



Review article

Thallium pollution in China and removal technologies for waters: A review

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ABSTRACT

Thallium (Tl) is a typical toxic metal, which poses a great threat to human health through drinking water and the food chain (biomagnification). China has rich Tl-bearing mineral resources, which have been extensively explored and utilized, leading to release of large amounts of Tl into the environment. However, research on Tl pollution and removal techniques is relatively limited, because Tl has not been listed within the scope of environmental monitoring in China for several decades. This paper reviewed Tl pollution in wastewater arising from various industries in China, as well as the latest available methods for treating Tl-containing industrial wastewater, in order to give an outlook on effective technologies for controlling Tl pollution. Conventional physical and chemical treatment technologies are efficient at removing trace amounts of Tl, but it proved to be difficult to achieve the stringent environmental standard ($\leq 0.1\text{--}5\ \mu\text{g/L}$) cost-effectively. Adsorption by using newly developed nanomaterials, and metal oxide modified polymer materials and microbial fuel cells are highly promising and expected to become next-generation technologies for remediation of Tl pollution. With the potential for greater Tl contamination in the environment under accelerated growth of industrialization, researches based on lab-scale implementation of such promising treatment technologies should be further expanded to pilot and industrial scale, ensuring environmental protection and the safety of drinking water for sustainable development. Comprehensive insights into experiences of Tl pollution in China and in-depth perspectives on new frontier technologies of Tl removal from wastewaters will also benefit other nations/regions worldwide, which are susceptible to high exposure to Tl likewise.

1. Introduction

Thallium (Tl) is a typical rare element widely dispersed in the natural environment. It is used in chemical, electronic, pharmaceutical, aerospace and optical industry as well as in superconducting materials and high-energy physics (Nriagu, 1998; Karbowska, 2016; Belzile and Chen, 2017). However, it is extremely toxic, far exceeding the toxicity of As and Hg, with a lethal dose of only 8–10 mg/kg for human adults (Dmowski et al., 2015; Osorio-Rico et al., 2017; Puccini et al., 2018). The acute toxicity of Tl to human is characterized by vomiting, diarrhea, temporary hair loss, and effects on the nervous system, lungs, heart, liver, kidneys and even death (Viraraghavan and Srinivasan, 2011). Epidemiological data showed that exposure to Tl during

pregnancy may have a detrimental impact on birth outcomes, such as fetal death, congenital malformations, or decreased birth weight (Hoffman, 2000; Qi et al., 2019). Chronic exposure may occur at Tl concentration levels in the range of 0.1 to 100 $\mu\text{g/L}$ (Campanella et al., 2016; Biagioni et al., 2017; Campanella et al., 2017). Thallium and its compounds are therefore considered major hazardous wastes by the World Health Organization (WHO, 2008). It is also listed as one of the technology-critical elements by European COST Action TD1407, bearing consequential environmental risks and potential human health threats (Cobelogarcía et al., 2015). In order to minimize health risks arising from Tl, the United States Environmental Protection Agency (USEPA) has suggested the maximum permissible level at 2 $\mu\text{g/L}$ in drinking water, with the goal of lowering it to 0.5 $\mu\text{g/L}$ (USEPA, 2006).

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Table 1
Standards of thallium concentrations in waters for different provinces in China and for other countries.

Source	Concentration ($\mu\text{g/L}$)	References
Environmental Quality Standards for Surface Water regulated by MEP, China	0.1	SEPA, 2006
Inorganic Chemical Industry Pollutant Discharge Standard by MEP, China	5	SEPA, 2006
Emission Standard for Industry Wastewater regulated in the Hunan Province, China	5	HPEPB, 2014
Emission Standard for Industry Wastewater in the Guangdong Province, China	5	GPEPA, 2017
Emission Standard for Steel Industry Wastewater in the Jiangsu Province, China	2	EPDJP, 2018
Industry Wastewater Discharge Standard in Shanghai, China	5	SEPB, 2017
Primary Drinking Water Regulations, Maximum Contaminant Level (MCL) by USEPA	2	USEPA, 2018
Primary Drinking Water Regulations, Maximum Contaminant Level Goal (MCLG) by USEPA	0.5	USEPA, 2018
Human Health Effects in Seawater by USEPA	4	USEPA, 2004
Wastewaters (for RCPA categories: P113, P115, U214, U215, U216, and U217) BDAT, US	140	Peter and Viraraghavan, 2005
Water Quality Guideline for Freshwater in Canada	0.8	CCME, 2003
Maximum Contaminant Level of Drinking Water in Russia	0.1	WHO, 2008

Meanwhile, a more stringent limit of $0.8 \mu\text{g/L}$ was adopted in Canada (CCME, 2003), and an even lower limit of $0.1 \mu\text{g/L}$ was fixed in China (MOH and SAC, 2006) (Table 1).

Thallium was discovered by William Crookes in 1861 *via* spectral analysis of residues from a sulfuric acid plant (Crookes, 1861; Nriagu, 1998; Viraraghavan and Srinivasan, 2011). With an atomic number of 81 (electron configuration: $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$) and a relative atomic mass of 204.3833, Tl is the heaviest element in the Group IIIA. The atomic radius, the ionic radius and the covalent radius are 0.208, 0.15 and 0.148 nm, respectively, and the atomic volume is $17.2 \text{ cm}^3/\text{mol}$. There are two naturally occurring stable isotopes, ^{203}Tl (29.46%) and ^{205}Tl (70.54%), and 26 artificial isotopes with masses ranging from 191 to 210 and half-lives ranging from 2.1 ms (^{201}Tl) to 3.8 years (^{204}Tl) (Nriagu, 1998).

Thallium is insoluble in water, alkali and liquid ammonia, but it is readily dissolved in nitric acid to form soluble salts. Dilute sulfuric acid reacts with Tl considerably slower than dilute nitric acid. Thallium occurs in two oxidation states in nature, Tl(I) and Tl(III), and exhibits a versatile chemistry in aqueous systems (Nriagu, 1998; Wick et al., 2017; Böning et al., 2018). The industrially valuable products of Tl compounds mainly include thallium oxide (Tl_2O_3), thallos oxide (Tl_2O), thallos hydroxide (TlOH), thallos sulfide (Tl_2S), thallos sulfate (Tl_2SO_4), thallos chloride (TlCl) and others (Zhou and Chen, 2008). Thallium in organic compounds is generally only stable at the trivalent state. Cyclopentadienyl Tl(I) is the only stable organic compound of monovalent Tl. Thallium can be alloyed with a variety of other heavy metals (Zhou and Chen, 2008).

The unique properties of Tl and its compounds are utilized in numerous applications. For example, thallium-barium-calcium-copper oxide is used as a high-temperature superconductor (HTS) in filters for wireless communication. Thallium is contained in gamma radiation detection equipment (e.g. NaI scintillator crystals) as an activator (Cvjetko et al., 2010). It is also used in an alloy with mercury to measure low temperatures (CCME, 2003; USGG, 2017). In China, Tl is used at quantities of about 3 t/a, mainly for the production of photocells (Zhou and Chen, 2008). Thallium also serves as an additive in optical lenses, as a component in high-density liquids for imitation jewelry, and as a catalyst for synthesis of organic compounds.

