



Geochemical transfer and preliminary health risk assessment of thallium in a riverine system in the Pearl River Basin, South China



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ABSTRACT

Thallium is a highly toxic element, whose geochemical dispersion, transfer and potential health risks in aquatic systems are far from understood. This study aims to investigate the distribution of Tl in the surface water from an ultra-large Tl-bearing pyrite open-mining site and its associated riverine system of Yunfu city, western of the Pearl River Basin (PRB). Concentrations of 2.75–194.4 µg/L of Tl were found in the surface water from the mining site. Compared with other trace metals measured (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn), Tl experienced little precipitation by conventional lime-dosing treatment of mine water and readily moved through the river trace. The distribution of Tl in the river watershed during both the dry season (Tl: 0.01–9.15 µg/L) and wet season (Tl: 0.03–1.92 µg/L) generally followed a decreasing concentration pattern downstream of the pyrite mining site for the upper and middle reaches. However, some unexpected Tl elevations were observed in the lower reaches. Concentrations of Tl correlated well with concentrations of Ca, Mn, Sr, sulfate, total dissolved solids and water conductivity values for both the dry season and the wet season. Finally, health risk assessment suggests that Tl may pose non-carcinogenic health risks to local residents over a long time. This study highlights not only anthropogenically-induced but also hidden naturally-occurring Tl enrichment in the hydrosphere of the PRB, and enhances the understanding of aqueous geochemistry of Tl.

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1. Introduction

Surface water contamination with trace metals has become a serious environmental concern worldwide, owing to their toxicity, persistence and bioaccumulation (Babula et al., 2008; Klavins et al., 2000; Muhammad et al., 2011). The Pearl River Basin (PRB) covers an area of roughly 461,000 km² with a population of 21.4 million people, including many big cities like Guangzhou, Hong Kong, and Macao (Sun et al., 2010). It bears abundant sulfide metal ores in the upper and middle reaches, and excessive metal mining and smelting has resulted in large amounts of potentially toxic trace metals since the end of the 1970s (Ouyang et al., 2006).

Thallium (Tl) is a typical trace metal of toxicity to mammals higher than that of Cd, Pb and Hg, and it is reported to have induced many therapeutic, occupational and accidental poisoning (Anagboso et al., 2013; Xiao et al., 2003; Peter and Viraraghavan, 2005). However, compared to Cd, As, Pb, Hg, Cu and Zn, the environmental behavior of Tl is much

less studied, and many aspects are still unknown (Law and Turner, 2011; Peter and Viraraghavan, 2005). As a rare but widely spread element, Tl is present in natural environments usually at very low concentrations, with an average concentration of 0.49 µg/g in the continental crust and of 0.013 µg/g in the oceanic crust (Peter and Viraraghavan, 2005). Independent thallium minerals are very rare. To date, only fifty-six have been found in nature, but Tl is an abundant minor component, relatively concentrated in many sulfide minerals (e.g. pyrite, galena, sphalerite, chalcopyrite) and in minerals of potassium (Jakubowska et al., 2007; Karbowska et al., 2014; Vaněk et al., 2012). Therefore, Tl is usually recovered as a byproduct of the smelting of Pb, Zn and Cu ores and of sulfuric acid production, where pyrite (FeS₂) is used as raw material. While less than 15 t of Tl are produced worldwide annually, it is estimated that 2000–5000 tons per year are mobilized by industrial processes (Kazantzis, 2000; Peter and Viraraghavan, 2005).

There are many sulfide mineral resources enriched in Tl in China, but its recycling in the mining or smelting or related industrial activities has not ever been considered (Xiao et al., 2012; Zhou et al., 2008). Specifically, two ultra-large Tl-bearing sulfide ore deposits (the Pb–Zn bedrock and the pyrite bedrock) are located in the Pearl River Basin (PRB). As documented, minerals of the Pb–Zn bedrock and the pyrite bedrock

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showed an average Tl content around 10 µg/g and 50 µg/g, respectively. However, Tl pollution has been often ignored in China, partly due to its relatively low abundance and associated difficulties with analysis in natural water samples (Das et al., 2007; Lukaszewski et al., 1996; Krasnodębska-Ostręga et al., 2013), though the maximum contaminant level in drinking water of China has been fixed at 0.1 µg/L since 2006 (MOH and SAC, 2006), much lower than the limiting value of 2 µg/L for drinking water in the USA (US EPA, 2006). Therefore, enormous amounts of Tl have been mobilized and discharged into the PRB intentionally or accidentally until an incidental Tl pollution (0.18–1.03 µg/L) of a drinking water source in the northern PRB broke out, mainly caused by hidden discharges from a Pb–Zn smelting plant using Tl-bearing Pb–Zn ores, which aroused severe public concern all over China in 2010 (Xinhua News Agency, 2010).

Apart from the Pb–Zn smelting, recent investigations have also revealed serious Tl contamination of surface soils and fluvial sediments due to open mining activities at Tl-bearing pyrite deposits in Yunfu city, located in the western PRB (Liu et al., 2010a, 2010b, 2012; Yang et al., 2005). The pyrite mine is one of the world's largest metallogenic region with massive sulfide reserves of more than 200 Mt (Liu et al., 2010a; Yang et al., 2005). The deposits are stratiform ores, mainly consisting of pyrite, followed by some pyrrhotite (Fe_{1-x}S), limonite (Fe_2O_3) and small proportions of sphalerite (ZnS) and chalcopyrite (CuFe_2S). Gangue minerals include silica, calcite, sericite, carbon and minute amounts of clay, sphene, fluorite and zircon. Sulfides are present predominantly in veins, accompanied by several massive and disseminated occurrences, and contain various potentially toxic trace elements like As, Cr, Co, Ni, Tl (Yang et al., 1997). It was estimated that over 7000 t of Tl were preserved in the mine (Song and Liang, 1992). Up to commissioning in the late 1960s, 2–3 Mt pyrite ores have been extracted annually from the mine, leaving huge quantities of metal-rich waste legacies without proper environmental safeguards. Drainage from the mine wastes with low pH due to various kinds of chemical and microbiological weathering usually results in excessive amounts of dissolved metal and sulfide particles. All these materials have been dispersed downside and are now hazardous to the local environment, particularly by water flow and transportation by the river system, which originates near the mine mountain and flows southeast through the city center and then northeast across small villages at a length of 40 km until it reaches the Pearl River. However, environmental impacts of the mining activities on a larger scale across the city are unknown, except for some studies focused on the minerals, rocks, soils and fluvial sediments within the mining area itself (Liu et al., 2010a, 2010b, 2012; Yang et al., 2005). The river system is used as the main source of irrigation and portable water to the villagers and of drinking water for the urban agglomeration area in the western PRB. In this unique context, investigations of Tl transfer paths are of vital importance. In addition, very little is known regarding its distribution, mobilization, fate and impacts in fresh water systems worldwide (Laforte et al., 2005; Turner et al., 2010; Xiao et al., 2003), despite the high toxicity of Tl.

The objectives of this study are to: (i) investigate the distribution of Tl and other potential anthropogenically-related trace metals in surface water of different locations in the riverine system, (ii) identify possible geochemical transfer of Tl in the hydrosphere; (iii) characterize the potential human health risks of Tl and associated metals with hazard quotients (HQs). As a part of ongoing multidisciplinary environmental studies on Tl, this investigation not only promotes the understanding of Tl hydrogeochemistry, but also urges to establish a goal for reducing Tl loads and to develop a water conservation strategy in order to preserve public health in urban regions around Tl-bearing mines.

2. Materials and methods

2.1. Study area

Yunfu city, located in the western Guangdong Province, China, is situated between 22°43′–23°08′N and 111°56′–112°20′E and featured by

some hilly to undulating slopes and several flatlands. The pyrite mine, situated within the NE limb of the Yunfu Daqianshan anticline, is approximately 10 km² in size and is situated at an elevation of 300–600 m above sea level, constituting the city peak (Liu et al., 2010a; Song and Liang, 1992). The mineralization deposit is primarily a stratiform massive sulfide orebody produced by submarine exhalative deposition with later metamorphism and hydrothermal metasomatism. The deposit consists of volcanic fragment and carbonate rock, while the outcropping rock mainly includes metamorphic rock, sandstone, clastic rock, siltstone (Song and Liang, 1992). The open mining activities since 1970s have produced huge amounts of tailings and wastewater. Mining activities generate 300 Mt acid effluents annually, which are partly conveyed and enter into the city's chief river network downstream (Song and Liang, 1992). This causes surface water contamination by some toxic heavy metals, although several simple wastewater treatment facilities using lime-dosing are available.

