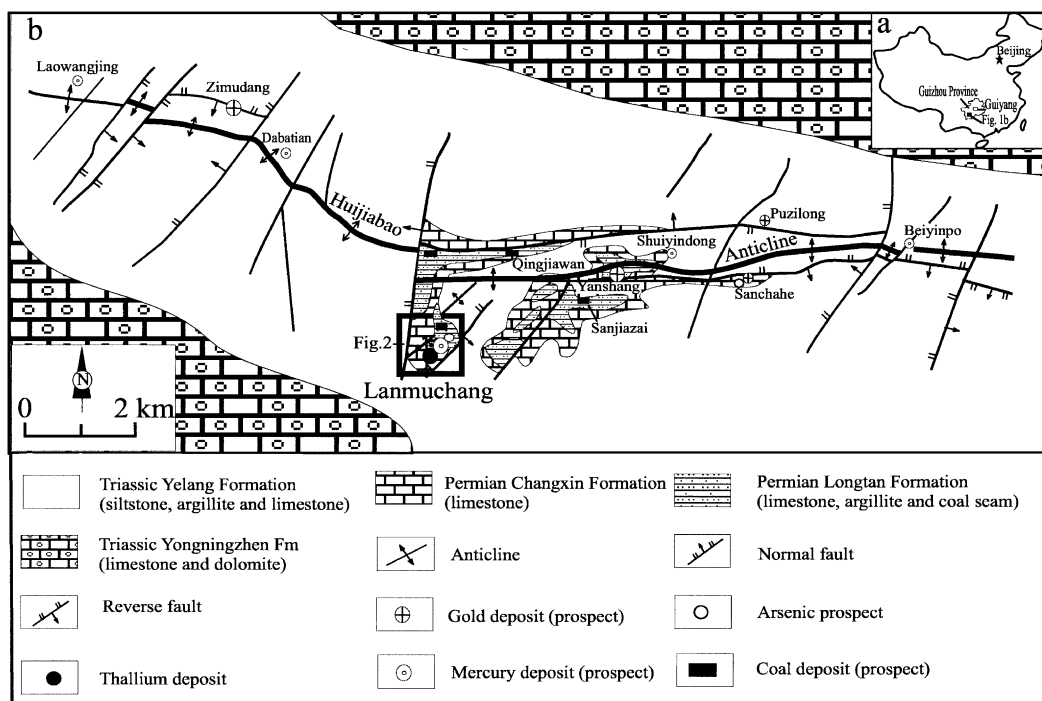
Fig. 1. Geological sketch map of the Huijiabao anticline metallogenic belt in SW Guizhou, China (modified after Wang et al., 1994).

the Permian Longtan Formation (P$_2$l: limestone, argillite and coal seam), Changxing Formation (P$_2$c: limestone), Triassic Yelang Formation (T$_1$y: siltstone, argillite and limestone), and Yongningzhen Formation (T$_1$yn: limestone and dolomite).

Thallium mineralization mainly occurs within the strata of P$_2$l and P$_2$c, and the host rocks are intensively altered by silicification, decalcification, argillization, pyritization, kaolinization and baritization (Chen, 1989b). The sulfides lorandite, cinnabar, realgar, orpiment, arsenopyrite and pyrite are the main minerals containing Tl, As and Hg (Chen, 1989b; Li, 1996). The Hg–Tl ore veins occur in 14 different horizons. The individual veins are generally 60–240 m long, 40–80 m wide, and 2–5 m thick. The veins present stratified, banded and bedded structures, and strike approximately 25° NE, dipping nearly parallel to the host rocks (Chen, 1989b; Li, 1996).

3.2. Hydrogeology

Previous researches on the hydrogeology of the Lanmuchang area include the hydrogeological survey of the Lanmuchang Hg deposit area (Guizhou Geological Bureau, 1960) and the regional hydrogeological survey at the scale 1:200,000 of Xingren quadrangle (Guizhou Hydrogeological Survey, 1985). According to these surveys, the study area is cut by a number of NE–SW and E–W-trending faults and fractures, producing complex aquifer characteristics. The Hg–Tl ore bodies are located

between the Lanmuchang and Huangnijiang faults, parallel to the Huijiabao anticline. Groundwater in the Lanmuchang Hg–Tl mineralized area is mainly recharged by wet season rainfall and seeps through the faults and fractures to deeper aquifer (Guizhou Geological Bureau, 1960). As a result, the groundwater table fluctuates strongly during the year. Borehole pumping tests (Guizhou Geological Bureau, 1960; Guizhou Hydrogeological Survey, 1985) showed that the groundwater table was strictly controlled by faults, and is relatively deep, 50–150 m below the local streambed elevation of 1399–1404 m a.s.l. The groundwater drains to the deeper parts of the ore body in a southerly direction. At the marginal areas of the Tl ore body, especially at the south margin, the groundwater table is a little higher, up to 1380–1420 m a.s.l., the maximum being 1448 m a.s.l., with a fluctuation of 2–5 m between winter and summer. As a result, the groundwater at the southern margin of the Tl-mineralized area may discharge to the surface streambed.

The Qingshui Stream is the only surface water available in the Lanmuchang area, but its sources are mainly from discharges of 3 different groundwater outlets (creeks A, B and C) within or around the Tl mineralized area (Fig. 2). The Qingshui stream is close to the Tl-mineralized area and runs through the main populated area located between creeks B and C (Fig. 2). All stream water drops into a sinkhole located about 3 km downstream. During the rainy season, the seepage of this
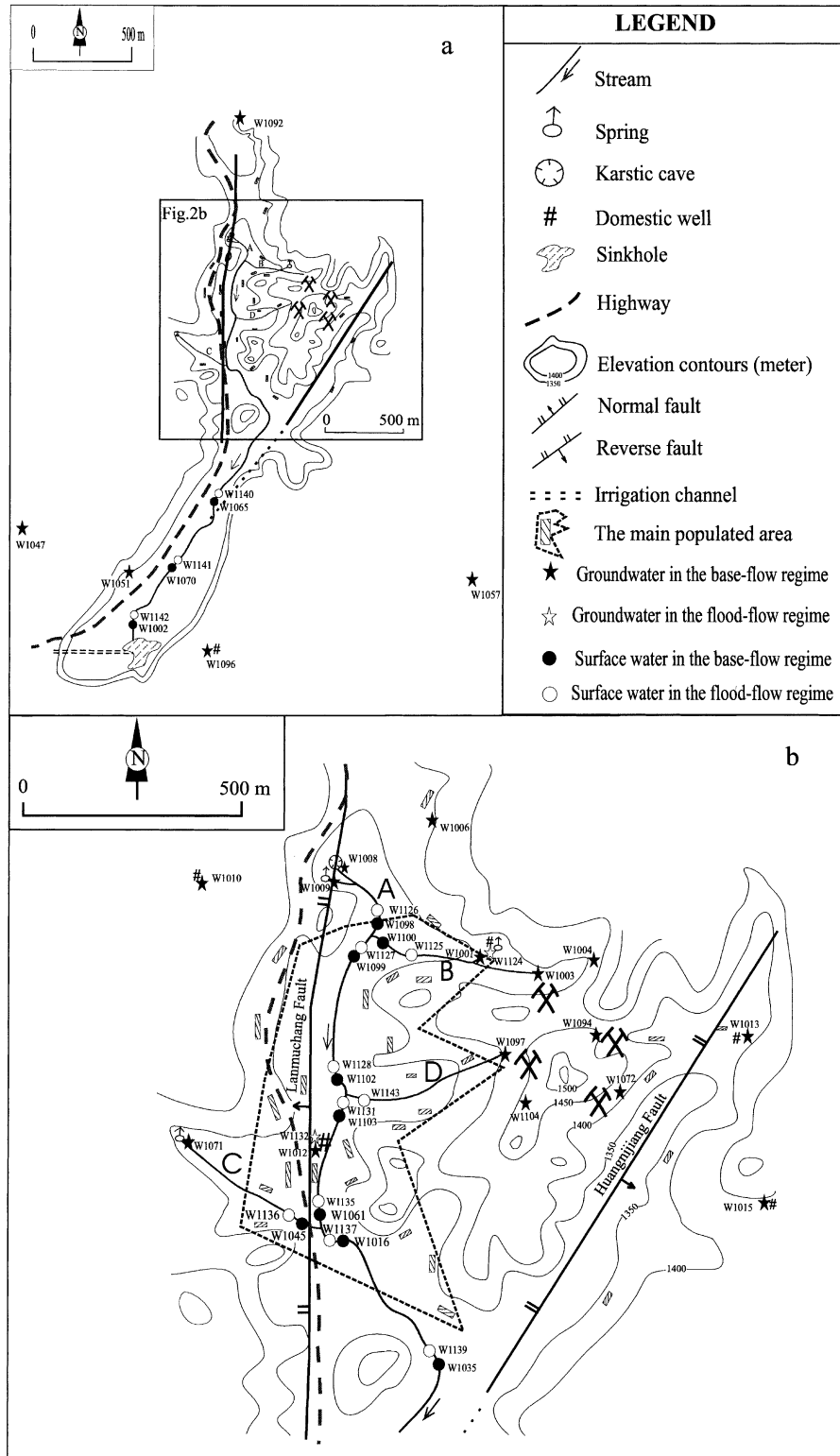
Fig. 2. Location of water sampling sites.