Owing to its scarcity and high toxicity, Tl and its compounds are used only at small amounts by industry. The worldwide production of pure Tl is very low (Fig. 1a). In 1975, about 8 t were produced in Germany and 3 t in the USA (Zitko, 1975). From 1985 to 2003, the total world annual production of Tl remained fairly constant at approximately 15–16 t (Cvjetko et al., 2010; USGG, 2009; USGG, 2017). From 2004 until present, the world production of Tl experienced a reduction to approximately 10 t. The price of Tl increased in recent years (Fig. 1b), as the supply worldwide continued to be relatively tight. The price tripled from 2005 to 2008 (USGG, 2009; USGG, 2017). Since 2012, the price has persisted at a high level. Sources for commercial production of Tl are flue dust from the roasting of zinc, lead, and copper

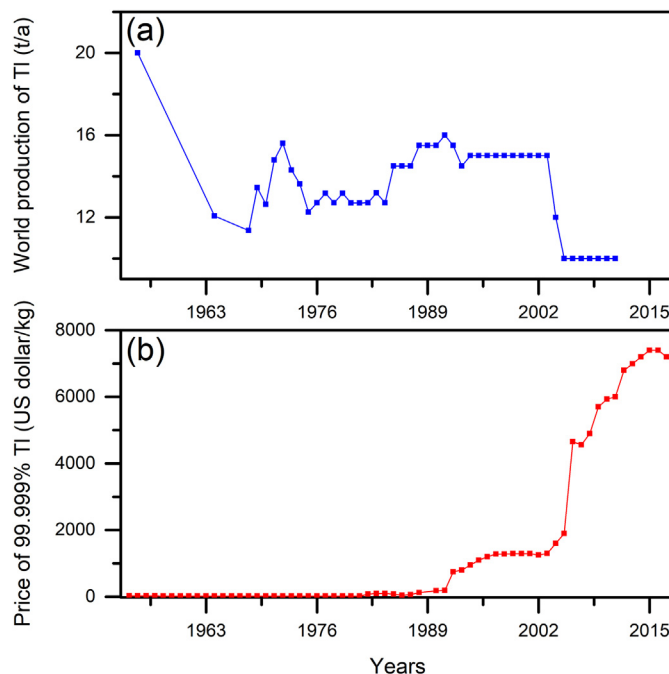


Fig. 1. Variations of thallium production and price. Data compiled from USGG (2009, 2017).

ores in smelters and sometimes from pyrite roasting in sulfuric acid plants (Zitko, 1975; Smith and Carson, 1977; Vaněk et al., 2018; USGG, 2017).

Thallium has both lithophilic and chalcophilic properties (Xiong, 2009; Lin and Nriagu, 1999). As a lithophile, Tl can enter mica, alunite, potassium feldspar, and jarosite by isomorphic substitution, replacing K^+ owing to their similar ionic radii: 1.49 \AA for Tl^+ and 1.33 \AA for K^+ . The sulfur-binding property promotes the coexistence of Tl with Pb, Zn, Cu, As, Sb, Fe, Hg, and Au in various sulfide minerals (Xiong, 2009), where it is widely distributed. Mining and processing of sulfide ores is a major source of Tl contamination in ecosystems (Xiao et al., 2003; Laforte et al., 2005; Turner et al., 2010; Casiot et al., 2011). In total, it was estimated that 2000–5000 t of Tl were mobilized annually before the year of 2000, by industrial processes worldwide (Dmowski and Badurek, 2002; Peter and Viraraghavan, 2005).

In recent years, serious Tl pollution incidences have occurred in different provinces of China, affecting large rivers which act as main drinking water sources (Fig. 2), e.g., the North River of Guangdong in October 2010, the Hejiang River of Guangxi in July 2013, several main rivers of Xinyu in Jiangxi in April 2016, the Jialing River across Sichuan Province and Shanxi Province in May 2017, and the Lu River crossing Hunan Province and Jiangxi Province in August 2018 (Liu et al.,

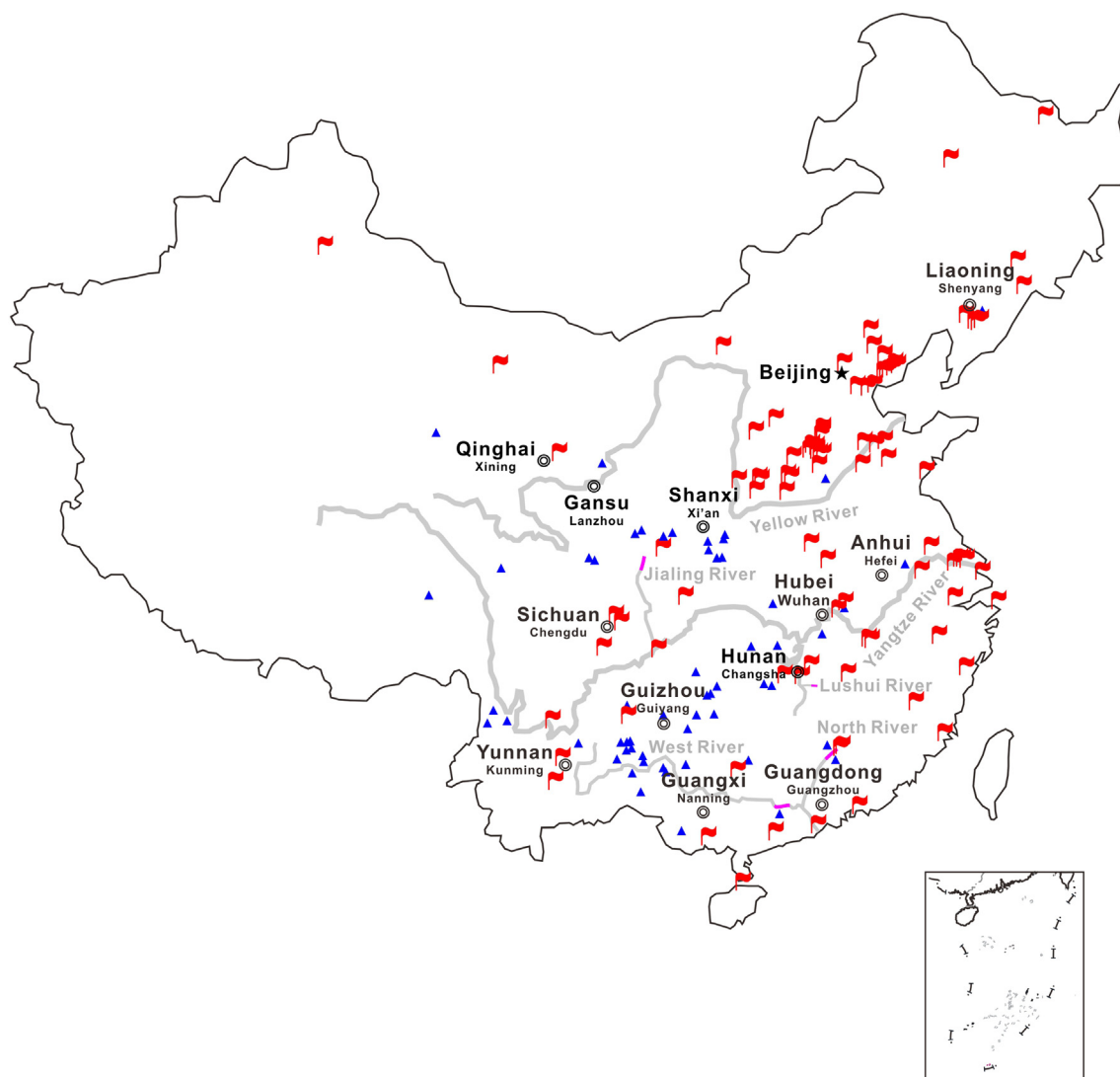


Fig. 2. Map showing the areas where Tl-containing deposits (blue triangles) and steel-iron making factories (red flags) in active production have been identified to pollute minor (pink lines) and major (gray lines) rivers in China. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Modified after Liu et al. (2018a, 2018b).