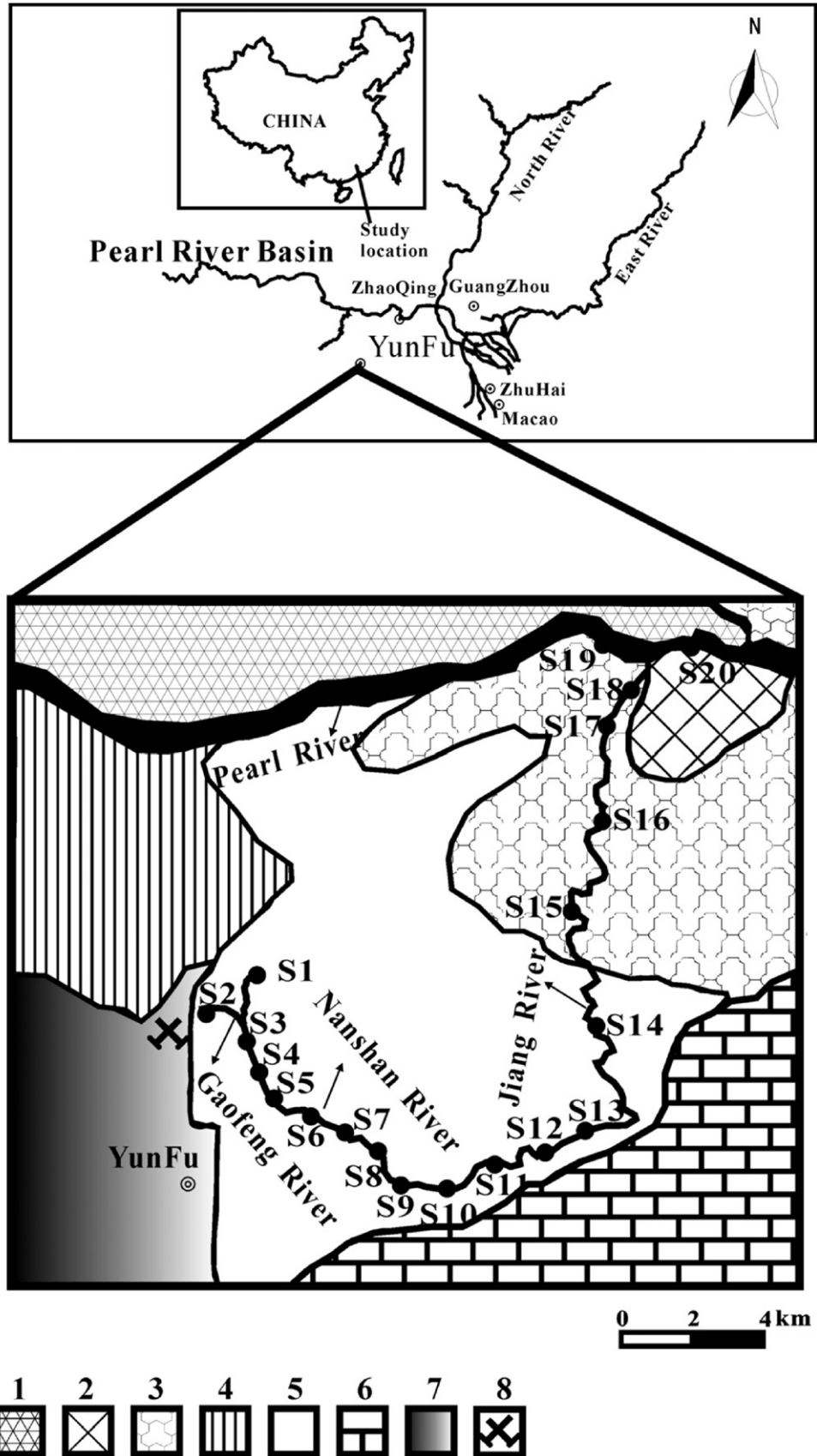
As shown in Fig. 1, the network system includes three main rivers – the Gaofeng River, the Nanshan River and the Jiang River – providing domestic water for local residents. The Gaofeng River is a small river with a mean width of 2 m and depth of 0.25 m, which originates near the mine mountain. The main section of the river acts as a recipient of mine discharge, and stretches for about 4 km along some major roads leading to the city center and then converges with the Nanshan River, a larger river with an average width of 50 m and depth of 1.5 m. It receives water discharge from both the mining-impacted Gaofeng River and some other unaffected rivers. As reported, the riverbed of the Gaofeng River and Nanshan River shares common geological bedrock, which mainly consists of dolomite, silica, coal-containing shale, limestone or marl. The Nanshan River lasts for about 10 km in the city center and then connects with the Jiang River. The Jiang River is another chief river, winding along several small villages with intensive agricultural production for over 20 km and finally converges to the Pearl River, the 3rd longest river in China which provides chief drinking water for the huge urban agglomeration area including Hong Kong, Macao, and Guangzhou. Different from the above mentioned studied rivers, the Jiang River is based on bedrock mainly consisting of granite, such as rhyolite, dacite, andesite and granite porphyry. All these rivers drain an area of about 760 km², and the total population of this region is about 0.30 million. The city of Yunfu is well-known for its ultra-large-scale open pyrite mining, which acts as local pillar industry. This area lies within the south subtropical-monsoonal climate zone. It is warm and humid with a mean annual temperature of 21.5 °C and the highest and the lowest temperatures being 39 °C and 2 °C, respectively. Annual mean precipitation is about 1608 mm, and more than 80% of the rainfall occurs between April and September (Song and Liang, 1992). The wet season lasts from April to October. (See Fig. 2.)

2.2. Sampling, samples treatment and analysis

Water sampling was conducted over two campaigns. In the first campaign (March 2014, representing dry season), samples were taken from twenty locations along the river systems with the aim to cover the whole river basin from the mine to the Pearl River inlet (Fig. 1). The first one (S1) is the head section of the Gaofeng River located above the mining-influenced area and was chosen to represent the regional geochemical background. The 2nd to 4th stations (S2–S4) are also in the Gaofeng River, but located in the immediate downstream of the mining site which directly collects mine discharge at various distances. As shown in Fig. 1, the six subsequent sampling locations (S5–S10) are relatively evenly distributed in the Nanshan River, which flows through the city center where sewage discharges occur. The 11th to 13th stations (S11–S13) are located in the transition zone from city to countryside of the Jiang River. The 14th to 18th stations (S14–S18) are also in the Jiang River located in the rural area of intensive farming, representing a link between the Nanshan River and the Pearl River. For comparison, the upstream (S19) and downstream (S20) of the Pearl River inlet

were also included. In the second sampling period (November 2014, representing wet season), more extensive investigation was performed by collecting various surface waters both from the aforementioned

twenty locations of the rivers and from the pyrite industrial site, including acid drainage water (WP1), pond water (WP2), pipelined effluent (WP3), mine adit water (WP4) and tailing seepage (WP5).



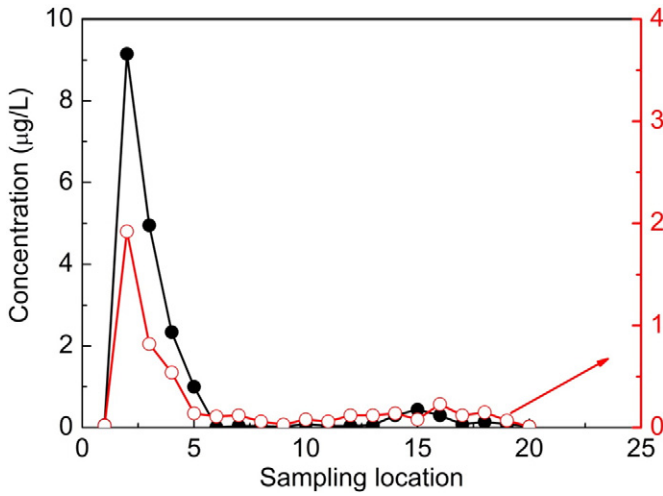


Fig. 2. Thallium distribution in the river waters (black: dry season, red: wet season).

For the surface river waters, replicates of the water near river banks and center were collected at a depth of about 15 cm and then mixed in-situ using polypropylene (PP) plastic bottles. For the surface waters from the mining site, samples (approximately 1 L each) were collected manually with plastic containers from the top surface. Water pH, electrical conductivity (EC) and total dissolved solids (TDS) were measured in-situ using a portable pH meter and a TDS probe. The samples were then filtered through pre-washed 0.45 µm disposable membrane filters (Whatman GmbH, Germany) on the sampling day. The anions Cl and SO₄ were measured by ion chromatography. Samples destined for metal analyses were acidified to pH <2 using ultrapure HNO₃ and stored in coolers at -4 °C until analysis.

The trace metals Al, As, Co, Cr, Cu, Mn, Ni, Pb, Rb, Sr, Tl, and Zn were determined by a Perkin-Elmer Élan 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) under standard operating conditions. The calibration standard solutions were prepared by successive dilution of a high-purity ICP multi-element standard solution (Merck, Darmstadt, Germany) with double-deionized water (Milli-Q Millipore, 18.25 MΩ/cm). Each sample was analyzed five times, and quality control standards were run after every 10 samples to ensure consistent instrument performance during the analysis. The precision obtained was generally better than 5%. All the acids and reagents used were of super-pure grade. The determination limits for the metals were 0.01 µg/L for Al, Cd, Co, Ni, Cu, Rb, Sr, Tl and Pb, 0.1 µg/L for Cr and Mn, and 0.5 µg/L for As and Zn. The major elements Ca, Mg, Na and K were measured by a Leeman Prodigy Spectrum ICP Atomic Emission Spectrometer (ICP-AES). Here, the analytical precision was better than 10%.