sinkhole is not rapid enough to discharge the floodwater from upstream and midstream. Instead, the water inundates the whole sinkhole and its surroundings, up to an area of 10 ha. During the wet season, some AMD from discharge of deep mine groundwater through mine adits flows to the stream, particularly through creek D, although the water volume is very small.

4. Water sampling and analysis

During the 1998 dry season (October–December), groundwater was sampled from springs, domestic shallow wells and deep mine groundwater which discharges from hydraulically conductive fractures and drainage ditches on the mine adit floor. Stream water was collected throughout the Qingshui Stream (Fig. 2). In the 1999 wet season (June–August), surface water was also collected throughout the Qingshui Stream (Fig. 2), 2 days after a flood event. All the water for geochemical analysis was filtered on site by using Millipore Sterivex syringe capsules containing 0.45 μm cellulose acetate filters. Three filtered sub-samples of water were sealed in pre-cleaned 60 ml Nalgene® bottles, one for anion analysis, one for cation determination (preserved with 0.4% ultra pure HNO_3 to acidify the sample pH to 2.0), and the third for Hg determination [preserved with ultra pure HNO_3 (0.4%) BrCl (3%) solution]. A field duplicate was collected at every 10th site. The parameters water temperature, pH, electrical conductivity (EC) and dissolved O_2 (DO) were measured in the field. All the apparatus were calibrated with standards each morning and rechecked during field tests. Three buffer solutions (pH = 4, 7 and 10) were used to calibrate the pH electrodes. The electrode was moved slowly in order to be in contact with different portions of the water at each site, and a stable reading was recorded at each site. In a similar manner, an EC meter was calibrated by using deionized water; a YSI 55 DO meter with a detection limit of 0.01 mg/L was calibrated using 5% sodium sulfite for zero calibration and pure water saturated with air for span calibration. All samples were sealed with screw caps and stored in coolers at 4 °C and then shipped to the laboratory where they were kept in coolers at the same temperature. The water samples were finally air-shipped to the Analytical Chemistry Research Laboratories of the Geological Survey of Canada (GSC) in Ottawa for geochemical analysis.

The trace metals were analyzed by direct inductively coupled plasma–mass spectrometry (ICP–MS) and Hg by hydride ICP–MS. The major elements Na, K, Ca, Mg and Si were determined by ICP emission spectrometry (ICP–ES), the anions Cl and SO_4 by ion chromatography, and HCO_3 by acid-base titration. The analytical precision, determined by QA/QC through the duplicates, the blanks and the reference sample OTT96

(GSC, Ottawa), is better than 15% for major ions and trace metals.

5. Results

5.1. Geochemistry of major elements

Results of major ion determination and water parameters are listed in Table 1. The observed ion balance is better than ±15%, except for samples of rainy season. The waters generally show a weak alkalinity with a pH range of 7.1–8.3, except for deep mine groundwater which has low pH values (2.6–3.6). The values of EC fall into the range of 200–400 μS/cm, except for higher values in deep mine groundwater up to 2000 μS/cm. The observed water temperature varied from 14 to 23 °C; the warmer waters were collected during the rainy summer period.

A piper plot of major elements allows for the recognition of the chemical types of ground and surface waters (Fig. 3). This plot indicates that Ca is the major cation whereas SO_4 and HCO_3 dominate the anion components. Deep mine groundwater is characterized by high contents of Ca and SO_4, and shallow groundwater is chemically dominated by enrichment of Ca and HCO_3. Na, K and Cl are generally in low concentrations.

5.2. Distribution of Tl and other trace elements

The water analysis results of trace metals are listed in Table 2. Distribution of Tl in groundwater shows 3 distinct patterns (Fig. 4). Firstly, the concentrations of Tl in the deep mine groundwaters (group I), at sites W1003, W1072, W1094, W1097 and W1104, range between 13 and 1100 μg/L, representing the highest enrichment in the study area. The average is 340 μg/L, 4 orders of magnitude higher than the background value (< 0.005 μg/L at sites W1047 and W1057) in water. Secondly, slightly away from the Tl mineralized area, the shallow groundwater (group II) from the Tl–Hg-coal-hosted strata (P_2c and P_2l), at sites W1001, W1004, W1006 and W1012, shows an average concentration of 0.36 μg/L. The water at site W1012, taken from a domestic well, shows a slightly higher Tl content of 0.38 μg/L. Finally, the shallow groundwater (group III) from outside the Tl mineralized area yields lower Tl levels with an average of 0.03 μg/L.

The Tl-rich deep mine groundwater is characterized by lower values of pH and DO, and higher values of EC than the shallow groundwater (Fig. 5). The pH is strongly acidic with values down to 3.0, and the DO is very low, down to 0.59 mg/L. Away from the Tl mineralized area, these parameters change to increasing pH and DO values and decreasing EC values.

Table 1
Concentrations of major ions and field parameters of waters in the Lanmuchang area