2018a). These pollution incidents have evoked great public concerns, and Tl pollution regulation and surveillance has been increasingly adopted in China. In 2014, Hunan Province has promulgated the first standard for Tl discharge in China (“Emission Standard of Thallium Pollutants for Industrial Wastewater in Hunan Province” (DB43968-2014)) (HPEPB, 2014). Thereafter, Guangdong (GPEPA, 2017), Jiangsu (EPDJP, 2018), and Shanghai (SEPB, 2017) have also established Tl pollution discharge standards, mostly requiring total effluent Tl concentrations below 5 µg/L before discharge (Table 1).

This paper aims to review emerging Tl pollution in China and the latest removal technologies for Tl-containing wastewater, and to give an outlook on effective technologies for controlling Tl pollution. Recent studies showed that chronic exposure to Tl is a global phenomenon (Turner et al., 2010; Casiot et al., 2011; Voegelin et al., 2015; Campanella et al., 2016; Karbowska, 2016; Vaněk et al., 2018; Biagioni et al., 2017; Belzile and Chen, 2017; Campanella et al., 2017; Aguilar-Carrillo et al., 2018; Grösslová et al., 2018; Cruz-Hernández et al., 2018; López-Arce et al., 2017, 2019; George et al., 2018). Therefore, new insights into experiences with Tl pollution in China and evaluating available technologies is beneficial for other nations/regions worldwide, where similar pollution incidences may occur due to industrial

activities, such as mining, smelting, and coal burning.

2. Typical sources of Tl in waters

Sources of Tl in water can be classified into two categories: natural and anthropogenic. Thallium is widely distributed in natural waters at concentrations < 0.1 µg/L (Peter and Viraraghavan, 2005). However, Tl concentrations are generally higher in watersheds near Tl-bearing minerals. Areas hosting Tl-bearing sulfide ores are prone to Tl contamination in surface and/or ground waters (Casiot et al., 2011; Campanella et al., 2016; Liu et al., 2016; Biagioni et al., 2017; Campanella et al., 2017; Perotti et al., 2017). For example, Tl concentrations were in the range of 0.11–0.37 µg/L for the River Canon and the Red River in England, whose catchments are partly mineralized (Law and Turner, 2011). Anthropogenic sources mainly arise from mining and smelting activities using Tl-bearing ores (especially PbS, FeS₂ and ZnS) and coals (Lis et al., 2003; Peter and Viraraghavan, 2005; Jakubowska et al., 2007; Yang et al., 2009; Liu et al., 2010; Turner et al., 2010; Lukaszewski et al., 2012; Anagboso et al., 2013; Vaněk et al., 2010a, 2010b, 2013; Karbowska et al., 2014; Gomez-Gonzalez et al., 2015; Voegelin et al., 2015; Cruz-Hernández et al., 2018; Ghezzi

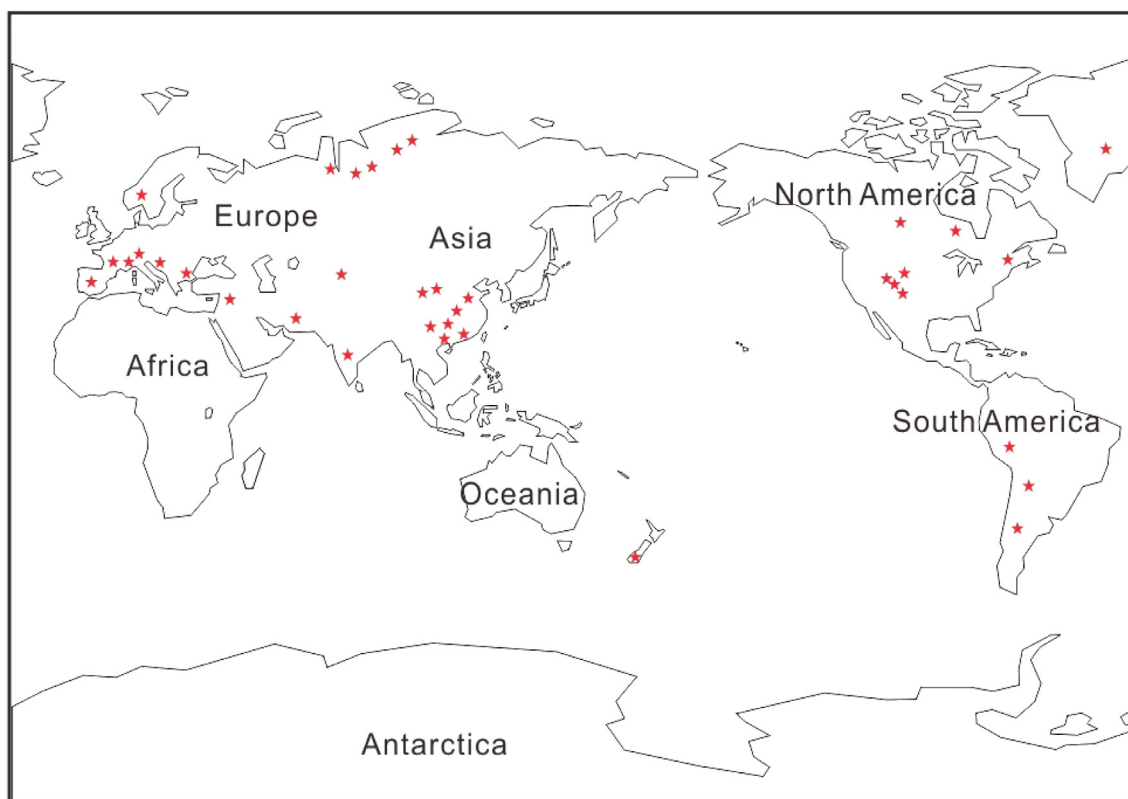


Fig. 3. Distribution of thallium deposits in the world (★: Tl-containing deposits). Modified after Fan et al. (2005).

et al., 2019; López-Arce et al., 2019).

2.1. Distribution of Tl deposits

According to the available data, there are not many locations of Tl deposits. As shown in Fig. 3, the global distribution is extremely uneven. Most of the Tl deposits are concentrated in the northern hemisphere (Europe, Asia and North America). Only a few exist in the southern hemisphere (South America and Oceania). The countries with the most Tl deposits are Macedonia, Switzerland, the United States, France and China (Ikramuddin et al., 1986; Janković, 1989; Hofstra, 2000; Fan et al., 2005; Xiao et al., 2012 and references therein). More than half of Tl minerals are produced from deposits in these countries, such as the Alchar As-Sb deposit in Macedonia, the Carlin gold deposit in Nevada, USA, the Lengnabach deposit in Switzerland, the Jason Roux As-Sb deposit in the French Alps, and the Lanmuchang Hg-Tl deposit in Guizhou Province, China (Table 2). Thallium deposits are typically concentrated in low-temperature ore-forming domains, e.g., in the Mediterranean Alpine region, in the southwestern China, in North America (Carlin-type Au deposits), and in the Russian North Caucasus (Fig. 3). The geological environment of Tl minerals is different in various parts of the world, but most Tl is found in sulfide deposits of Pb, Zn, Fe, Cu, As, Au, Ag, Hg, Sb, Se or Sn; especially in such deposits with high contents of realgar and orpiment (Jakubowska et al., 2007; Karbowska et al., 2014; Xiong, 2009; Vaněk et al., 2012; Zitko, 1975). Independent Tl minerals are very rare. To date, merely 48 have been discovered in nature. They include 33 sulfosalt minerals, 7 sulfide minerals, 3 selenide minerals, 3 sulfate minerals, a sulfur chloride mineral and an oxide mineral (Table 3). Nine kinds of independent Tl minerals have been discovered in China (Table 4). They were mainly found in Yunnan Nanhua, Guizhou Lanmuchang, Tibet Luolong Maoshui and Anhui Xiangquan (Jiang et al., 2014; Mao and Wu, 1989). Lanmuchangite is a new Tl sulfate mineral which was discovered in China by

Chen and Zhou (2000).