2.3. Human health risk assessment

According to the US Environmental Protection Agency (EPA), metals in water enter into the human body through several pathways, including direct ingestion of water, dermal adsorption of metals in water adhered to exposed skin, and inhalation of water odor (USEPA, 1999). However, the latter two pathways are negligible compared with the oral intake (USEPA, 1999; Liu et al., 2012). Consequently, for risk characterization only the exposure doses via ingestion were considered in this study. Potential non-

Table 1 Daily reference dose (R_fD: µg/kg·day) of the studied trace metals.

Element	R _f D	Element	R _f D	Element	R _f D
Tl	0.01	Co	0.3	Ni	20
Al	1000	Cr	3	Sr	600
As	0.3	Cu	40	Pb	1.4
Cd	0.5	Mn	24	Zn	300

carcinogenic risks, estimated by the hazard quotient (HQ), were defined as the ratio of the average daily intake dose (D_i) and the daily reference dose (R_fD) using Eqs. (1) and (2). An HQ >1 indicates potential concerns of non-carcinogenic effects, i.e., an adverse effect on human health. If the HQ value is less than unity, non-cancer risks are not expected to occur (Kelepertzis, 2014; Li and Zhang, 2010; USEPA, 1999, 2004).

$$D_i = (C_w \times IR \times EF \times ED) / BW \times AT \tag{1}$$

In this equation, D_i (µg/kg·day) is the daily exposure dose via ingestion of water, and C_w (µg/L) is the metal concentration in water. Based on the Guangdong Provincial investigation (Wang et al., 2012), an intake rate (IR) of 1.5 L/day, an exposure duration (ED) of 70 a, an exposure frequency (EF) of 365 days/a, a body weight (BW) of 64.3 kg and an average exposure time of 25,550 days were used in the calculation. The hazard quotient was calculated by Eq. (2)

$$HQ_i = D_i / R_{fD_i} \times 10^{-6} \tag{2}$$

where R_fD_i (µg/kg·day) is the daily reference dose. The values of the daily ingestion reference dose (R_fD_i) for As, Co, Cr, Cu, Mn, Ni, Pb, Tl, and Zn originate from the US EPA risk-based concentration table (USEPA, 2015) and are listed in Table 1.

2.4. Statistical analysis

In order to better identify elemental associations and to understand geochemical transfer of Tl, parameters measured in-situ (pH, TDS and EC), major elements (Ca, Mg, Na and K), anions (SO₄ and Cl) and trace metals (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Rb, Sr and Zn) in the river water samples were included in the data matrix of a statistical analysis using the SPSS software version 19.0. Since not all measured data fitted a normal distribution, they were analyzed using the non-parametric procedure of the Kruskal–Wallis test (Rodriguez et al., 2014). The Spearman rank correlation matrix was used to identify relationships between water variables (pH, TDS, EC, Ca, Mg, Na, K, SO₄, Cl) and trace metals (Al, As, Cd, Co, Cr, Cu, Mn, Ni, Pb, Rb, Sr and Zn) in surface waters from the river for the wet season and for the dry season.

3. Results and discussion

3.1. Physio-chemical properties and major element distribution in surface water

As shown in Table 2, the pH values of water samples from the studied rivers ranged from 6.90 to 7.90 with an average of 7.38 in the dry season, and ranged from 7.00 to 8.05 with an average of 7.22 in the wet season. Surface waters from the mining site (WP1–WP5) showed almost invariant strong acidity with pH values of 2.54–2.81. Exceptionally high values of TDS and EC were observed in mine water, ranging from 2110 to 8560 mg/L and 3010 to 12,200 µS/cm, respectively. The

Fig. 1. Sampling sites in the studied river network of the mine city, in the Western Guangdong Province, China. The topmost insertion depicts the location of YunFu City (22°53'N and 112°00'E) in China. The interjection map shows a magnification of the study area, showing the Pearl River Basins with the main branches of the Pearl River in solid lines, and the major cities (○). The main map in the lower insertion shows the surface water sampling points along the studied river network (●) flowing between the pyrite mining area and the Pearl River inlet against a background of geological structure (Ordovician: 1 = sandstones and shale stones; 2 = sand shale, silica and limestone. Late Jurassic: 3 = rhyolite, dacite, andesite and granite porphyry. Devonian: 4 = limestone, silica, sand shale. Triassic: 5 = dolomite, silica, coal-containing shale, limestone or marl. Carboniferous: 6 = clastic rock. Jurassic: 7 = volcanic fragment, carbonate rock, metamorphic rock, sandstone, clastic rock, siltstone; 8 = pyrite ore mine).

Table 2
Concentration of major ions and chemical characteristics of surface waters.

Sample description	Sample no.	Ca	Mg	Na	K	SO ₄	Cl	TDS	EC	pH
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	µS/cm	
<i>Surface water from mining site</i>										
	WP1	409.9	49.35	10.50	6.50	15.62	0.005	6930	9900	2.63
	WP2	446.6	45.99	9.60	5.70	9.62	0.001	5562	6823	2.72
	WP3	431.6	45.66	9.80	5.30	6.05	0.001	8560	12,200	2.81
	WP4	300.8	43.20	8.60	5.60	20.60	0.004	5320	6231	2.54
	WP5	489.6	50.14	9.20	6.10	2.13	0.005	2110	3010	2.62
<i>Surface river water</i>										
<i>Dry season</i>										
	WS1	0.70	1.97	1.98	0.25	1.11	0.268	92.0	45.0	7.10
	WS2	29.61	30.48	5.95	0.92	23.81	0.144	2120	3020	7.50
	WS3	17.35	20.47	10.04	1.43	17.40	0.321	1570	2250	6.90
	WS4	2.33	4.51	5.70	0.64	1.83	0.154	387	550	7.40
	WS5	1.42	1.89	3.39	0.46	0.79	0.110	229	323	7.90
	WS6	1.73	3.26	5.28	0.72	0.27	0.154	313	440	7.30
	WS7	1.54	2.93	3.49	0.53	0.24	0.110	238	339	7.60
	WS8	2.05	3.97	6.63	0.95	1.01	0.248	360	500	7.20
	WS9	1.44	2.90	4.38	0.58	0.05	0.023	262	376	7.40
	WS10	2.51	5.35	7.15	0.89	1.09	0.219	415	570	7.40
	WS11	1.83	3.99	6.10	0.76	0.82	0.222	346	500	7.40
	WS12	1.94	4.62	5.92	0.77	0.94	0.257	361	510	7.30
	WS13	1.86	4.34	5.70	0.80	1.09	0.241	334	477	7.40
	WS14	1.98	4.43	6.26	0.79	0.90	0.231	361	520	7.30
	WS15	2.07	4.39	6.36	0.81	1.10	0.268	358	499	7.30
	WS16	1.87	4.06	5.03	0.72	1.09	0.187	340	620	7.10
	WS17	1.60	4.25	5.98	0.84	1.04	0.202	341	482	7.30
	WS18	2.19	4.68	3.54	0.46	0.61	0.124	256	360	7.50
	WS19	1.62	4.60	2.87	0.37	0.40	0.108	210	298	7.50
	WS20	1.19	1.40	2.14	0.31	0.38	0.065	24.2	34.6	7.90
<i>Wet season</i>										
	WS1	0.95	3.12	0.86	0.12	0.01	0.010	150	73.0	7.05
	WS2	9.52	20.14	3.83	0.63	0.49	0.007	1700	2390	7.70
	WS3	8.26	10.83	5.62	0.85	0.19	0.010	477	670	7.00
	WS4	4.65	5.81	3.25	0.52	0.10	0.012	337	489	7.30
	WS5	3.41	5.61	2.16	0.38	0.06	0.012	116	166	7.42
	WS6	3.16	5.44	3.56	0.59	0.04	0.014	163	228	7.23
	WS7	3.03	5.21	2.35	0.42	0.04	0.014	158	224	7.25
	WS8	2.28	5.67	4.18	0.63	0.04	0.016	177	247	7.19
	WS9	2.04	5.12	3.53	0.43	0.05	0.016	256	125	7.17
	WS10	3.06	6.30	4.21	0.69	0.04	0.016	314	447	7.13
	WS11	2.36	7.77	3.85	0.63	0.03	0.008	368	530	7.14
	WS12	3.25	6.13	2.81	0.65	0.00	0.002	206	288	7.05
	WS13	3.13	6.95	3.67	0.61	0.01	0.030	291	460	7.14
	WS14	3.56	7.15	2.69	0.59	0.01	0.001	266	130	7.15
	WS15	2.66	7.79	3.72	0.61	0.01	0.003	217	106	7.13
	WS16	5.63	8.62	2.86	0.58	0.06	0.005	211	302	7.02
	WS17	4.01	7.56	2.31	0.35	0.03	0.011	198	285	7.05
	WS18	2.54	0.81	1.89	0.21	0.03	0.013	207	101	7.08
	WS19	2.10	8.78	1.32	0.18	0.02	0.006	163	225	7.17
	WS20	0.95	0.87	0.53	0.05	0.01	0.004	31.5	50.0	8.05