| Samples	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	SiO$_2$ (mg/l)	SO$_4$ (mg/l)	Cl (mg/l)	HCO$_3$ (mg/l)	TDS (mg/l)	EC (µS/cm)	DO (mg/l)	pH	T (°C)
Shallow groundwater													
W1001	59	9.1	2.9	0.9	5.5	56	0.93	114	248	326	7.9	7.7	17
W1004	48	5.5	0.9	0.8	3.9	26	0.33	98	183	241	7.4	8.0	15.9
W1006	200	34	5.3	2	6	354	2.6	200	803	929	1.6	6.6	16.8
W1008	49	2.8	1.2	0.6	3.3	11	0.77	108	177	227	8.3	8.3	16.2
W1009	47	3.1	1.3	0.9	4.8	9.3	0.56	113	179	222	8.3	8.3	16.2
W1010	56	1.5	0.5	0.5	2.3	11	0.6	125	197	263	4.0	7.5	16.4
W1012	104	6	7.3	6.4	10	111	13	143	400	628	3.5	7.1	16.3
W1013	35	3.1	2.6	0.8	6.2	8.1	0.37	93	149	181	8.0	8.0	16.7
W1015	47	3.7	2.2	0.5	4.8	12	0.22	110	180	229	7.9	7.2	16.3
W1051	52	3.9	2.2	1.0	4.7	7.3	1.2	145	217	294	6.0	7.3	16.5
W1071	58	4.3	1.2	1.0	5.4	3.4	0.49	143	218	255	5.0	7.7	16.5
W1092	71	5.7	1.6	0.7	2.7	41	1.5	134	258	329	4.4	7.6	16.5
W1096	45	3.4	0.5	0.5	3	2.4	0.42	127	182	238	8.7	8.3	10.6
W1124	65	10	3.2	0.9	5.5	na	na	na		346	na	5.8	17.1
W1132	110	4.2	5.5	4.5	5.4	na	na	na		502	na	7.2	16.6
Deep mine groundwater													
W1003	300	34	1.6	3.6	2.4	612	0.74	151	1105	1300	1.8	6.6	18.5
W1072	240	21	5.9	0.8	10	806	1.8	nd	1085	2000	0.7	2.6	16.3
W1094	290	2.4	0.9	0.8	7.5	225	0.63	nd	527	2000	1.3	3.6	17.8
W1097	480	54	3.3	0.9	29	1800	7.7	nd	2375	2000	0.8	2.9	16
W1104	290	31	2.3	nd	59	870	13	nd	1262	2000	0.6	2.9	21.5
Background groundwater													
W1047	76	3.6	1.6	0.7	3	24	0.98	170	279	395	5.6	7.2	16.4
W1057	43	3.4	1.9	0.5	5	17	0.31	118	189	252	7.0	7.3	17.3
Stream water in the base-flow regime													
W1002	65	5.5	3.6	3	7.8	68	2.5	97	252	331	8.2	7.7	14
W1016	55	5	3.4	1.4	3.2	29	1.5	119	217	283	5.5	7.9	16.5
W1035	50	5.7	4	2	4.4	40	2	133	240	325	8.2	7.6	13.3
W1045	46	4	2.5	0.9	1.9	10	1.1	109	176	331	9.2	8.6	16.6
W1061	77	7.4	8.4	3	6.9	70	3	135	311	402	7.5	7.1	14.4
W1065	65	5.9	4.2	2.8	9	70	2	137	295	333	6.9	6.2	14.5
W1070	67	6.2	3.8	3.3	9.4	90	2.5	78	260	355	8.5	7.1	14.6
W1098	55	4.5	2.1	1.3	4.7	23	0.91	123	215	276	7.3	7.9	17
W1099	62	6	2	1.4	5.3	41	0.93	118	236	313	6.9	7.6	16.7
W1100	110	15	3.3	2.3	9.4	164	1.3	124	429	319	6.8	7.6	16.6
W1102	64	6.5	2.2	1.5	5.6	48	0.99	120	249	318	6.3	7.6	16.8
W1103	67	6.9	2.7	1.9	6	54	1.4	121	260	336	5.3	7.4	16.7
Stream water in the flood-flow regime													
W1125	100	16	3.3	1.3	6.4	na	na	na		610	na	6.3	17.7
W1126	47	4.2	2	1.3	4.2	na	na	na		232	na	7.0	17.4
W1127	56	6.2	2.4	1.3	4.6	na	na	na		274	na	6.9	17.5
W1128	62	7.1	2.5	1.5	4.8	na	na	na		305	na	6.8	19.2
W1131	63	7.1	2.9	1.9	5.1	na	na	na		342	na	7.4	17.8
W1135	65	7	3.2	2.1	5.2	na	na	na		347	na	6.8	18.3
W1136	48	3.6	1.8	1.1	3.9	na	na	na		235	na	7.5	19.8
W1137	53	4.8	2.2	1.4	4.3	na	na	na		288	na	7.7	18.7
W1139	56	5.3	2.6	1.7	4.6	na	na	na		312	na	6.7	20.1
W1140	57	5.3	2.6	1.8	4.9	na	na	na		298	na	6.2	20.4
W1141	57	5.3	2.7	1.9	5	na	na	na		301	na	6.4	22.5
W1142	57	5.2	2.8	27	5	na	na	na		290	na	6.4	23
Acid mine drainage from discharge of an abandoned mine adit													
W1143	400	39	nd	nd	24	na	na	na		869	na	3.8	21.1

na = Not analyzed; nd = not detectable.
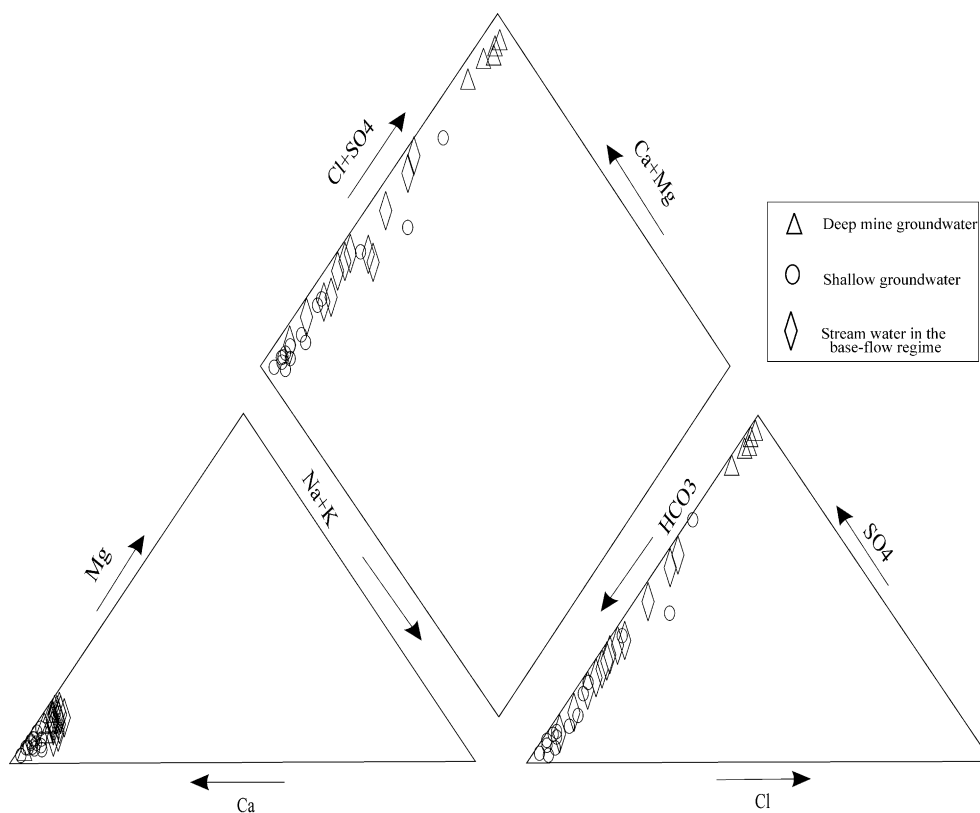
Fig. 3. Piper plot showing the variation in major cations and anions for ground- and surface water samples from the Lanmuchang area.

Average concentration of Tl in stream water is 8.1 μg/L during the dry season (the base-flow regime). The dispersion pattern of Tl in the base-flow regime along the stream is illustrated in Fig. 6. Note that samples representing the source discharge (e.g. sites W1098, W1110 and W1045 from creeks A, B and C, respectively) of stream water were not plotted on Fig. 6. This pattern is characterized as follows. Firstly, upstream, Tl concentration is from 0.76 to 0.99 μg/L (site W1099 where the water merges from creeks A and B, and site W1102) (Fig. 2). In creek A, the water source is groundwater discharge from a karstic cave (site W1008) and a spring (site W1009). Tl content in source groundwater from these two sites is very low (< 0.005 μg/L), but at site W1098 it increases up to 0.09 μg/L. In creek B, the water source is from a spring (site W1001). Tl content is 0.12 μg/L from this spring, but it jumps to a high level of 4.8 μg/L at site W1100. Secondly, midstream, Tl concentrations are in the range of 1.4–2.1 μg/L (from sites W1103 and W1061), and at site W1016 it decreases to 0.8 μg/L. In creek C, Tl is 0.12 μg/L at site W1045 (Fig. 2). Thirdly, downstream, Tl concentrations clearly increase from 3.1 μg/L (site W1035) to the very high level of 33 μg/L at site W1065. At the sinkhole (site W1002) Tl concentration is 19 μg/

L, and the Tl-rich water recharges slowly into the sinkhole (Fig. 2).