In addition, Tl^+ can be enriched in the fluids of the late pegmatitic during magmatic differentiation processes, owing to the similarity to K^+ and Rb^+ regarding charge and ionic radius (Tl^+ : 1.49 Å, K^+ : 1.33 Å, and Rb^+ : 1.48 Å). Therefore, Tl is found in pegmatites of the igneous rocks, acid and intermediate magmatic rocks consisting of K-feldspar, plagioclase, biotite or muscovite (Jović, 1998 and Tu et al., 2004). High contents occur in organic-rich shales as well (Kazantzis, 2000). Table 5 shows Tl contents in different minerals from different rocks.

Rich Tl resources have been discovered in China. As can be seen in Table 2 and Fig. 2, abundant Tl-bearing sulfide mineral resources are widely distributed over different provinces. Examples are the Guangdong Yunfu Tl-bearing pyrite (Yang et al., 2005; Li et al., 2009), the Yunnan Lanping-bearing Tl-Pb-Zn mine (Zhang et al., 1998), the Guangxi Yilan-containing Tl-Hg mine (Zhang et al., 1998), the Xiangquan Tl-bearing pyrite deposit in Anhui (Hu, 2007; Zhou et al., 2008), the Guizhou Getang Tl-bearing Sb-Au deposit, the Kezhai Tl-bearing Se deposit, the Sichuan Dongbeizhai Tl-bearing Au-As ore (Zhang et al., 1998), and the Jiangxi Chengmenshan Tl-bearing Pb deposit (Zhang et al., 1998). The Tl content of Hg-Tl ore in Guizhou Lanmuchang amounts to 3800 mg/kg, with Tl reserves of around 390 t (Zhang et al., 1997); the average Tl content of Pb-Zn ore in Yunnan Jinding is 110 mg/kg, with Tl reserves of 8200 t (Jiang et al., 2014); Tl content in Anhui Xiangquan pyrite ore can reach 3000 mg/kg, with proven reserves of 459 t (Fan et al., 2005); and the average Tl content in Guangdong Yunfu pyrite ore is approximately 50 mg/kg, with proven reserves of nearly 7000 t (Liu et al., 2017b; Song and Liang, 1992). In total, Tl reserves in sulfide ore deposits in China are estimated to be approximately 16,000 t (Tu et al., 2004).

Table 2
Compilation of thallium deposit in the world.

Continent	Country	Thallium deposit	References
Asia	China	Lanmuchang deposit, Yata deposit and Getang deposit in Guizhou Province, Xiangquan deposit in Anhui Province, Jinding deposit and Nanhua deposit in Yunnan Province, Yilan deposit in Guangxi Province, Tongmu trench and Tongjiawan deposit in Shanxi Province, Yunfu pyrite deposit in Guangdong Province, Chengmenshan copper deposit in Jiangxi Province	Chen and Zhou, 2000; Zhu et al., 2002; Zhang et al., 2003; Chi et al., 2005; Xiao et al., 2007; Zhou et al., 2008; Liu et al., 2010; Zhou et al., 2013
	India	Rajpura-Dariba deposit, Rajasthan	Sobott et al., 1987; Grzetic and Moh, 1995
	Japan	Kuroko deposit in Akita, Beihai	Glasby et al., 2008
North America	Uzbekistan	Malkand Zirabulaksk Mountains	Sobott et al., 1987; Grzetic and Moh, 1995
	USA	Mercur deposit in Utah, Getechll deposit and Garlin deposit in Nevada, Franklin deposit in New Jersey, Rambler deposit in Wyoming.	Ikramuddin et al., 1986; Hofstra and Cline, 2000
South America	Canada	Hem Luo deposit in Thunder Bay area, Poudrette deposit in Saint-Hilaire area	Muir, 2002
	Greenland	Illimaussaq deposit	Karup-Møller and Makovicky, 2001
Europe	Argentina	Capillitas deposit in Catamarca Province, Tuminico deposit in LaRiaja Province	Sobott et al., 1987; Grzetic and Moh, 1995
	Peru	Quiruvilca deposit in Santiago Province	Sobott et al., 1987; Grzetic and Moh, 1995
Oceania	Czech Republic	Ronaz deposit in Bohemia, Bukov deposit in Moravia	Janković, 1989
	France	Viges deposit in Limousin Province, JasRoux deposit in Hautes-Alpes Province	Johan and Mantiene, 2000; Topa et al., 2013
	Germany	Segen Gottes mine in Baden-Württemberg, Weintraube mine in Lower Saxony	Janković, 1989
	Macedonia	Alsar deposit, Lojane deposit	Radusinovic, 1966; Janković, 1989; Volkov et al., 2006; Jelenkovic and Boev, 2011
	Russia	Murun Mountains in Eastern Siberia, Norilsk deposit in Eastern Siberia, Beshtau deposit in North Caucasus, Verkhnyaya Kvaisa deposit in South Caucasus, Turzinsk region of Ural Mountains	Arndt et al., 2003; Kekelia et al., 2008; Novruzov, 2011
Oceania	Sweden	Kalmar deposit in Smaland Province	Janković, 1989
	Switzerland	Lengenbach deposit	Hofmann, 1994; Hofmann and Knill, 1996
	New Zealand	Rotokawa mountainous area	Krupp and Seward, 1987

2.2. Thallium pollution in waters from mine areas and industrial sites

Extensive mining during the last several decades entailed release of enormous amounts of Tl into the environment, posing a serious threat to human health (Xiao et al., 2003; Xiao et al., 2012). Extremely high Tl concentrations were mostly found in the Guizhou and Yunnan Province (Southwest China) within a large-scale epithermal metallogenesis area of 900,000 km² (Fig. 4; Xiao et al., 2012). As shown in Fig. 4, this typical low-temperature epithermal metallogenic domain is characterized by metal mineralization of Tl, Sb, Hg, Pb, Au, As, and Zn (Xiao et al., 2012). The average Tl contents in rocks of the domain were in the range from 1.63 to 3.81 mg/kg, resulting in several typical zones with high geochemical baselines of Tl (Fig. 4; Tu et al., 2004; Xiao et al., 2012). In particular, various independent Tl minerals were discovered in the

Xingren Hg-Tl mine, Guizhou Province (Li et al., 1989; Li, 1996; Chen and Zhou, 2000) and in the Nanhua As-Tl mine, Yunnan Province (Zhang et al., 1996, 1998) (Table 4).

As displayed in Table 6 and Fig. 5, the mine pit water, groundwater and surface water of the Xingren Hg-Tl mine show Tl concentrations of 26.6–26.9 µg/L, 13–1966 µg/L, and 1.9–8.1 µg/L, respectively (Xiao et al., 2004a, 2004b, 2004c, 2012). Such high levels of Tl are mainly ascribed to Tl mineralization in the Lanmuchang area. As reported, Tl mineralization with sulfide generally occurs as lorandite, cinnabar, realgar, orpiment, arsenopyrite and pyrite (Zhang et al., 1997; Tu et al., 2004). Thallium contents in different minerals and wall rocks in this area are listed in Table 7.