TDS values fell into a range from 32.0 to 1700 mg/L with a mean of 300 mg/L in the wet season, and from 24.0 to 2120 mg/L with a mean of 446 mg/L in the dry season. The EC values ranged from 50.0 to 2390 µS/cm with an average of 377 µS/cm in the wet season, and ranged from 35.0 to 3020 µS/cm with a mean of 636 µS/cm in the dry season. Surface water samples from both the rivers and the mining site were characterized by obviously higher concentrations of Ca and Mg compared to K and Na, suggesting that Ca and Mg are the major cations in the hydrosphere of this area. As the solution pHs from the mining site were quite low, it is reasonable that high levels of Ca and Mg could be resulted from the dissolution of carbonate minerals, such as calcite, dolomite, and magnesite. For the anion components, the surface waters were chemically dominated by enriched amounts of SO₄ as compared to Cl (Table 2).

3.2. Thallium and trace metal concentrations in surface water

Surface waters taken at the pyrite mining site serve as negative "reference samples" for the surface water quality assessment of the rivers. As shown in Table 3, washing process water (WP1), waste pond

water (WP2), pipelined effluent (WP3), and mine adit water (WP4) were particularly enriched with Tl (101.1–194.4 µg/L), when compared to the local background (WS1) and the unpolluted rivers elsewhere (Nielsen et al., 2004; Ouyang et al., 2006). Similarly enriched levels of Tl were found in the mine water systems of some other mine areas (Xiao et al., 2003; Li, 2007). For instance, the concentration of Tl was 13–1966 µg/L in deep mine groundwater from a Hg–Tl mineralized zone in China (Xiao et al., 2003). For another Pb–Zn mine area also in China, the Tl levels were 13.2–193 µg/L in groundwater (Li, 2007). Though pure Tl minerals such as lorandite (TlAs₂) and avicennite (Tl₂O₃) have not been found in this region, Tl is known to be encountered in many sulphidic minerals, such as pyrite, chalcopyrite and sphalerite (Tremel et al., 1997; Turner et al., 2010). For example, the mean concentration of Tl in the pyrite (FeS₂) and sphalerite (ZnS) minerals in this area, as reported, can reach 50 mg/kg and 10 mg/kg, respectively. The severe contamination with Tl in WP1–WP4 thus can probably be ascribed to the dissolution of these sulfide minerals, which occur abundantly in the Ediacaran rocks of the Dagan Mountains (Feng, 2010). In addition, as shown in Table 3, the water samples also exhibited high concentrations of As (60.20–482.1 µg/L), Cd (288.3–313.8 µg/L),

Table 3
Thallium and other trace metal concentrations (in $\mu\text{g/L}$) in the surface waters.

Sample description	Sample no.	Tl	Al	As	Cd	Co	Cr	Cu	Mn	Ni	Rb	Sr	Pb	Zn
<i>Surface water from mining site</i>														
	WP1	126.2	52,500	482.1	281.6	363.7	211.6	32.80	205,460	837.9	56.58	732.8	577.1	3600
	WP2	106.3	48,620	251.2	313.8	409.0	232.8	19.35	227,319	931.0	102.2	738.5	468.2	2657
	WP3	194.4	38,700	122.4	299.0	371.1	221.5	10.20	217,203	855.7	34.75	492.8	494.1	2647
	WP4	101.1	39,200	60.20	288.3	282.9	172.6	76.11	146,834	625.3	42.26	702.3	93.21	2078
	WP5	2.75	45,200	200.70	978.4	879.8	80.82	949.9	18,380	1212	49.23	81.57	178.3	1800
<i>Surface river water</i>														
<i>Dry season</i>														
	WS1	0.06	4.90	1.26	0.03	0.05	0.55	0.81	3.98	1.34	5.21	50.19	0.28	3.25
	WS2	9.15	776.5	3.95	2.15	11.34	0.33	1.25	14,993	5.87	36.99	436.8	1.84	124.4
	WS3	4.95	135.1	3.46	0.34	13.84	0.34	0.98	9075	5.28	24.99	302.0	0.75	67.80
	WS4	2.34	39.43	3.41	0.25	0.39	0.26	0.79	843.9	2.17	8.28	104.4	2.42	24.44
	WS5	1.00	1.85	3.32	0.01	0.11	0.31	0.68	5.79	1.58	7.37	45.71	0.15	17.62
	WS6	0.01	19.37	7.30	0.03	0.27	0.23	0.71	34.6	1.83	9.58	63.22	0.44	2.94
	WS7	0.04	73.14	6.83	0.08	0.30	0.34	1.05	55.3	1.27	6.59	59.09	0.51	2.85
	WS8	0.04	1.08	5.60	0.01	0.25	0.63	0.66	1.25	2.62	12.07	74.04	0.44	2.94
	WS9	0.02	48.28	5.90	0.05	0.24	0.35	0.85	46.2	1.25	7.25	51.68	1.77	4.41
	WS10	0.09	2.86	5.17	0.02	0.35	0.59	0.68	404.1	2.64	11.51	97.12	0.44	2.94
	WS11	0.04	27.51	5.03	0.03	0.51	0.30	1.00	36.95	2.52	10.16	75.76	0.46	3.71
	WS12	0.04	41.81	4.60	0.03	1.02	0.42	1.32	78.60	2.51	9.80	83.94	0.39	4.10
	WS13	0.06	28.65	4.26	0.03	1.10	0.34	0.96	63.50	2.37	10.47	79.01	0.65	4.50
	WS14	0.30	21.86	4.25	0.02	1.62	0.30	0.72	124.10	2.76	10.42	83.00	0.84	20.87
	WS15	0.44	25.63	4.51	0.03	1.30	0.33	0.77	161.00	2.83	10.83	84.09	0.56	18.13
	WS16	0.30	35.33	4.21	0.03	0.60	0.56	0.69	157.00	2.65	9.58	74.89	0.93	12.04
	WS17	0.08	6.06	4.61	0.01	0.76	0.54	0.84	188.20	2.75	5.08	86.87	1.34	12.91
	WS18	0.14	34.81	2.87	0.05	0.14	0.47	0.50	1.92	1.35	10.63	87.09	0.15	12.06
	WS19	0.08	31.64	2.53	0.03	0.22	0.38	0.76	25.93	1.38	3.17	96.87	0.35	2.49
	WS20	0.03	5.72	2.21	0.03	0.12	0.27	0.64	8.76	2.75	3.09	25.21	1.83	3.99
<i>Wet Season</i>														
	WS1	0.02	43.12	1.77	0.02	0.14	0.28	1.12	3.88	2.56	4.28	24.73	0.70	2.61
	WS2	1.92	217.20	1.05	0.18	2.38	2.59	1.84	4394	6.67	28.78	267.3	2.38	32.30
	WS3	0.82	50.12	1.22	0.22	1.46	0.06	1.16	1482	3.49	20.44	125.1	1.21	15.70
	WS4	0.54	40.26	4.16	0.01	0.26	5.33	2.20	2.30	1.03	7.36	39.30	2.50	16.40
	WS5	0.14	20.13	5.30	0.01	0.75	7.39	2.36	5.23	2.38	15.00	90.80	2.09	1.84
	WS6	0.11	8.56	3.91	0.13	0.14	0.45	2.15	4.20	1.50	11.27	52.51	0.23	0.52
	WS7	0.12	9.28	8.42	0.02	0.12	7.34	5.32	3.52	0.60	6.25	38.40	2.84	0.48
	WS8	0.06	23.12	4.56	0.19	0.12	0.05	0.92	1.49	1.98	13.11	57.56	0.21	0.51
	WS9	0.03	2.03	7.53	0.03	0.07	0.22	1.00	12.44	0.79	3.84	29.04	0.12	0.98
	WS10	0.08	25.16	1.78	0.12	0.24	0.09	0.98	15.18	2.13	16.39	73.10	0.25	0.96
	WS11	0.06	1.36	1.21	0.08	0.58	0.05	0.88	54.16	2.43	15.36	67.87	0.32	1.03
	WS12	0.12	32.53	0.84	0.03	0.12	0.34	0.63	1.50	0.60	6.25	38.40	0.18	1.21
	WS13	0.12	33.65	1.48	0.11	0.20	0.19	1.32	40.66	2.00	14.07	72.38	0.23	1.32
	WS14	0.14	31.27	0.53	0.09	0.75	0.39	2.36	50.58	2.38	15.00	90.80	0.12	2.51
	WS15	0.08	26.31	1.37	0.10	0.22	0.34	0.80	66.50	2.36	14.20	79.67	0.15	1.13
	WS16	0.23	32.16	1.13	0.40	0.45	0.05	0.96	178.0	3.26	13.00	77.87	0.10	1.05
	WS17	0.12	8.23	1.12	0.11	0.27	0.16	1.03	114.9	3.01	12.07	74.32	0.11	0.25
	WS18	0.15	25.43	0.59	0.42	0.03	0.28	1.29	6.44	0.80	6.91	8.98	0.13	2.05
	WS19	0.07	21.36	0.52	0.12	0.10	0.13	4.13	1.20	1.84	4.04	87.80	0.02	0.62
	WS20	0.01	5.93	0.10	0.02	0.02	0.25	1.52	1.01	0.73	0.17	2.81	0.49	4.12
Surface water limit (China), Grade I ^{a)}		NG _{Tl}	NG	50	1	NG	10	10	100	NG	NG	NG	10	50
Surface water limit (China), Grade V ^{a)}		NG	NG	100	10	NG	100	1000	1000	NG	NG	NG	100	2000
Water quality criteria for drinking water														
China ^{b)}														
	WHO ^{c)}	0.1	200	10	5	1000	50	1000	100	20	NG	NG	10	1000
	USEPA MCL ^{d)}	2	NG	10	5	NG	100	1300	50	NG	NG	NG	15	NG
	USEPA MCLC ^{d)}	0.5	NG	NG	5	NG	100	1300	50	NG	NG	NG	NG	NG
	Pearl River, China ^{e)}	0.05	134.17	0.16	0.05	0.14	11.4	5.82	44.73	7.62	8.73	76.61	0.4	7.73
	Yangtze River, China ^{f)}	NG	NG	13.2	4.7	NG	20.8	10.7	5.4	13.4	NG	NG	55.1	9.4
	Ghana stream ^{g)}	<0.01	NG	18	1.3	1.3	0.52	2.65	682	0.85	4.65	214	0.85	138
	Background world average ^{h)}	0.007	NG	NG	0.08	0.06	1	0.56	3	0.34	NG	NG	0.1	3.35