Thallium concentration in stream water during the flooding regime shows very similar dispersion to that in the base-flow regime (Fig. 6), although the average concentration of Tl decreases to 1.9 μg/L due to dilution effects. However, in the mid-stream section the Tl average concentration (1.9 μg/L) is almost the same as that (1.8 μg/L) in the base-flow regime. Due to dilution of elements in the flood regime, the mass loads of dissolved Tl during the rainy season in the mid-stream waters, therefore, should be smaller than those during the dry season. Downstream, Tl also shows the highest concentrations, ranging from 3 to 4.5 μg/L (sites W1140, W1141 and W1142). A sample collected from the inundated sinkhole area (site W1142) contains 4.5 μg/L of Tl.

Two other toxic elements of interest (As and Hg) also show considerable concentrations in the water system. The average level of As in deep mine groundwater, shallow groundwater and surface water are 211, 0.5 and 10 μg/L, respectively. The dispersion patterns of As in both groundwater and stream water are similar to Tl, and stream water downstream also shows an increase in As concentration in both flow regimes (Fig. 6). For mercury, the enrichment compared to the background

Table 2
Concentration of trace elements in groundwater and stream waters (µg/L)

| Samples	Al	Fe	Mn	Li	B	Rb	Sr	Sb	As	Tl	Hg
Shallow groundwater											
W1001	32	43	9.5	3.9	5.2	0.8	1500	0.07	<0.2	0.12	1.3
W1004	1.5	7	0.3	1.5	2.8	1.5	220	<0.05	0.2	0.75	0.17
W1006	3	420	32	9.7	15	2.2	4100	0.27	1.4	0.18	0.36
W1008	6.8	<3	0.25	0.04	1.7	0.5	380	0.08	0.3	<0.005	0.49
W1009	7.6	6	0.37	0.39	1.2	1.4	340	0.27	0.3	<0.005	0.64
W1010	6.4	8	8.2	0.18	<0.5	0.7	280	0.32	0.3	0.04	0.19
W1012	5.0	40	32	0.47	12	2.6	520	0.44	2.3	0.38	0.25
W1013	2.8	3	0.18	1.5	1.6	0.7	230	<0.05	<0.2	0.006	0.51
W1015	3.1	10	12	0.62	1.7	0.8	250	0.12	<0.2	0.006	0.78
W1051	5.2	33	0.49	0.15	1.7	1	550	<0.05	0.2	0.04	0.28
W1071	3.3	<3	0.16	0.99	1.0	1.8	360	0.18	0.6	0.01	0.34
W1092	6.7	12	1.3	0.36	1.3	1.1	430	0.13	0.7	0.03	0.11
W1096	26	33	3	0.33	<0.5	0.8	190	<0.05	0.2	0.09	0.2
W1124	16	1100	19	3.2	4.6	0.8	1600	0.1	0.1	0.3	<0.003
W1132	2.7	<3	2.7	0.27	8.1	1.8	440	0.35	0.5	0.22	0.004
Deep mine groundwater											
W1003	55	72 382	1870	17	5.2	4.7	12 380	0.13	540	13	0.9
W1072	37 000	130 000	2100	25	16	10	610	1.3	250	1100	1.3
W1094	20 350	7950	275	10	3.2	3.8	80	0.01	44	62	0.2
W1097	300 000	420 000	4600	249	232	18	880	3	200	54	0.24
W1104	460 000	450 000	7300	254	231	38	450	0.06	23	470	0.2
Background groundwater											
W1047	7.6	10	28	0.1	1.5	0.6	510	<0.05	0.6	<0.005	0.16
W1057	7.2	<3	1	1.1	1.4	0.6	380	<0.05	<0.2	<0.005	0.14
Stream water in the base-flow regime											
W1002	18	100	270	1.9	10	4.7	450	0.24	14	19	0.24
W1016	26	74	48	0.79	3.1	1.8	440	0.55	5.6	0.8	0.63
W1035	22	140	51	1.1	4.2	2.3	510	0.50	7.9	3.1	0.2
W1045	31	64	19	0.16	1.4	1.2	330	0.56	1	0.12	0.22
W1061	15	240	150	2.1	7.2	3.9	830	0.56	20	2.1	0.17
W1065	4	<3	270	3.5	14	5	530	0.37	10	33	0.21
W1070	53	780	450	2.5	13	5.5	500	0.28	25	31	0.21
W1098	26	210	28	0.48	8.1	1.9	460	0.41	1.6	0.09	0.08
W1099	14	130	38	1.1	5.3	2	670	0.34	4.1	0.76	0.08
W1100	8	720	100	4.6	9.3	2.9	1900	0.1	18	4.8	0.1
W1102	9.6	33	19	1.32	4.9	2.1	740	0.34	3.8	0.99	0.06
W1103	12	210	47	1.56	5.3	2.7	780	0.39	14	1.4	0.06
Stream water in the flood-flow regime											
W1125	28	2100	290	6	6.8	1.5	1900	0.08	1.9	3.3	0.07
W1126	32	33	31	0.46	3.5	1.5	380	0.16	0.8	0.19	0.04
W1127	54	300	78	1.4	4.1	1.6	620	0.16	0.9	0.73	0.04
W1128	11	6	0.21	1.6	5.0	1.8	750	0.28	0.3	1.1	0.08
W1131	12	10	0.27	1.7	5.8	2.1	740	0.3	1.3	1.6	0.08
W1135	13	12	0.18	1.7	6.5	2.3	730	0.49	2.1	2.1	0.006
W1136	8.9	<3	0.14	0.15	1.6	1.4	310	0.37	0.4	0.07	<0.003
W1137	12	7	0.10	0.61	3.5	1.7	460	0.34	1.3	0.67	0.05
W1139	13	12	0.11	0.88	4.4	2.1	510	0.38	2.3	1.4	0.004
W1140	9.8	9	0.27	0.87	4.5	2.2	500	0.32	1.8	3	<0.003
W1141	7.8	4	0.13	0.9	5.0	2.5	500	0.35	3	4.2	<0.003
W1142	25	210	2.9	1.1	5.3	3.9	480	0.42	6.5	4.5	<0.003
Acid mine drainage from discharge of an abandoned mine adit											
W1143	220	150	2.9	200	188	17	1100	0.06	48	59	0.01

< below detection limit.
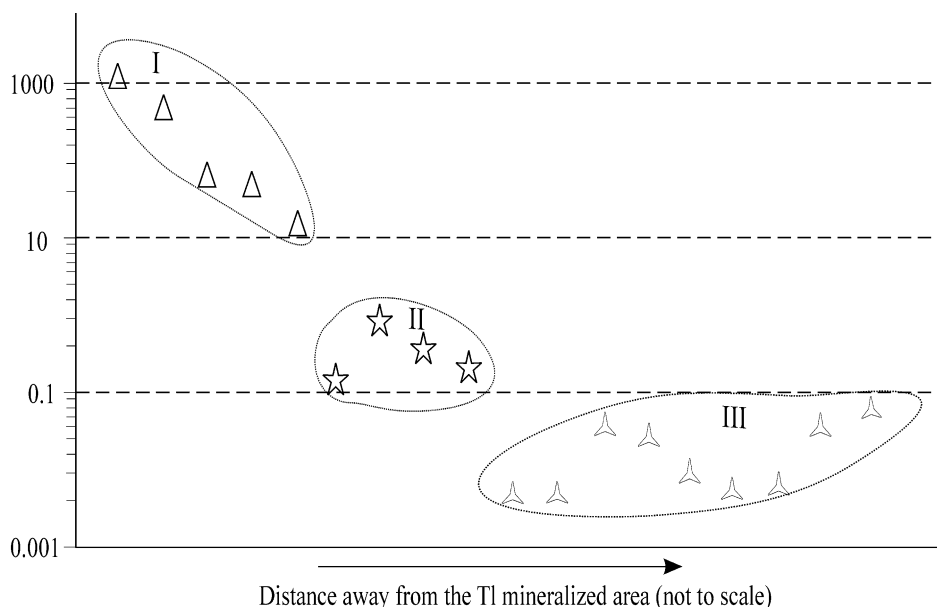
Fig. 4. Concentration of Tl in groundwaters relative to distance from the Tl mineralized area outwards. (I) deep mine groundwater; (II) shallow groundwater close to the Tl mineralized area; (III) shallow groundwater away from the Tl mineralized area.

level is not as strong as Tl and As. Average levels of Hg in deep mine groundwater and shallow groundwater are 0.57 and 0.38 μg/L, respectively. Mercury concentration in stream water ranges from 0.06 to 0.63 μg/L in the base-flow regime and from <0.003 to 0.08 μg/L in the flooding flow regime. The average concentration of Hg in the base-flow is about 0.19 μg/L, slightly above the background level (0.15 μg/L). However, this background value (0.15 μg/L) for Hg is higher than the world background level in fresh water (0.0001–0.1 μg/L) (Fergusson, 1990), and indicates that the whole region is somewhat anomalous with respect to Hg.