The surface water and mine water from Nanhua As-Tl mine in Yunnan Province have Tl concentrations of 2.91 and 16.5 µg/L,

Table 3
Independent thallium minerals (adapted from Nriagu (1998) and Zhang et al. (2004)). Independent thallium minerals (adapted from Zhang et al. (2004)).

Mineral	Chemical formula	Mineral	Chemical formula	Mineral	Chemical formula
Avicennite	Tl ₂ O ₃	Gillulyite	Tl ₂ (As,Sb) ₈ S ₁₃	Rebulite	Tl ₅ Sb ₅ As ₈ S ₂₂
Bernardite	Tl(As,Sb) ₅ S ₈	Hatchite	(Pb,Tl) ₂ AgAs ₂ S ₅	Rohaite	TlCu ₅ Sb ₄
Bukovite	Cu _{3+x} Tl _{1-x} FeSe _{4+x}	Hutchinsonite	(Pb,Tl)As ₅ S ₉	Routhierite	TlCu(Hg,Zn) ₂ (As, Sb) ₂ S ₃
Carlinite	Tl ₂ S	Imhofite	Tl ₆ CuAs ₁₆ S ₄₀	Sabatierite	TlCu ₄ Se ₃
Chabourneite	(Tl,Pb) ₅ (Sb,As) ₂₁ S ₃₄	Jankovicite	Tl ₅ Sb ₃ As ₃ Sb ₂ S ₂₂	Sicherite	TlAg ₂ (As,Sb) ₃ S ₆
Chalcostibite	Cu ₆ Tl ₂ Sb ₄	Jentschite	TlPbAs ₂ Sb ₃ S ₆	Simonite	TlHgAs ₃ S ₆
Chalcothallite	(Cu,Fe) ₆ Tl ₂ Sb ₄	Lanmuchangite	TlAl(SO ₄) ₂ ·12H ₂ O	Stalderite	TlCu(Zn,Fe,Hg) ₂ As ₂ S ₆
Christite	TlHgAs ₃ S ₃	Lorandite	TlAs ₂ S ₂	Thalcosite	Cu _{3-x} Tl ₂ Fe _{1+x} S ₄
Criddleite	TlAg ₂ Au ₃ Sb ₁₀ S ₁₀	Monsmedite	H ₈ K ₂ Tl ₂ (SO ₄) ₈ ·11H ₂ O	Thalphenisite	Tl ₆ (Fe,Ni,Cu) ₂₅ S ₂₆ Cl
Crookesite	Cu ₇ (Tl,Ag)Se ₄	Parapirotite	Tl(Sb,As) ₃ S ₈	Thallipyrrite	(Fe,Tl)(S,As) ₂
Cuprostibite	Cu ₂ (Sb,Tl)	Perillalite	K ₈ Tl ₁₄ Al ₁₂ Si ₂₄ O ₇₂ ·2OH ₂ O	Thalliusulphate	Tl ₂ SO ₄
Dorallcharite	Tl _{0.8} K _{0.2} Fe ₃₊₃ (SO ₄) ₂ (OH) ₆	Picotpaulite	TlFe ₂ S ₃	Thalliusulphoacidite	Tl ₂ S ₂ O ₃
Edenhartherite	TlPbAs ₃ S ₆	Pierrotite	Tl ₂ Sb ₆ As ₄ S ₁₆	Vaughanite	TlHgSb ₄ S ₇
Ellisite	Tl ₃ As ₃ S ₃	Raguinite	TlFeS ₂	Vrbaite	Tl ₄ Hg ₅ Sb ₂ As ₈ S ₂₀
Emigliiite	Tl ₂ SnAs ₂ S ₆	Rathite	(Pb,Tl) ₃ As ₅ S ₁₀	Wallisite	TlPb(Au, Ag)As ₂ S ₅
Galkhaite	(Cs,Tl)(Hg,Cu,Zn) ₆ (As,Sb) ₄ S ₁₂	Rayite	Pb ₈ (Ag,Tl) ₂ Sb ₈ S ₂₁	Weissbergite	TlSb ₂

Table 4
Independent thallium minerals discovered in China.

Mineral	Chemical formula	Discovery place	References
Abicennite	Tl ₂ O ₃	Luolong, Tibet	Mao and Wu, 1989
Lorandite	TlAsS ₂	Lanmuchang, Guizhou Province	Chen and Zhou, 2000
Christite	TlHgAsS ₃		Li et al., 1989
Lanmuchangite	TlAl(SO ₄) ₂ ·12H ₂ O		Chen and Zhou, 2000
Raguinite	TlFeS ₂		Li, 1996
Hutchinsonite	PbTlAs ₅ S ₉	Nanhua, Yunnan Province	Zhang et al., 1998
Picotpaulite	TlFe ₂ S ₃		Zhang et al., 1998
Ellisite	Tl ₃ AsS ₃		Zhang et al., 1996
Thallipyrrite	(Fe,Tl)(S,As) ₂		Zhang et al., 1996

respectively (Table 6; Zhang, 1998). Thallium concentrations in the spring water ranged from 0.078 to 0.437 µg/L (Zhang, 1998). Extremely high contents of Tl (> 4000 mg/kg) were found in arsenopyrite minerals (Zhang, 1998).

High Tl contents (50 mg/kg on average) in pyrite originating from epithermal metallogenesis were also found in the Yunfu pyrite deposit of Guangdong Province (Liu et al., 2010; Liu et al., 2017b). The deposit bears massive sulfide reserves of > 200 Mt (Liu et al., 2017b), mainly composed of stratiform pyrite ores, followed by pyrrhotite (Fe_{1-x}S), sphalerite (ZnS) and chalcopyrite (CuFe₂S). Nearly 7000 t of Tl was preserved in the mine (Song and Liang, 1992). Approximately 2–3 Mt pyrite ores have been extracted annually from the mine since the late 1960s, discharging huge quantities of Tl (Liu et al., 2017b). It is estimated that about 15–20 t of Tl have been discharged into the environment (Chen et al., 2013). Dedusting wastewater of a local sulfuric acid plant also had Tl concentrations of 15.4–400 µg/L (Table 6; Liu et al., 2010). Concentrations of 101.1–194.4 µg/L of Tl were found in the surface water from the mining site (Table 6). High concentrations 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 (Fig. 6), located downstream of the mining site (Liu et al., 2017b).

A Tl ore deposit formed by epithermal metallogenesis was recently uncovered in Xiangquan (Anhui Province, eastern China) (Zhou et al., 2005). Up to 5000 mg/kg Tl was observed in pyrite from this deposit (Zhou et al., 2008). The well water, pond water, and hot spring water from the Xiangquan Tl mine showed Tl concentrations of 0.05–0.089 µg/L, 0.05–0.15 µg/L, and 0.62–0.65 µg/L, respectively (Zhou et al., 2008).

In May 2017, Tl concentrations in the Jialing River (Shanxi Province) amounted to 0.46 µg/L, which could be mainly attributed to mining activities. The Tl concentrations in ditch water from the tailing pond ranged from 0.14 to 2.33 µg/L. Exceptionally higher Tl concentrations (up to 1520 µg/L) were found in the mine water (Zhang, 2017).

Owing to high volatility (Table 8), Tl and its compounds can easily enter flue gas as aerosols at high temperature (800–1500 °C) and enter wastewater in subsequent wet dedusting processes. Industrial smelting of Tl-bearing sulfide ores (PbS, FeS₂ and ZnS) at high-temperature

constitutes another significant source of Tl pollution (Nriagu, 1998; Peter and Viraraghavan, 2005; Vaněk et al., 2013). For example, Pb blast furnace soot contains 500–2000 mg/kg Tl (Zhou and Chen, 2008).