^{a)}The values for metal concentrations are taken from SEP and GAQIQ (2002); ^{b)}the values are taken from MOH and SAC (2006); ^{c)}the values are taken from WHO (2008); ^{d)}the values are taken from USEPA (2006); ^{e)}the values are taken from Ouyang et al. (2006); ^{f)}the values are taken from Wu et al. (2009); ^{g)}the values are taken from Asante et al. (2007); ^{h)}the values for metals are taken from Klavins et al. (2000) except Tl from Nielsen et al. (2005); ⁱ⁾NG: not given.

Cr (172.6–232.8 $\mu\text{g/L}$), Mn (146,833–227,319 $\mu\text{g/L}$), Ni (625.3–931.0 $\mu\text{g/L}$), Pb (93.21–577.1 $\mu\text{g/L}$), and Zn (2078–3600 $\mu\text{g/L}$). The runoff from the randomly disposed tailing constitutes another source of surface water contamination in the mining area, as illustrated by the tailing seepage (WP5), which displayed highly concentrated As, Cd, Cu, Mn, Ni and Zn. When compared to other surface waters from the mining site, WP5 has a considerably lower Tl concentration (2.75 $\mu\text{g/L}$) which, however, still exceeds the permissible drinking water limit (MOH and SAC, 2006; USEPA, 2006) by an order of magnitude. All these results demonstrate that the concentrations of Tl and associated trace metals in the

surface waters from the mining site generally exceed both the drinking water limit (MOH and SAC, 2006; USEPA, 2006; WHO, 2008) and the safe concentration for aquatic life and industrial, agricultural or domestic use in China (SEP and GAQIQ, 2002). It is also higher than the Tl concentration in mine waters (0.48–1.38 $\mu\text{g/L}$) from an abandoned mine in the South West England (Law and Turner, 2011). The concentration of Tl here is comparable to those in streamwater from the Hg–Tl mineralized zone (1.9–8.1 $\mu\text{g/L}$) and the Pb–Zn mine area (0.92–45.9 $\mu\text{g/L}$) in China (Xiao et al., 2003; Li, 2007). Due to large open mining activities without proper environmental treatment, all these contaminated

surface waters and tailings stored in unlined ponds may be an environmental problem of extraordinary spatial dimensions during heavy rain falls or mountain torrents. Farmlands and croplands, distributed sporadically over the mine mountain and extensively at the mountain foot, are at a particularly high risk of serious Tl contamination as they frequently receive mining waters for irrigation. Worse still, all these contaminated waters and tailings are then conveyed to surrounding riverine systems, intentionally or accidentally over the dense surface and/or underground drainage network.

WS1 abstracted from the headwater of the Gaofeng River showed a very low concentration of Tl (0.02–0.06 µg/L), comparable to the reported background level in the Pearl River (Table 3, Fig. 2). However, the Tl concentration in WS2, sampled from the immediate downstream of the mining site, amounted to 1.92 µg/L in the wet season and 9.15 µg/L in the dry season, i.e., exceeding the official drinking water limit by two orders of magnitude (MOH and SAC, 2006; USEPA, 2006). This level of Tl represented the peak for the studied rivers during both seasons. The concentration then decreased by more than half in the WS3, collected 1 km downstream of WS2, probably due to dilution by other runoffs. Even WS4, gathered from the location 3 km away from the mine, showed an excessively high concentration of Tl. Elevations of Co, Cu, Mn, Ni and Zn were also observed in the samples of WS2–WS4, especially during the dry season. The overall elevation of Tl and other metals here may be ascribed to the anthropogenic impacts from pyrite mining and to the geogenic source from natural weathering of the river bedrock. The concentrations of Co, Cu, Ni and Zn, albeit enriched at some locations, are mostly lower than their respective drinking water limits (MOH and SAC, 2006; USEPA, 2006; WHO, 2008), while Tl levels across the whole Gaofeng river mostly exceeded the drinking water standard. These concentrations are slightly higher than the results for surface waters from the River Carnon and the Red River in England (0.11–0.37 µg/L), whose catchments are partly mineralized (Law and Turner, 2011). High concentrations of Tl (2.5–80.3 µg/L) were detected in river waters surrounding the base-metal sulfide mine areas in north-eastern New Brunswick, Canada (Zitko and Carson, 1975). The exclusive high concentration of Tl may presumably result from the particular geochemical properties of Tl that commonly occurs as free Tl⁺ species under conditions of most surface waters. As such, it has low affinities for suspended particles and is hardly removed from the mine waste water by the traditional precipitation treatment of lime-neutralization used at the pyrite mining site (Law and Turner, 2011; Peter and Viraraghavan, 2005; Song and Liang, 1992). The resident riverside communities with around 30,000 inhabitants who usually use the surface waters for irrigation of crops and vegetables, watering of livestock and even direct consumption are thus exposed to a great potential health risk arising from Tl.

In order to further investigate the contamination scale, more surface waters were collected from the Nanshan River, a larger river just downstream of the Gaofeng River. Surface waters in the Nanshan River generally showed much lower Tl concentrations than those in the Gaofeng River during both seasons, probably as a result of dilution by the “clean” drainage originating in foresting areas. However, Tl concentrations at some locations during the wet season still exceeded the drinking water limits (MOH and SAC, 2006; USEPA, 2006). The remarkable anomalies of Tl in these waters are most possibly caused by unidentified discharge of Tl-bearing groundwater in deep fractures of the mineralized area, where Pb–Zn–Ag polymetallic sulfide ores enriched with Tl were found (Feng, 2010). The elevation of the groundwater table above the riverbed during the wet season could facilitate release of dissolved Tl from groundwater seepage to surface water. Similar findings were reported for a small watershed of the Hg–Tl mineralized area and the Pb–Zn mine area from China (Xiao et al., 2003; Li, 2007). Surface water samples from the Jiang River, which drains catchments containing no metalliferous deposits and flows through several small villages, were also included in the investigation. During the wet season, relatively high concentrations of Tl were observed unexpectedly in WS12–

WS14 and WS16–WS18 from the lower reaches located more than 20 km away from the mineralized area, where scarce industrial activities are to be found. These concentrations are generally consistent with the range of Tl levels found in the ground colored water from the brown coal Miocene aquifer (Wojtkowiak et al., 2016), but approximately ten times higher than those in surface water from the River Warta and Odra (Lukaszewski et al., 1996) and surface river waters from the abandoned mine in England (Law and Turner, 2011). The above high levels of Tl in waters suggest that both weathering processes and mining activities can accelerate the release of Tl from the Tl-rich rocks and sulfide minerals into water.

Additionally, the concentrations of Co, Cr, Cu, Ni, Pb and Zn were generally low and comparable to their local background levels across the river course. In each sampling period, one more surface water sample was collected from the upstream and downstream of the Pearl River inlet for further comparison. The upstream surface water (WS19), which connects with the Tl-bearing mine city, overall exhibited an obviously higher Tl concentration than the downstream one (WS20) linking with another city.