Concentrations of the trace elements Sb, Rb, Sr, Li and B decrease in the order of mine groundwater, stream water and shallow groundwater, showing a spatial dispersion similar to Tl and As. Their concentrations in stream water were slightly diluted in the flood regime.

6. Discussion

Thallium usually occurs in a very dispersed state in nature, and its concentrations in natural water are normally low compared to many other metals. For instance, the range of Tl content is 0.001–0.25 μg/L in groundwater (Banks et al., 1995), and 0.001–0.036 μg/L in lake water (Cheam et al., 1995; Lin and Nriagu, 1999). However, concentrations of Tl in groundwater and groundwater-recharged stream water in the Lanmuchang study area are markedly higher compared to those in the natural waters mentioned above. Moreover,

the occurrence of Tl in the Lanmuchang watershed shows an excellent case related to recognizable Tl mineralization rather than sulfide mineralization of Pb, Zn, Fe and Cu, polymetallic ore-treatment plants or cement plant emissions. The general dispersion pattern of Tl in the Lanmuchang watershed follows a descending order in concentration from mine groundwater (deep groundwater) → stream water → shallow groundwater → background water. The occurrence and dispersion of Tl in the Lanmuchang aqueous system is constrained by Tl mineralization, water-rock interactions and hydrogeological conditions.

6.1. Contributions of Tl mineralization and water–rock interactions

Thallium mineralization occurs as the sulfide mineral lorandite ($TlAsS_2$), and other Tl-bearing sulfides of As, Hg and Fe (e.g. cinnabar, realgar, orpiment, arsenopyrite and pyrite) in the study area (Chen, 1989b; Li, 1996; Xiao, 2001). The above Tl-rich sulfides are the main suppliers of Tl to the local aqueous system, and the Tl-bearing host rocks are another source for Tl. In the supergene environment, Tl in the original sulfides and host rocks tends to be released into the water system. The intensive faults and fractures, and mining shafts in the supergene zones have probably permitted O_2-rich and/or CO_2-rich meteoric waters to migrate through the rock mass. The infiltrating meteoric waters are expected to react with Tl-bearing host rocks and Tl-rich sulfides. Since the solubility of sulfide is low (e.g. 0.2 g/L for Tl sulfide), and solubility of SO_4 is high (e.g. 48 g/L for Tl
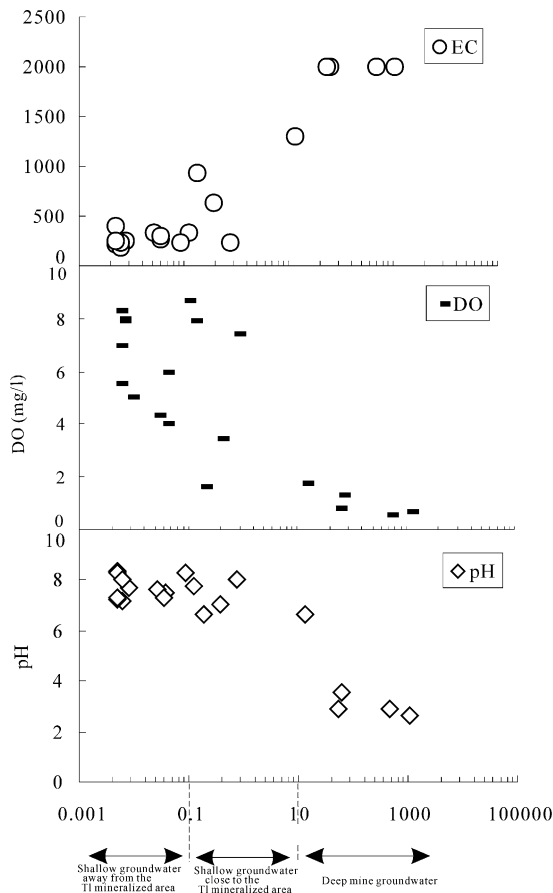
Fig. 5. Electrical conductivity (EC), dissolved O$_2$ (DO) and pH versus Tl concentrations in groundwater.

sulphate) (Zitko, 1975b; Sager, 1994), the breakdown and/or the weathering/leaching processes of Tl-bearing sulfides and host rocks may release significant amounts of Tl into the groundwater and meanwhile decrease the pH values by producing acidic fluids. Furthermore, lower pH waters, in turn, may enhance the dissolution of limestone and increase the Ca and the total dissolved solids (TDS) in groundwater.

Thallium mineralization also contributes to the dispersion of Tl in the groundwater. The locations of groundwater samples with high concentrations of Tl in the study area are restricted to the center of the Tl mineralization. In contrast, shallow groundwater samples collected away from the center of the Tl mineralized area shows decreasing Tl contents, further away from the mineralized core, some samples being below the detection limit (0.005 μg/L). These concentration differences reflect the impact of Tl mineralization and its host rocks on the hydrogeochemical composition of groundwater. In fact, the groundwater flow path in the study area is generally from north to south, and the intensive faults and fractures cause an independent groundwater

reservoir (e.g. deep mine groundwater) in the intensive Tl mineralized area. Concentrations of Tl in the host rocks range from 33 to 490 μg/g, and from 130 to 35,000 μg/g in Tl ores and Tl-bearing sulfides of As, Hg and Fe, whereas away from the mineralized area, the bedrocks show weak Tl mineralization or barren of sulfide mineralization, and contain Tl levels in the range 0.02–0.86 μg/g (Xiao, 2001).

High contents of Ca and SO$_4$ in both groundwater and stream water reflect a major contribution from reaction with carbonate and oxidation of sulfide minerals, and/or dissolution of gypsum (Fig. 3). The presence of carbonates in the area (mainly limestone) could also favour the dissolution of limestone as a main source for Ca in the water system. In contrast, Na and K play much lesser contributions to the major cations, as a result of the paucity of silicate minerals.

High contents of Tl in groundwater are accompanied by high concentrations of SO$_4$, Ca and TDS. Sulphate concentration ranges from 25 to 1800 mg/L. The elevated contents of SO$_4$ derived from the primary sulfide minerals or the secondary efflorescent salts, appear to correspond well to high Tl levels in groundwater (Fig. 7). The concomitant increases of Ca and TDS with Tl (Fig. 7) probably reflect the leaching of Tl-bearing sulfides and the dissolution of limestone, which is also supported by the negative correlation between Tl and pH values (Fig. 5).

Correlations between Tl and Al, Fe and Mn in groundwater also suggest contributions from mineralization and water–rock interactions (Fig. 8). These correlations are related to the fault zones with abundant fault gouges occupying the main groundwater conduit system of the bedrock. The gouge materials are characterized by high amounts of Fe, Al and Mn hydroxides [e.g. copiapite (MgFe$_4$(SO$_4$)$_6$(OH)$_2$·20H$_2$O), magnesia alum (MgAl$_2$(SO$_4$)$_4$·22H$_2$O), kalinite (KAl(SO$_4$)$_2$·11H$_2$O], epsomite (MgSO$_4$·7H$_2$O) and fibroferrite (Fe(SO$_4$)(OH)·5H$_2$O) identified by using X-ray diffraction] which contain considerable concentrations of Tl (25–1100 μg/g) (Xiao, 2001). Relatively reducing conditions indicated by low DO values and acidic conditions (Fig. 5) are expected to dissolve the Fe, Al and Mn hydroxides and release some of their absorbed or coprecipitated Tl into the groundwater.