As shown in Table 6, Tl concentrations in the wastewater of a Pb-Zn smelter in the northern Guangdong Province were reported to be as high as 19.5–370 µg/L even after lime-precipitation. Such extraordinarily high concentrations of Tl can be due to the fact that Tl often occurs as free Tl⁺ species under normal conditions of most surface waters. In addition, Tl has low affinities for suspended particles and is hardly removed from wastewater by the traditional precipitation treatment (lime neutralization) used at the industrial site (Campanella et al., 2016; Campanella et al., 2017; Law and Turner, 2011; Peter and Viraraghavan, 2005; Liu et al., 2016). Our previous survey throughout the northern section of the Pearl River, which serves as a major drinking water source for mega-urban cities (e.g. Guangzhou, Shaoguan and Qingyuan), discovered elevated levels of Tl in the surface waters and sediments over a distance of 100 km along the river in 2005 (Fig. 7). Water quality monitoring of major drinking water sources showed that Tl levels frequently exceeded the maximum permissible level (0.1 µg/L) during the period 2005–2008. This was mainly ascribed to effluent discharge from industrial sites on the upper reaches (Gao et al., 2008; Qi, 2009). It is reported that Tl-bearing effluents and wastes from different industries onshore were directly discharged into the northern branch of the Pearl River (Qi, 2009). In July 2013, a section (approximately 110 km) of the He River in Guangxi Province was contaminated with Tl at different degrees up to 0.56 µg/L, mainly caused by sewage discharge from an indium producing factory.

As a concomitant element, Tl can also be widely present or even enriched in various K-containing rocks (such as mica, alunite, and potassium feldspar) (Jović, 1998; Yu et al., 2018; Gomez-Gonzalez et al., 2015). In addition to the well-known sulfide-ore mining waste producers, steel-making industry using Fe-oxide minerals which bear K-rich rocks can be a source of Tl pollution. Our pioneering investigation on environmental impacts of a typical steel-making factory in Guangdong Province showed that even very low Tl contents (0.02–1.03 mg/kg) in the raw materials can finally lead to enriched levels of Tl up to 1000 µg/L in dedusting wastewater from sintering furnaces (Liu et al., 2017a). High urinary Tl levels (0.33 µg/L) for hypertensive populations were

Table 5
Thallium contents (mg/kg) in minerals of different rocks (based on Jović, 1998 and Tu et al., 2004).

	Granite pegmatites	Granotoid rocks	Basaltic	Alkaline rocks	Gabbroid rocks	Gneisses	Ultramafic	Granodiorite	Porphyry monzonite	Granite	Amazonite
K-feldspars	0.5–50	0.7–30	–	1.2–3.4	–	0.7–30	–	1.4	2.4	4.5–4.8	–
Hornblende	–	0.8–2.6	–	0.7	–	–	–	–	–	–	–
Magnetite	–	0.4	0.036–0.097	–	2.2	–	–	–	–	–	–
Plagioclase	–	–	0.030–0.052	–	0.05	–	–	–	–	–	10
Phlogopite	–	–	–	–	–	–	3	–	–	4.4	–
Biotite	3–15	3–15	–	3.2–7.6	–	–	–	0.7–8.4	–	3.4–4.1	–
Muscovite	1.5–3.7	1.5–3.7	–	–	–	–	–	–	–	–	–
Pyroxene	–	–	0.003–0.045	–	–	–	–	–	–	–	–
Olivine	–	–	0.008	–	0.05	–	–	–	–	–	–

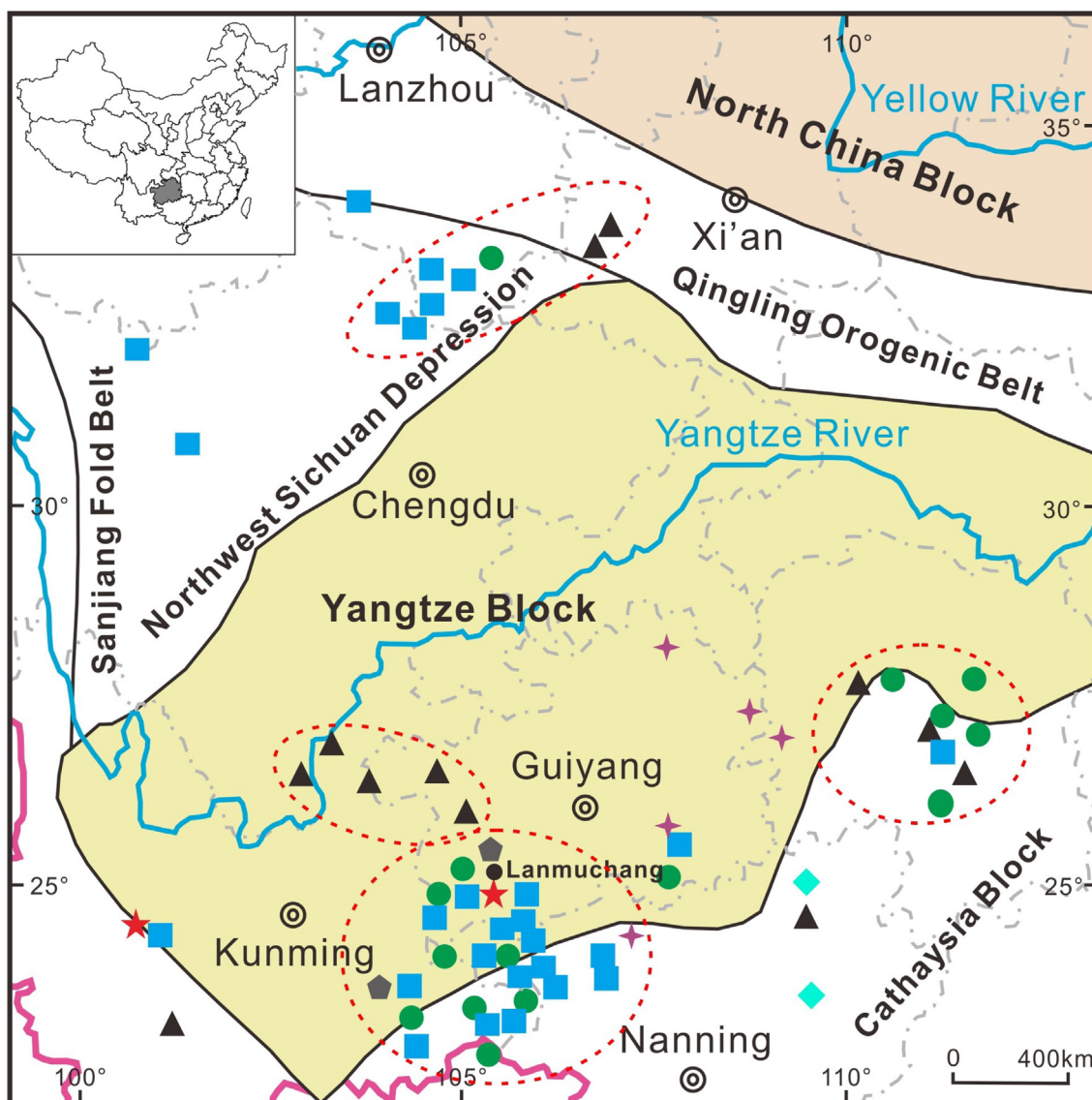


Fig. 4. Map showing the distribution of epithermal ore deposits in Southwest China (★ Tl; ▲ Pb/Zn; ■ Au; ◆ Ba; + Hg; ◆ As; ● Sb; ⊙ capital city; — Geotectonic boundary; - - - provincial boundary; — national boundary; — river; — typical zones with high geochemical baselines of Tl). Modified after Xiao et al. (2012) and Hu et al. (2007).

discovered very recently in Wuhan City, Hubei Province by Jiang et al. (2018). This may be also predominantly ascribed to the long-term human exposure to Tl-bearing metal emissions from a large steel production factory located in that city. Over 200 steel-making plants on a scale of million tonnages exist in China (Fig. 2). Their potential to induce Tl pollution needs further investigation.