3.3. Geochemical transfer processes of Tl in the river water

Thallium is a widely dispersed trace element, and its concentrations in natural waters are normally low, ranging from 0.012 to 0.016 µg/L in seawater (Flegal and Patterson, 1985), 0.001 to 0.003 µg/L in stream water (Dall'Aglio et al., 1994), from 0.001 to 0.036 µg/L in lake water (Cheam, 2001), and from 0.001 to 0.007 µg/L in river water (Nielsen et al., 2005). Compared to the values reported for normal natural waters, “natural” surface waters from the riverine system of this study were relatively enriched with Tl, with an average concentration of 0.96 µg/L in the dry season and 0.25 µg/L in the wet season, which both surpassed its threshold in drinking water of 0.1 µg/L. The general dispersion of Tl in the riverine systems followed a descending order for the sampling sites with increasing distance downstream from the pyrite mining site. However, some unexpected Tl elevations were observed in the lower reaches, which directly conjuncts with the Pearl River. The occurrence and geochemical transfer of Tl are likely to be governed by mine water discharge, pyrite tailing dispersion, and water-rock interactions.

The pyrite minerals as reported are accompanied by many toxic trace metals like As, Cr, Co, Mn, Ni, Cu, Pb, and Zn. Tl as an accompanying element is particularly enriched in the studied pyrite ore, with a mean content of 10–50 µg/g (Song and Liang, 1992). The extraction activities of pyrite ores which involve washing, flotation and some other processes facilitate the release of various accompanying toxic metals in the minerals. As shown in Table 3, waste waters from the mining site exhibited exceptionally high concentrations of the above mentioned trace metals. Concurrently, these surface waters also showed high concentrations of Ca, Mg, Na and K and SO₄ with high values of TDS and EC and low pH values (Table 2), as compared to values commonly observed in surface waters of rivers. The enriched levels of SO₄ due to the reactions of primary sulfide minerals or the release of secondary sulfate salts correlated well with Tl levels in the mine water. When compared to drinking water standards (MOH and SAC, 2006; USEPA, 2006; WHO, 2008) and concentrations in rivers farther away from the mining site, the Gaofeng river, whose main section acts as the mine water recipient, only showed enriched levels of Tl and Mn. This indicates that conventional lime-dosing for pretreatment of mine water before discharge is only effective for removing other trace metals like As, Cd, Co, Cr, Cu, Pb and Ni, but not Tl and Mn. It is well reported that lime-dosing is only suitable for removal of Tl(III) (Peter and Viraraghavan, 2005; Xiao et al., 2012). However, Tl(I) is the principal species in acidic mine waters, at least in the mine area under study. In equilibrium with air (O₂ = 0.21 bar), speciation computation then carried out by Phreeqc software (Phreeqc interactive, 2.12.5) additionally confirmed that Tl

exclusively exists as free Tl^+ species in the mine water with high contents of SO_4 and low contents of Cl.

Large quantities of annually produced pyrite tailing, rich in various sulfide minerals, may also contribute to the elevation of Tl in the rivers. As Tl is seldom recovered in the pyrite ore processing, as is usually done in metal-based mining or smelting operations elsewhere (Cheam, 2001; Peter and Viraraghavan, 2005), it is discarded into the environment as part of the tailings. Pyrite tailing dispersion in the rivers may occur by occasional tailing-dam failures or torrential flooding. For example, according to local documentations (Zhang et al., 1999), several tailing-dam failures in the 1970s–1990s transported a lot of tailing materials downstream up to 20–30 km away from the mining site. Alternatively, eolian transportation of tailing in fine particles from the mining site in NE direction might also be possible. The Tl level in the tailing seepage, though not comparable to those observed in the mine water, still amounted to 2.75 $\mu\text{g/L}$. Since the tailings are also rich in sulfide minerals, water-tailing interactions (during water flow through the tailing) by chemical and microbiological weathering may also release excessive Tl, thereby introducing Tl dispersion in rivers over long distances. This may also explain some elevations of Tl in the middle and lower reaches of the watershed farther away from the mining site.

Water-rock interactions represent another possible way for Tl dispersion in the river waters. The bedrock of the Gaofeng River and the Nanshan River is dominated by limestone, dolomite, silicstone and coal-containing shale, while that of the Jiang River is granite of andesite, rhyolite and dacite. Aside from the contribution of Ca from the mine

water, the presence of carbonates (mainly limestone) in the upper and middle reaches of the river system may additionally favor dissolution of Ca into the rivers. Since Tl is not only encountered in the sulfide minerals as a chalcophile element, but also occurs in minerals of K, Rb, and et al. as a lithophile element, elevated Tl concentrations in these parental rocks are also reported (Tremel et al., 1997; Law and Turner, 2011; Xiao et al., 2003). As a geochemical analog in many aspects, Tl^+ can replace K^+ , Rb^+ , and et al. in the alkali micas and feldspars (Tremel et al., 1997; Law and Turner, 2011). Water-rock interactions between groundwater and Tl-bearing minerals under the surface might also be possible. The investigation by Feng (2010) reported the presence of deep underground Pb–Zn–Ag polymetallic sulfide ores in the mineralized area along the upper reaches of the rivers. Therefore, unidentified discharge of Tl-bearing groundwater seepage due to water-rock interactions in deep fractures of the mineralized area may contribute to the occurrence of Tl in the surface water. The groundwater table elevation above the riverbed could facilitate release of Tl into the surface water, much more in the wet season than in the dry season. As shown in Fig. 3, high concentrations of Tl in the river waters were accompanied by enriched concentrations of Ca, Sr, Rb, Mn, SO_4 and high values of TDS and EC. These concomitant elevations probably reflect combined contributions from mine water, leaching of Tl-bearing sulfide minerals in the tailing or in the deep underground Pb–Zn–Ag polymetallic sulfide ores and the dissolution of limestone.

Another possible reason for Tl enrichment in the river consists in water-soil/sediment interactions. High contents of Tl ranging from 4.2

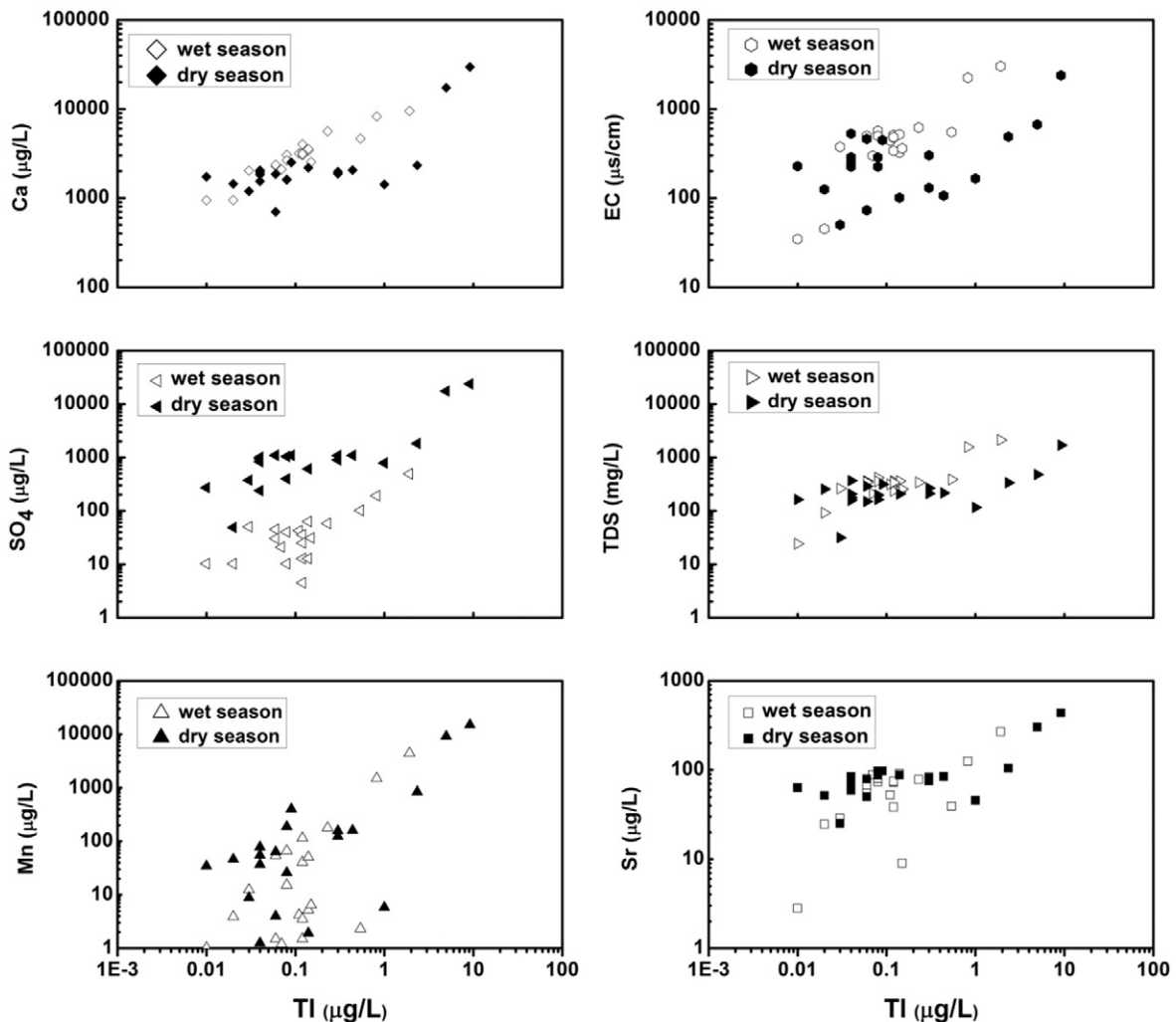


Fig. 3. Plots of concentrations of Ca, EC, SO_4 , TDS, Mn and Sr versus Tl concentration in the river waters.