Water–rock interactions also affect the distributions of As and Hg in the water system. Arsenic shows quite high concentrations in ground- and surface water within the Lanmuchang watershed, but Hg contents are relatively low. These different behaviours for As and Hg are probably attributable to the fact that the solubility and weathering of As sulfides is high and quite similar to Tl, but the low level of Hg in ground and surface water probably reflects the extremely low solubility and relative resistance of cinnabar to weathering and oxidation (Jonasson and Boyle, 1972; Engler and Patrick, 1975).
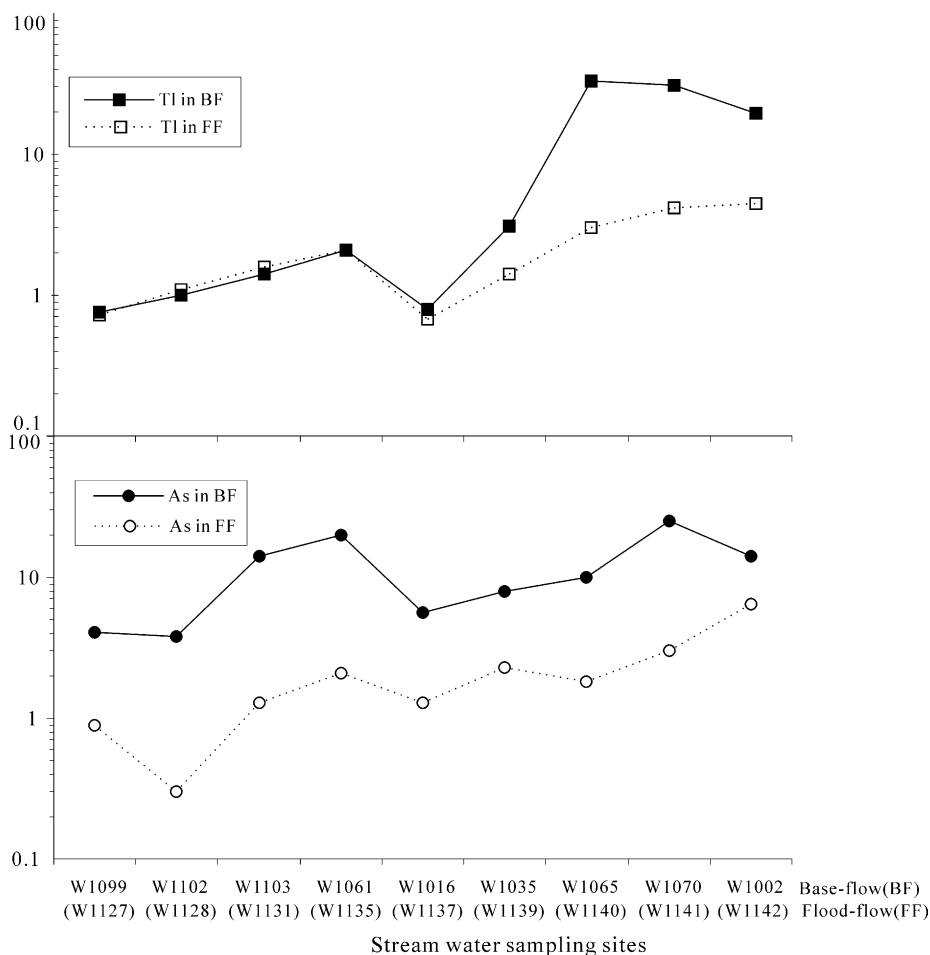
Fig. 6. Dispersion patterns of Tl and As in stream water [from upstream (left) to downstream (right); BF = base-flow; FF = flood-flow].

In addition, Rb also shows good correlations with Tl in ground- and surface waters (Fig. 9) which may reflect the close geochemical affinity of the two metals having very similar ionic radii (Shannon, 1976; Heinrichs et al., 1980), and the contribution of water–rock interactions to the water compositions as well. The abundant K-minerals (mainly illitic mica) (e.g. in fault gouges) (Li, 1996) are thought to be the major hosts of Rb.

Thallium shows much higher levels in stream water rather than in the observed shallow groundwater discharging to the stream. The average concentration of Tl in the stream water in the base-flow regime is about 80 times the value in the groundwater that serves as the stream's source, and 15 times the content in the flood-flow regime. This large concentration difference probably reflects stream water Tl contamination resulting from other discharging sources, such as AMD, soil–water interactions, and unidentified groundwater discharge.

The AMD had no apparent effect on the water volume of the Qingshui Stream, as the AMD from discharge of

deep mine groundwater through an abandoned mine adit, only contributed a small volume through creek D during the rainy season. However, it is important for solute transportation into the stream water as its pH value was down to 3.8, whereas creeks A, B, C show high pH values of 7.9, 7.6 and 8.6, respectively. A Tl concentration of 59 μg/L from the AMD was also detected at site W1143 in creek D during the rainy season, very similar to that in deep mine groundwater at site W1097 (54 μg/L of Tl). However, the Tl-rich AMD became less significant when mixed with the large volume of stream water as at site W1131 where Tl concentration is only 1.6 μg/L.

Water–soil interactions or soil water seepage may also represent one of the factors which contribute to the enrichment of Tl in stream water. Soil water was not analyzed in this study, but very high Tl concentrations ranging from 21 to 100 μg/g were detected, by using strong HNO_3 extraction, in the alluvial deposits along the bank of the Qingshui Stream (Xiao, 2001). The
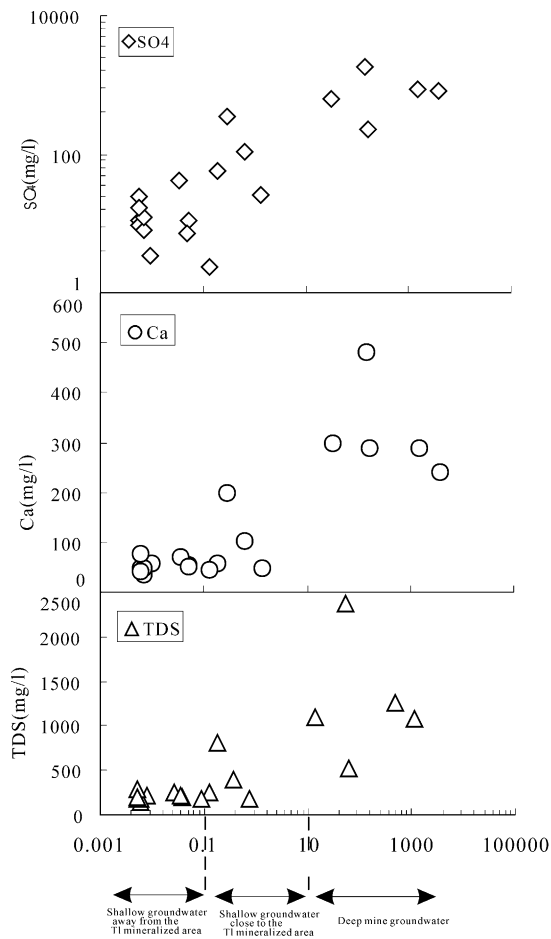
Fig. 7. Plots of SO$_4$, Ca and total dissolved solids (TDS) contents versus Tl in groundwaters.

Fig. 8. Plots of Al, Fe and Mn versus Tl concentrations in groundwaters.