Coal-burning and cement production are the other important anthropogenic sources of Tl (Antonia López Antón et al., 2013; Li and Sun, 2016). It is estimated that global resources of Tl in coal amount to 630,000 t (Karbowska, 2016). In coal, approximately 70% of Tl is associated with sulfides. The remaining content is bound to aluminosilicates and organic matters (Querol et al., 1995). Globally, it is estimated that up to one fifth of total Tl released into the environment originates from combustion of coal (Querol et al., 1995; Karbowska et al., 2016). Massive amounts of e-waste can be another major source of Tl input into waters, since trace quantities of Tl compounds are used in the e-industries (Kang et al., 2013). For example, Tl concentrations in wastewater from Li-batteries producing industries amounted to over 7 mg/L (Kang et al., 2013). The survey on Tl distribution in the waters and sediments of the northern branch of the Pearl River showed abnormally

high Tl levels in the vicinity of Shijiao and Longtang town, Qingyuan city. This area is used for incineration and improper disposal of e-waste (Gao et al., 2008; Qi, 2009).

Along with unprecedented economic growth, China is now facing an escalating level of Tl pollution and environmental risks from various industries, since there was practically no monitoring during the past three decades. Effective management and control measures for Tl-containing wastewater are still in the infancy stage, as compared to other metal contaminants (such as Pb, Zn, Cd, Cr, Hg, and As) (Carolin et al., 2017). The development of cost-effective techniques for removing Tl from wastewater is one of the most urgent tasks at present. Existing technologies for Tl pollution control are therefore reviewed in the following section.

3. Technologies for controlling Tl pollution in water

Suitable methods for removing Tl from wastewaters are dependent on the industrial source and the water chemistry. Chemical precipitation/coagulation, ion exchange, adsorption (also to nanoparticles), solvent extraction, and microbial fuel cells are challenging and

Table 6
Thallium concentrations in wastewater from various industrial sources in China.

Wastewater type	Industry/factory	Province	Tl concentration ($\mu\text{g/L}$)	References
Wastewater before lime treatment	Zn-making factory	Jiangxi	3000	Liu et al., 2018b
Wastewater after lime treatment	Zn-making factory	Jiangxi	1520	Liu et al., 2018b
Pond water	Zn-making factory	Guangdong	354.1	Liu et al., 2018b
Process water before pulping	Zn-making factory	Guangdong	19.5	Liu et al., 2018b
Process water after pulping	Zn-making factory	Guangdong	203.8	Liu et al., 2018b
Wastewater before lime treatment	Pb-Zn smelter	Guangdong	470	Liu et al., 2018b
Wastewater after lime treatment	Pb-Zn smelter	Guangdong	370	Liu et al., 2018b
Mine water	Yunfu pyrite mine	Guangdong	101.1–194.4	Liu et al., 2016
Dedusting wastewater	Sulfuric acid factory	Guangdong	15.4–400	Liu et al., 2010
Discharge effluent	Sulfuric acid factory	Guangdong	9.3–21.6	Chen et al., 2000
Discharge river water	Polymetallic mine deposit	Guangdong	2	Liu et al., 2018b
Sintering desulphurization wastewater	Steel factory	Guangdong	280.3–1400	GPEPA, 2017
Sintering desulphurization wastewater	Steel factory (A)	Jiangsu	2500	EPDJP, 2018
Sintering desulphurization wastewater	Steel factory (B)	Jiangsu	109	EPDJP, 2018
Sintering desulphurization wastewater	Steel factory (C)	Jiangsu	189	EPDJP, 2018
Sintering desulphurization wastewater	Steel factory (D)	Jiangsu	194	EPDJP, 2018
Sintering desulphurization wastewater	Steel factory (E)	Jiangsu	2.68–5.01	EPDJP, 2018
Sintering desulphurization wastewater	Steel factory (F)	Jiangsu	301	EPDJP, 2018
Sintering desulphurization wastewater	Steel factory (G)	Jiangsu	438	EPDJP, 2018
Mine water	Lanmchang Hg-Tl mine	Guizhou	26.6–26.9	Xiao et al., 2012
Mine water	Lanhua As-Tl mine	Yunnan	16.5	Zhang, 1998
Surface river water	Lanhua As-Tl mine	Yunnan	2.91	Zhang, 1998
Mine water	Cu mine	Shanxi	1520	Zhang, 2017
Mine water	Cu mine	Shanxi	0.14–2.33	Zhang, 2017

promising techniques currently in use or under development. Each technology has certain advantages and disadvantages, as displayed in Table 9. Conventional physical and chemical treatment technologies are efficient at removing trace amounts of Tl, but it is proved to be difficult to cost-effectively achieve the required standard of $\leq 5 \mu\text{g/L}$.

3.1. Chemical precipitation/coagulation

In chemical precipitation and coagulation methods, metals initially dissolved in wastewater are converted into sparingly soluble compounds. Thallium in water generally exists in the form of soluble Tl^+ . It can be directly transformed into a sparingly soluble Tl(I) salt (such as Tl_2S and TlCl) or it can be oxidized to trivalent Tl, which is then precipitated as Tl(OH)_3 .

Saturated NaCl solution can be used to precipitate Tl(I) as TlCl . In this way, the concentration of dissolved Tl can be reduced to $2 \mu\text{g/L}$ or below (Vink, 1993; Peter and Viraraghavan, 2005). Williams-Beam and Twidwell (2003) proposed that Tl can be effectively removed from wastewater to $< 2 \mu\text{g/L}$ by reductive sulfide precipitation. However, sulfide precipitates in water may generate acid gas as secondary pollution. Furthermore, in addition to pH, the redox potential must be controlled in order to achieve effective Tl removal (Williams-Beam and Twidwell, 2003).

Chemical oxidation-coagulation is more widely used than Tl(I) precipitation. Oxidants such as NaClO , KMnO_4 , and H_2O_2 are applied to oxidize Tl(I) to Tl(III) , which is then coagulated in alkaline solution (Kikuchi et al., 1990; Chen, 2013; Huangfu et al., 2015; Zhang et al., 2013b; Liu et al., 2018a). Owing to the extremely low solubility of Tl(OH)_3 in water, chemical oxidation-precipitation is one of the most effective methods for the treatment of industrial wastewater, also at high salinity and high contents of other metals. Concentrations of dissolved Tl can be reduced to below $0.1 \mu\text{g/L}$. Chemical oxidation-precipitation is a relatively mature technology and widely used in large-scale wastewater treatment. At present, research on this method is mainly focused on complex wastewater systems with different substrates, searching for suitable oxidants, and improving the oxidation efficiency of oxidants.