Table 4
Spearman correlation coefficients between TI and other parameters in surface water of the riverine system (a. dry season; b. wet season).

	TI	Al	As	Cd	Co	Cr	Cu	Mn	Ni	Rb	Sr	Pb	Zn	Ca	Mg	Na	K	SO ₄	Cl	TDS	EC	pH
<i>a.</i>																						
TI	1																					
Al	0.22	1																				
As	-0.47	0.03	1																			
Cd	0.19	<u>0.86</u>	-0.14	1																		
Co	0.44	0.47	0.25	0.21	1																	
Cr	-0.04	-0.14	0.06	-0.27	-0.13	1																
Cu	0.01	<u>0.65</u>	0.25	0.46	0.54	-0.12	1															
Mn	0.56	0.49	0.14	0.33	<u>0.81</u>	-0.12	0.48	1														
Ni	0.47	<u>0.00</u>	-0.06	-0.10	<u>0.72</u>	-0.11	0.04	<u>0.60</u>	1													
Rb	0.43	0.16	0.21	0.15	<u>0.59</u>	0.11	0.07	<u>0.36</u>	0.51	1												
Sr	0.64	0.43	-0.10	0.33	<u>0.61</u>	0.09	0.24	<u>0.68</u>	0.45	0.53	1											
Pb	<u>0.17</u>	0.39	0.08	0.35	0.49	-0.33	0.26	<u>0.63</u>	0.48	-0.01	0.19	1										
Zn	0.76	0.33	-0.32	0.27	<u>0.56</u>	-0.30	0.15	<u>0.57</u>	0.54	0.38	0.43	0.49	1									
Ca	<u>0.60</u>	0.34	0.06	0.30	<u>0.65</u>	0.06	0.06	<u>0.59</u>	0.55	<u>0.85</u>	<u>0.83</u>	0.19	0.47	1								
Mg	<u>0.58</u>	0.46	-0.09	0.33	<u>0.62</u>	0.16	0.23	<u>0.61</u>	0.43	<u>0.63</u>	<u>0.95</u>	0.07	0.39	<u>0.87</u>	1							
Na	0.28	<u>0.02</u>	0.47	-0.14	<u>0.74</u>	0.09	0.19	<u>0.57</u>	0.66	<u>0.75</u>	0.55	0.22	0.31	<u>0.72</u>	0.54	1						
K	0.31	0.09	0.45	-0.09	<u>0.79</u>	0.17	0.26	<u>0.61</u>	<u>0.70</u>	<u>0.77</u>	0.55	0.29	0.35	<u>0.70</u>	0.55	0.93	1					
SO ₄	0.70	0.11	-0.30	0.15	0.55	0.17	0.24	<u>0.61</u>	<u>0.57</u>	0.52	0.58	0.26	0.56	<u>0.60</u>	0.52	0.47	0.54	1				
Cl	<u>0.21</u>	-0.14	0.05	-0.18	0.51	0.26	0.23	<u>0.25</u>	<u>0.43</u>	0.52	<u>0.27</u>	-0.15	<u>0.18</u>	<u>0.39</u>	0.32	<u>0.63</u>	0.57	<u>0.66</u>	1			
TDS	0.49	0.29	0.29	0.15	0.79	0.01	0.33	0.75	0.64	0.76	0.72	0.36	0.50	0.86	0.72	0.87	0.85	<u>0.64</u>	0.50	1		
EC	0.52	0.36	0.24	0.18	<u>0.79</u>	0.07	0.28	<u>0.77</u>	<u>0.65</u>	<u>0.72</u>	<u>0.66</u>	0.42	0.50	<u>0.82</u>	<u>0.68</u>	<u>0.78</u>	<u>0.79</u>	<u>0.64</u>	0.44	0.94	1	
pH	-0.06	0.06	-0.17	0.15	-0.38	-0.36	-0.11	-0.21	-0.31	-0.29	-0.12	-0.02	-0.12	-0.23	-0.14	-0.48	-0.46	-0.47	<u>-0.79</u>	-0.39	-0.45	1
<i>b.</i>																						
TI	1																					
Al	0.58	1																				
As	-0.09	-0.13	1																			
Cd	0.31	0.18	-0.27	1																		
Co	0.60	0.39	0.02	0.10	1																	
Cr	0.31	0.14	0.21	-0.51	0.05	1																
Cu	0.28	0.00	0.03	-0.22	0.03	<u>0.57</u>	1															
Mn	0.50	0.27	-0.09	0.44	<u>0.74</u>	-0.19	-0.25	1														
Ni	0.34	0.37	-0.14	0.35	<u>0.82</u>	-0.29	-0.14	<u>0.77</u>	1													
Rb	0.49	0.33	0.05	0.36	<u>0.85</u>	-0.11	-0.14	<u>0.71</u>	<u>0.70</u>	1												
Sr	0.51	0.32	-0.14	0.34	<u>0.79</u>	-0.06	0.14	<u>0.61</u>	<u>0.71</u>	<u>0.76</u>	1											
Pb	0.18	0.23	0.43	-0.43	<u>0.26</u>	0.46	0.31	-0.09	<u>0.00</u>	<u>0.23</u>	-0.07	1										
Zn	0.40	0.64	-0.31	-0.18	0.31	0.30	0.17	0.15	0.23	0.19	0.10	0.42	1									
Ca	<u>0.90</u>	0.50	-0.05	0.25	<u>0.77</u>	0.21	0.13	<u>0.59</u>	0.48	<u>0.60</u>	<u>0.64</u>	0.15	0.27	1								
Mg	0.41	0.35	-0.32	0.40	<u>0.67</u>	-0.32	-0.14	<u>0.62</u>	0.66	<u>0.62</u>	<u>0.85</u>	-0.18	0.05	<u>0.57</u>	1							
Na	0.18	0.20	0.33	0.41	<u>0.44</u>	-0.35	-0.42	<u>0.48</u>	0.31	<u>0.70</u>	0.39	0.16	-0.07	0.33	0.48	1						
K	0.28	0.33	0.13	0.34	0.47	-0.25	-0.46	0.43	0.26	<u>0.71</u>	0.42	0.14	0.02	0.44	0.52	0.90	1					
SO ₄	0.54	0.12	0.42	0.30	0.44	0.03	0.22	0.32	0.29	0.41	0.36	0.34	0.12	0.52	0.21	0.44	0.25	1				
Cl	-0.12	-0.20	0.71	0.10	-0.23	-0.07	0.10	-0.12	-0.22	-0.02	-0.28	0.21	-0.36	0.50	-0.41	0.28	0.04	0.37	1			
TDS	0.46	0.41	-0.06	0.31	0.56	-0.22	-0.25	0.66	0.40	0.65	0.42	0.07	0.33	0.58	0.59	0.73	0.69	0.38	0.001	1		
EC	0.51	0.35	0.06	0.30	0.61	-0.26	-0.13	0.45	0.41	<u>0.62</u>	0.49	0.25	0.07	0.66	<u>0.67</u>	<u>0.69</u>	<u>0.70</u>	0.51	0.11	0.72	1	
pH	-0.11	-0.30	0.21	-0.39	-0.13	0.53	<u>0.58</u>	-0.42	-0.35	-0.12	-0.07	0.44	0.10	-0.14	-0.27	-0.13	-0.24	0.26	0.16	-0.22	-0.12	1

Underlined numbers: $P < 0.01$ (2-tailed); bold numbers: $P < 0.05$ (2-tailed).

to 30.5 µg/g with a mean of 11.4 µg/g were detected in the alluvial soils near the river (Liu et al., 2010a, 2010b), and 4.58 µg/L of Tl were found in the soil water. The river sediments also showed a high accumulation of Tl (2.06–17.31 µg/g). River flow, especially when acid water discharge occurs, may also enhance Tl release from the bank soils and river sediments.