Tl-rich alluvial deposits are expected to contain an appreciable part of the mobile portion (to be analyzed in the follow-up study) which could facilitate the release of Tl into soil water. Stream flow may also enhance Tl release during soil erosion along the stream bank. This migration mechanism may contribute to Tl dispersion in mid-stream, as the average flood-stage Tl concentrations (1.9 μg/L) are similar to ones from base-flow samples (1.8 μg/L), despite the fact that one would expect flood-flow concentration to be smaller due to dilution effects (Fig. 6). The greater concentrations of Tl in creeks A (site W1100) and B (site W1098) compared to their recharge sources (sites W1008, W1009 and W1001) also suggest contribution of stream bank soil erosion in the upper stream waters. However, Tl concentrations (25–40 μg/g) in bank soils downstream are not as high as those in upstream and mid-stream bank soils (Xiao, 2001), and thus soil erosion cannot contribute to the dramatic increase of Tl in downstream waters. The probable cause for this observation is discussed below.

6.2. Hydrogeological constraint

The hydrogeological constraint in the Lanmuchang area can be illustrated by the dispersion pattern of Tl in the downstream waters. In general, it is observed that concentrations of metals in stream waters decrease downstream from upper point-source discharges. In the case of the Qingshui Stream, however, Tl levels show the opposite trend: Tl concentrations in the stream water are much higher downstream than upstream and mid-stream in both base-flow and flooding regimes (Fig. 6).

The unexpected concentration increase for Tl in the downstream waters cannot be interpreted by contribution from bank soil erosion as discussed above. In addition, no known AMD sites drain to the downstream reaches. Therefore, sources other than soil water seepage and AMD should be considered to explain the increased Tl concentration in downstream waters.

From the above discussion it is evident that the creeks feeding the Qingshui Stream cannot account for the higher Tl levels in the downstream waters. Topographically, the Huangnijiang fault zone corresponds to a dry valley that only holds the runoff during the heavy
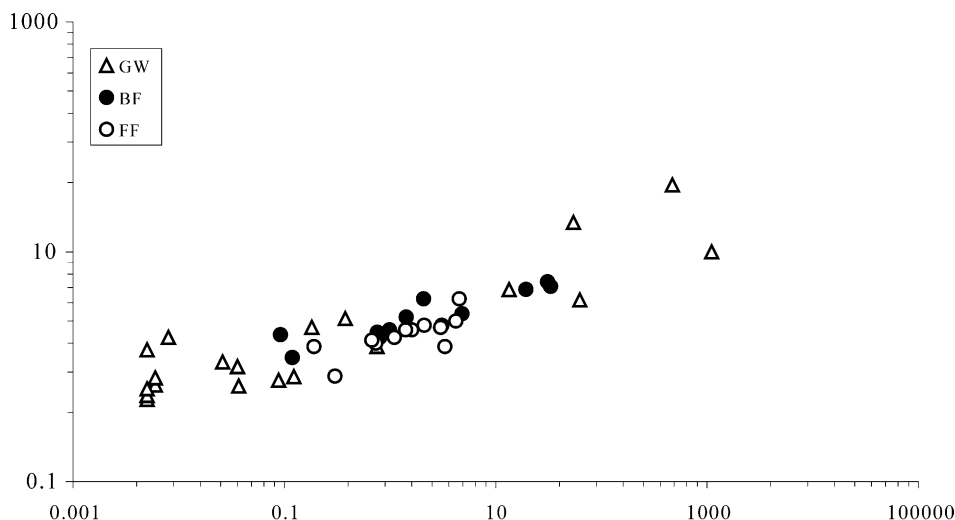
Fig. 9. Plots of Rb versus Tl concentrations in groundwater and stream water (GW = groundwater; BF = base-flow; FF = flood-flow).

rainy season. No surface waters were observed in this valley draining to the Qingshui Stream during the dry season. So, this excludes the possibility that any surface water bringing Tl from this valley, contributes to the higher Tl concentrations in the downstream waters during the dry season.

Without apparent surface sources, a probable underground source should be considered. Indeed, sites W1065 and W1070, representing very high concentrations of Tl (31–33 μg/L), are within the traces of the Huangnijiang fault and the Lanmuchang fault. Previous hydrogeological drilling data (Guizhou Geological Bureau, 1960) showed that groundwater in deep fractures within the Tl mineralized area may discharge outwards through the fault zones and flow to the southern margin. Also, the groundwater table is a bit higher at the south margin than elsewhere. The groundwater table elevation, with a 0–20 m relative elevation above the local streambed and with a fluctuation of 2–5 m between the dry season and the rainy season, could facilitate the groundwater discharge to the surface streambed if such an outlet of discharge is available. Therefore, unidentified groundwater seepage probably explains the unexpected high Tl contents in the downstream waters, that is, the unidentified groundwater seepage transports the Tl-rich solution or particles from the Tl mineralization area to discharging points (e.g. the traces of the confluence of the above two faults) at the downstream surface, and causes high contents of Tl in the downstream waters, although the flow capacity of stream water was not measured in this study. The increased concentrations of As, Rb and SO_4, and the decreased content of HCO_3 also suggest an unidentified groundwater discharge. A similar case study of the Farr creek drainage basin in Cobalt, Canada, also suggests that at this site, some unidentified groundwater passing through fault zones contributes to the increase in As in downstream waters (Percival et al., 1996).

6.3. Impacts of groundwater related thallium transfer

Thallium generally exists in natural waters as the species Tl^+ and Tl^{3+}, but the Tl^+ species is dominant in the aqueous environment (Fig. 10) (Vink, 1993). The solubility of Tl^+ compounds is quite high, ranging from 40 to 800 g/L (Zitko, 1975b; Sager, 1994), and suggests that Tl^+ would not precipitate from solution in most aqueous environments. Speciation computations have further predicted that the most common form of Tl^+ in ground-, river and lake waters would be the free Tl^+ species, but in water with high organic matter or high ionic strength, Tl^+ would be expected to exist in complex species (Kaplan and Mattigod, 1998). Kaplan and Mattigod (1998) also pointed out that Tl adsorption to geological materials (e.g. Fe–Mn–Al oxyhydroxides) appears to be dominated by cation exchange, as opposed to (co)-precipitation, or absorption into the structure of the solid phase. Cation exchange is a process that does not bond the metals very strongly. Therefore, Tl may move rather readily with groundwater flow and its attenuation by sediments would be limited. All these factors would indicate that Tl is a very mobile metal in most aqueous environments, rather than being locked-up into solid oxides, and can disperse easily during oxidation of Tl-bearing sulfides. Furthermore, the dominant Tl^+ in water systems can readily enter the food chain through drinking water or crop uptakes, as Tl^+ may substitute for K^+ in biogeochemical processes because of their very similar ionic radii (Shannon, 1976; Britten and Blank, 1968).
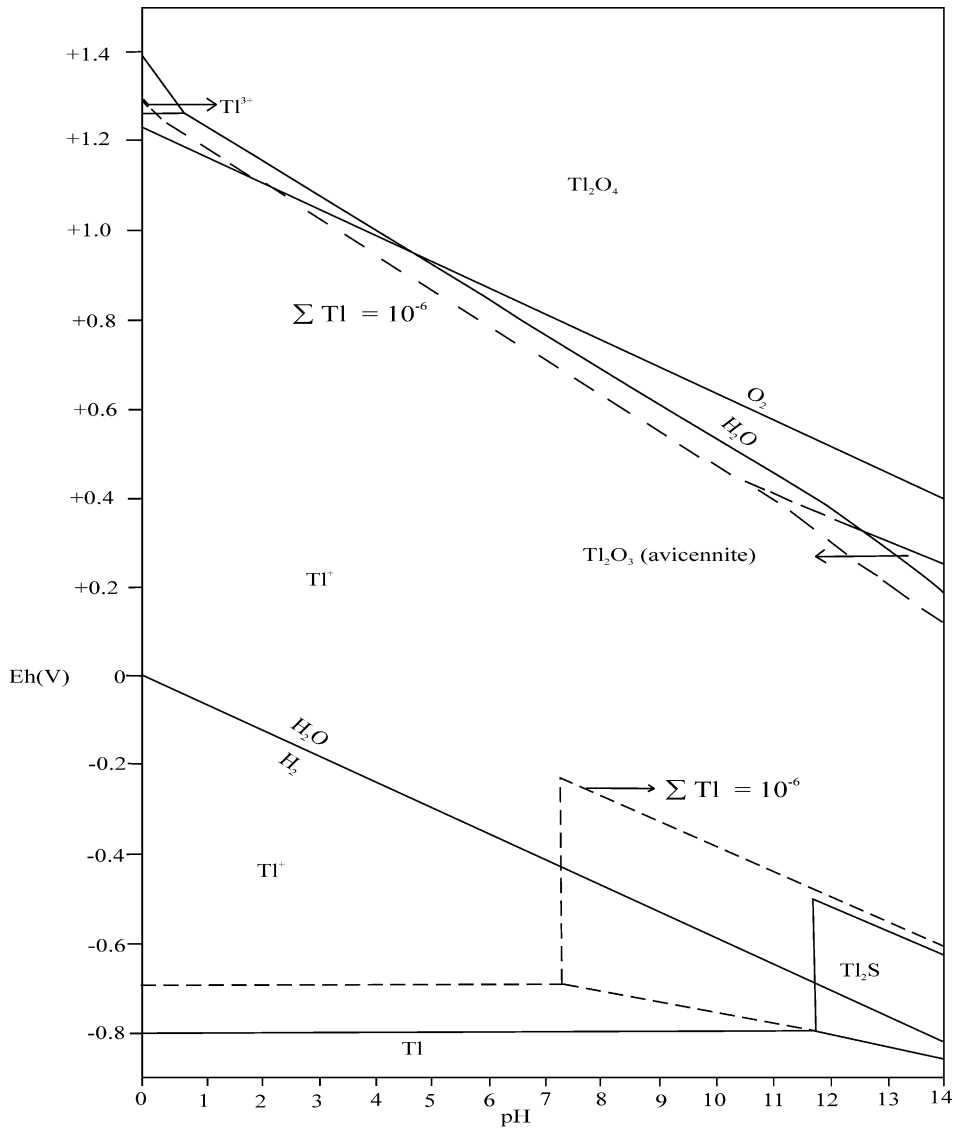
Fig. 10. Eh–pH diagram for the system Tl–S–O–H–"normal area". Activity for total dissolved Tl species: 10^{-8} M, and activity of total dissolved S species: 10^{-3} M (Vink, 1993).

In this study, groundwater further contributes Tl to surface waters in two ways: firstly, by direct AMD, and secondly, by discharge or seepage through fault zones or soil zones. These groundwater Tl transfer processes have certain environmental impacts on the local ecosystem of the Lanmuchang watershed, mainly drinking water supply and agricultural irrigation.

Domestic wells can be easily contaminated by Tl-rich groundwater as it seeps to shallow aquifers where the wells are located. In fact, very high concentrations of Tl (17–40 μg/L) were detected in well waters within the Tl mineralized area in 1977 by Zhou and Liu (1985). These Tl-rich wells were used to supply drinking water before the 1980s, and were assumed to have caused chronic Tl

poisoning (Zhou and Liu, 1985). At present, some of the wells have been sealed and abandoned, and other wells still supplying drinking water show much lower levels of Tl (0.12–0.38 μg/L from this study). For the domestic wells investigated by Zhou and Liu (1985), the locality and the Tl concentration in water for each well were not specifically indicated. The analytical QA/QC documentation for Tl determination in their study was also unknown. Therefore, it is difficult to compare the Tl data of the drinking water between the present study and the earlier study. It has been shown that groundwater seepage proximal to the fault-mineralized area is the most plausible reason for the Tl distribution pattern in the stream waters. If a single well from the present

study is located in the vicinity of a well or is one of the wells from the 1985 study by Zhou and Liu (1985), the data in this present study suggests a major reduction in the Tl level of the groundwater. If so, 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 for Tl-bearing sulfides or host rocks actually tend to deplete the Tl over the years, and thus release less Tl into the groundwater recharging to the wells. Another possible explanation is that prior to the 1980s, when the domestic wells were producing water, the groundwater flow paths were altered by the effects of shallow groundwater withdrawal, bringing Tl-rich waters into the shallow aquifer. Now that those wells no longer produce water, the flow paths have returned to their pre-pumping condition, and Tl-rich waters remain in deeper strata.

To date, the threshold of Tl in drinking water has not been regulated by the World Health Organization, but it was set as 2 μg/L by the US Environmental Protection Agency (USEPA) in 1993, with 0.5 μg/L for maximum contaminant level goal (USEPA, 2002). This concentration is much lower than many other toxic metals (e.g. 10 μg/L for As, 5 μg/L for Cd and 6 μg/L for Sb) (USEPA, 2002). In Russia, the limit is much stricter, down to 0.1 μg/L (cited from Frengstad et al., 2000). The Tl content in the well water in the Lanmuchang area (0.12–0.38 μg/L) is thus over the Tl safe limit of Russia and lower than that of the USEPA. Therefore, the potential risk of Tl poisoning from the drinking water in the Lanmuchang area should be constantly monitored. Furthermore, any future mining in the area must keep in mind the potential Tl contamination to the drinking water through Tl-rich groundwater transfer processes.

The stream water is the only source for domestic use and irrigation in the Lanmuchang area. The local villagers use the Tl-rich stream water for daily washing (e.g. washing clothes or vegetables), making it possible for Tl to enter the human body through the skin or through the vegetables consumed. The exposure of skin to Tl causing Tl poisoning was mentioned by Dmowski et al. (1998), but this type of effect on residents of the Lanmuchang area is not clear. The Tl-rich stream water can also cause Tl contamination in soils through irrigation. Thallium-rich soils, in turn, contaminate vegetables or cereals by uptake of Tl, providing a Tl source to the food chain (Tremel and Mench, 1997; Xiao, 2001). If the totality of Tl sources were summed, irrigation water containing 1 μg/L of Tl would contribute Tl ranging from 0.26 to 1 μg/g (dry weight) to plant materials (Sager, 1998), which can be regarded as the upper limit for human and farm animal consumption (Sager, 1998). At this point, it is worth noting that a new underground irrigation channel (Fig. 2) was constructed in 1998 to pipe part of the sinkhole waters (containing 19 μg/L of Tl in the base-flow regime and 4.5 μg/L of Tl in the flood-flow regime) to a neighbouring farming area, south of and outside the Lanmuchang watershed. Therefore, there is a definite possibility that Tl contamination may extend its impact outside the Lanmuchang watershed. This also implies that natural Tl in the aqueous system can multiply its effect through soil and agricultural contamination, and finally reach the food chain.

7. Conclusion

The specific geological context of the Lanmuchang area shows an enrichment of toxic Tl to the aqueous system. The distribution of Tl in groundwater is controlled by Tl mineralization, water–rock interaction, and hydrogeological conditions. The distribution of Tl in the aqueous system corresponds to the groundwater transfer processes, and shows specific patterns. Firstly, there are high levels (13–1100 μg/L) in deep mine groundwater within the Tl intensive mineralized area, with a decreasing trend away from this area to the background level. Secondly, the Qingshui Stream, supplied by discharge of groundwater from the mineralized and surrounding areas, shows higher Tl concentrations in the downstream waters than in the up- and midstream waters. The sources of Tl in the stream water are most likely from the groundwater transport of Tl from the leaching of Tl-rich sulfides or rocks, and from possible Tl-rich soil water seepage, and finally from small amounts of AMD during the rainy season. The markedly high levels of Tl in the downstream waters are likely caused by unidentified discharge of deep groundwater through fracture zones at the south margin of the Tl mineralized area.

The enrichment of Tl related to the groundwater transfer demonstrates that the Lanmuchang watershed is an excellent case study for toxic Tl related to natural Tl mineralization. The high Tl concentrations in the ground- and surface waters affect not only the aqueous system, but also the agricultural lands and products, and may have long-term health impacts, although Tl levels in the current drinking waters are not high. Moreover, this enrichment can be increased by human activity, such as mining or irrigation. Thus, the results of this study demonstrating groundwater-related Tl transfer through natural processes are important for health-related environmental planning and regulations, and serve as baseline data for future research on Tl natural dispersion processes.

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