Moreover, metals like Pb, As, Cr and Cu showed several enriched levels at some locations of the Nanshan River in the city center, probably showing impacts from improper disposal of urban sewage, traffic emission and/or other industrial activities. Meanwhile, almost no Tl elevation was observed at the locations with intensive urban activities. This suggests that urban sewage, traffic emission and some other industry are not important contributors of Tl to the aquatic environment in this study, though it is reported that Tl compounds, used at small quantities in industrial, construction and household products (e.g., dyes, imitation jewelry, electronic devices and pigments), may release Tl into the aquifer system out of solid waste (Law and Turner, 2011).

In summary, all these results suggest that the geochemical transfer of Tl in the rivers is mainly governed not only by anthropogenically-induced discharges of active pyrite mining, but also by local natural dispersion processes based on water-rock interactions. As well documented, Tl ($4f^{14}5d^{10}6s^26p^1$) commonly exists in two oxidation states, Tl^+ and Tl^{3+} (Vink, 1993; Kaplan and Mattigod, 1998), in the aqueous environment. Thermodynamic speciation computations predicted that the monovalent thallos cation (Tl^+) is the predominant species in natural waters. It is not expected to form complex species unless organic matter is present at high concentrations, since Tl^+ typically exhibits a low tendency for polymerization and forms weak aqueous complexes (Kaplan and Mattigod, 1998; Plavšić and Cosovic, 1994; Vink, 1993). The exclusive occurrence of Tl as free Tl^+ species was observed in the groundwater of a Hg–Tl mineralized area in China (Xiao et al., 2003) and in the surface water of the Amous River, which is affected by acid mine drainage downstream from an abandoned Pb–Zn mine in France (Casiot et al., 2011). However, predominance of Tl^{3+} was reported in freshwater from the Great Lakes in North America. This was ascribed to bacterial activity that oxidized Tl(I) into Tl(III), followed by stabilization of this valence state by complexation with organic and inorganic ligands or formation of dimethylthallium (Lin and Nriagu, 1999a, 1999b; Schedlbauer and Heumann, 2000; Twining et al., 2003). For river waters with relatively low concentrations of halide ions (such as Cl) and high concentrations of SO_4 as in this study, Tl mostly exists as free Tl^+ species as demonstrated by the speciation calculation with Phreeqc software. In addition, Tl^+ is weakly affiliated to solid minerals (Kaplan and Mattigod, 1998; Peter and Viraraghavan, 2005), all these greatly enhance its mobility in the whole river system.

3.4. Correlation analysis

In order to identify correlations between Tl and other analyzed parameters, non-parametric Spearman rank correlation coefficients

between water parameters (pH, TDS, EC, Ca, K, Na, Mg, SO_4 , Cl) and concentrations of Tl and other trace elements were calculated. They are presented in Table 4. In the dry season, Tl showed strong positive correlation coefficients at $P < 0.01$ with Sr (0.64), Zn (0.76), Ca (0.60), Mg (0.58) and SO_4 (0.70). Trace metals (like Mn and Ni) and water parameters (TDS and EC) also displayed significant positive correlation coefficients at $P < 0.05$ with Tl. Significant negative correlation at $P < 0.05$ was found between Tl and As. In the wet season, very significant positive correlation coefficients at $P < 0.01$ were found between Tl and Al (0.58), Co (0.76) and Ca (0.90). Furthermore, Tl exhibited strong positive correlation coefficients with Mn (0.50), Rb (0.49), Sr (0.51), SO_4 (0.54), TDS (0.46) and EC (0.51). Evidently, there are differences in the relationships represented by the correlation coefficients for the two seasons. The most plausible explanation for such differences is that there are variations of seasonal hydrological routing, which could cause different weathering effects for the parental rocks and induce changes in seasonal non-point pollution inputs from anthropogenic activities, such as pyrite mining and domestic sewage. All these seasonal variations could result in variables which correlate well with the Tl distribution in one environment, but become less significant in another environment. In spite of some differences between the two seasons, Tl concentrations displayed a good positive correlation with concentrations of Ca, Mn, Sr, SO_4 , TDS and EC, and showed negative correlations with As and pH for both seasons. The striking similarities between the two seasons further confirm that the geochemical transfer of Tl in the rivers is mostly controlled by the Tl-bearing pyrite mining and by natural weathering of the parental rocks regardless of the seasonality.

3.5. Preliminary health risk assessment of trace metals in the river water

As presented in Table 5, the average HQ value descends in the order $Tl > Mn > As > Co > Pb > Cd > Sr > Cr > Ni > Al > Zn > Cu$ in the dry season. In the wet season, the average HQ value decreases in the order $Tl > Mn > As > Co > Pb > Cr > Cd > Sr > Ni > Al > Zn > Cu$, slightly different from that in the dry season. Although some differences exist for the order of HQ values between the dry and wet seasons, Tl is the most important contributor to non-carcinogenic health risk concerns in both seasons. In the dry season, the average HQ value of Mn and in particular Tl exceeds the safe limit. Specifically, samples from the Gaofeng River exhibit HQ values of Tl mostly higher than 1. This indicates that Tl may cause health risks through drinking water to local residents. Additionally, since the solubility of thallos compounds is relatively high, Tl can be transferred from waters to crops via irrigation.

4. Conclusions

This study investigated the geochemical distribution and potential health risk of Tl in the surface water of the main riverine system in a pyrite mine city in the western Pearl River Basin, China. Results generally showed elevated Tl concentrations, exceeding the drinking water safe limit, across the rivers studied. The distribution of Tl in the aqueous system exhibited specific patterns, corresponding to the combined effects

Table 5 Health risk assessment for Tl and other trace metals in the surface water of the rivers.

		Tl	Al	As	Cd	Co	Cr	Cu	Mn	Ni	Sr	Pb	Zn
Dry season	Average	2.24E+00	2.14E-03	3.39E-01	7.59E-03	1.34E-01	3.05E-03	4.86E-04	1.28E+00	2.90E-03	5.25E-03	1.38E-02	1.35E-03
	Standard deviation	2.80E+00	4.94E-03	1.05E-01	4.04E-03	2.39E-01	9.13E-04	1.09E-04	2.00E+00	1.06E-03	4.55E-03	1.03E-02	1.18E-03
	Minimum	2.33E-02	3.09E-05	1.72E-01	4.67E-04	3.89E-03	1.79E-03	2.92E-04	1.22E-03	1.46E-03	2.18E-03	2.50E-03	1.94E-04
	Maximum	2.13E+01	2.22E-02	5.68E-01	1.00E-01	1.08E+00	4.90E-03	7.70E-04	1.46E+01	6.85E-03	2.08E-02	4.03E-02	9.67E-03
Wet season	Average	5.74E-01	9.65E-04	1.89E-01	5.64E-03	3.27E-02	1.01E-02	9.90E-04	3.13E-01	2.48E-03	3.63E-03	1.20E-02	3.41E-04
	Standard deviation	4.52E-01	1.32E-03	1.90E-01	5.49E-03	2.73E-02	1.91E-02	7.03E-04	3.26E-01	1.05E-03	2.55E-03	1.46E-02	3.67E-04
	Minimum	1.63E-02	3.89E-05	7.47E-03	4.67E-04	1.71E-03	3.50E-04	3.67E-04	9.80E-04	7.00E-04	1.34E-04	3.67E-04	1.94E-05
	Maximum	4.49E+00	6.21E-03	6.55E-01	1.95E-02	1.85E-01	5.75E-02	3.10E-03	4.27E+00	7.78E-03	1.27E-02	4.73E-02	2.51E-03

of mine water discharge, pyrite tailing dispersion, and water-rock interactions. With the exception of the head water, high levels of Tl (1.00–9.15 µg/L in the dry season and 0.54–1.92 µg/L in the wet season) were observed in surface waters sampled from the Gaofeng River. Tl concentrations then decreased obviously in the Nanshan River, but contamination with Tl also appeared at some of these locations during the wet season. Quite unexpected Tl anomalies were observed at the lower reaches of the Jiang River, which is based on granitic bedrock and is located most distant from the mining site. Non-parametric Spearman rank correlation analysis uncovered that Tl concentrations showed a good positive correlation with concentrations of Ca, Mn, Sr, SO₄, TDS and EC, and showed negative correlations with As and pH for both seasons, which further confirms that the geochemical transfer of Tl in the rivers is controlled not only by the mining of Tl-bearing pyrite (including mine water discharge and pyrite tailing dispersion), but also by local natural dispersion processes. They result from interactions between water and sulfide minerals of the host rock and from natural weathering effects of the parental bedrock (limestone, granite etc.), regardless of the seasonality. A preliminary non-carcinogenic health risk assessment by calculating hazardous quotient (HQ) indices proved that Tl in the river waters (especially Gaofeng River) may cause health risks through drinking water and via irrigation.

This study particularly highlights not only anthropogenically-induced but also hidden naturally-occurring enrichment of Tl in the hydrosphere of the PRB, and drives special attention to surveillance and remediation.

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