Chemical precipitation/coagulation is a simple and easily automated treatment method, which is efficient for the removal of heavy metals from wastewater. However, it may create by-products like

flocks, which are considered as a secondary pollutant, and the added chemical reagents may be harmful to human health and the environment (Carolin et al., 2017). Moreover, the sulfide precipitation process requires pre- and post-treatment and accurate control of reagent additions due to the toxicity of sulfide ion, and the potential to generate H_2S (Azimi et al., 2017). Therefore, the increased costs of sludge disposal, poor settling, and slow metal precipitation make it an impractical method (Wingenfelder et al., 2005).

3.2. Ion exchange

Ion exchange treatment is based on a reversible interchange of ions between the solid and liquid phases (Kurniawan et al., 2006), which initiates with ion-exchange reactions, then physical absorption of heavy metal ions, followed by complexation between counter-ions and functional groups, and finally hydration at the solution-adsorbent interface (Ferreira et al., 1999). The effectiveness of ion-exchange methods can be affected by different factors such as pH, anions, temperature, contact time, and the initial concentration of the adsorbent and sorbate (Gode and Pehlivan, 2006).

Albert and Masson (1994) proposed that Tl can be extracted from acidic solutions by using ion exchange resins and developed a viable procedure. Li et al. (2017a) used modified anion exchange resins to remove Tl and Cl from high-salinity industrial wastewater. The removal of Tl is based on oxidization of Tl(I) to Tl(III) by hydrogen peroxide under saline conditions to form a chloro complex (TlCl_4^-). More than 97% of Tl and 90% of Cl could be removed.

Ion exchange resins are preferably in treating wastewaters for elimination or separation of heavy metal ions (Kang et al., 2004). Because of its simple and convenient operation, the ion exchange method has been recommended by the US EPA (US EPA, 2004), which exhibited superior advantages than chemical precipitation attributed to high efficiency, low sludge production, recovery of valuable metals, and high selectivity (Chiarle et al., 2000; Rengaraj et al., 2001). However, due to the high content of matrix elements in industrial wastewater, the ion exchange capacity is strongly affected by other solutes. Moreover, matrix fouling occurs when treating solutions with high concentrations of competing metals (Barakat, 2011). Regeneration of ion exchange resins using hazardous chemical reagents is another disadvantage, which potentially causes secondary pollution. Additionally, the high

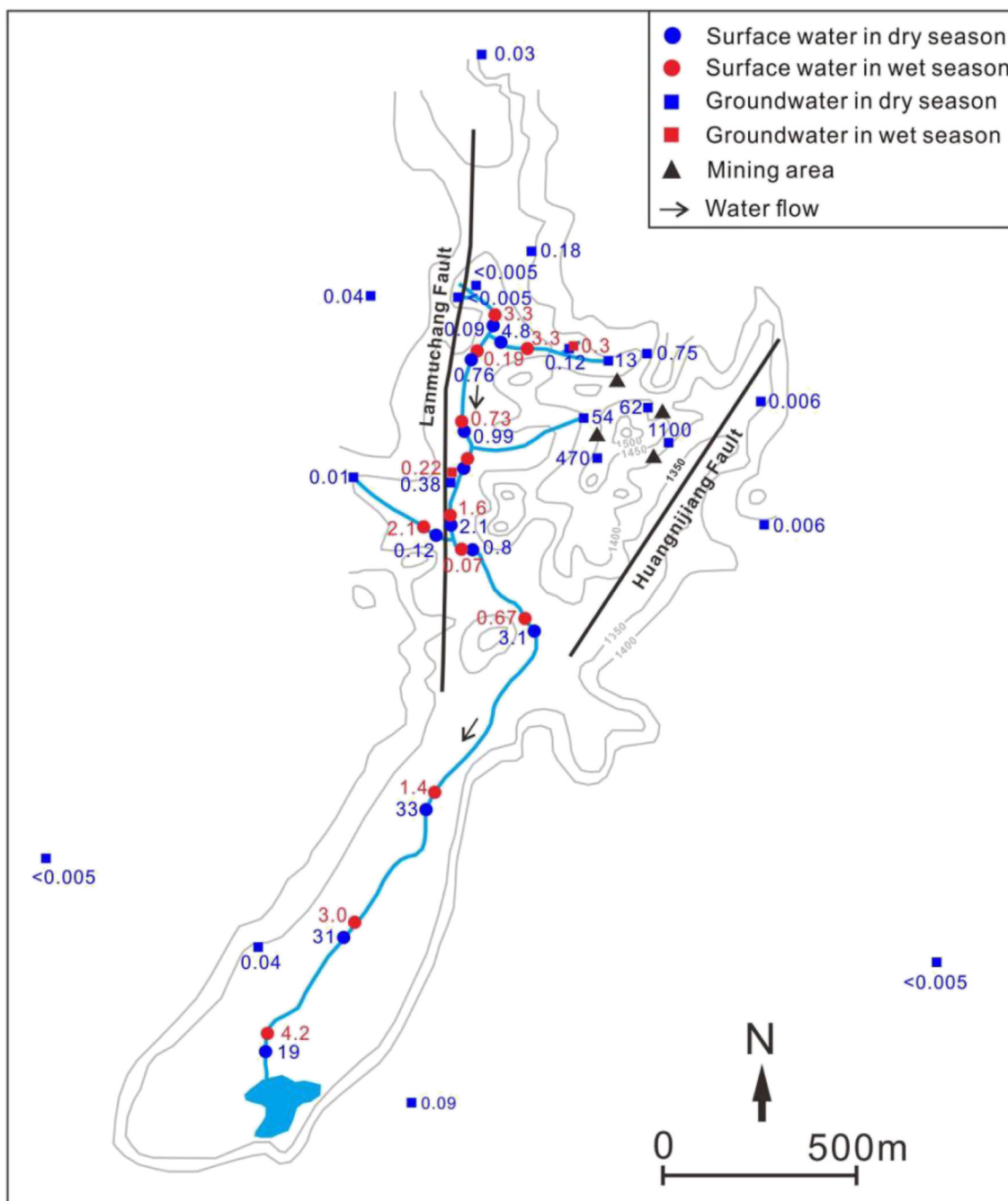


Fig. 5. Map showing Tl concentrations ($\mu\text{g/L}$) in the water system of the Lanmuchang Tl mineralized area (○ contour (m); → rivulet; Luoshui cave). Modified after Xiao et al. (2004d; 2012).

operational cost limits its large-scale utilization for wastewater treatment (Bilal et al., 2013).

3.3. Solvent extraction

Solvent extraction is based on the partitioning of compounds between two mutually immiscible (or sparingly miscible) solvents. The compound is transferred from one solvent to another solvent in repeated extraction steps. Effective extraction agents for Tl include tributyl phosphate (TBP), di-(2-ethylhexyl)phosphoric acid (DEHPA), and di(2-ethylhexyl)dithiophosphoric acid (DEHDTPA) (Hasegawa et al., 1980; Sato and Takahashi, 1986; Sato and Sato, 1992; Sato et al., 1996; Sato et al., 1997; Liu et al., 2005). Yang et al. (2017) developed an emulsion film method with 2-ethylhexyl phosphate as a carrier,

aviation kerosene as an organic solvent, polyisobutylene succinimide as a surfactant, polyisobutylene as an additive, and sulfuric acid as an internal reagent for removal of Tl from flue gas desulfurization wastewater generated in ferrous metal smelting. The extraction efficiency reached 99.76% within 15 min. The concentration of Tl was reduced to $< 5 \mu\text{g/L}$. Acidic conditions facilitated Tl removal in the presence of interfering ions (e.g. Ca^{2+} and Mg^{2+}). Solvent extraction has the advantage of high efficiency and selectivity, but is not suitable for every solution composition. Furthermore, the scale of application is limited by the large quantities of organic waste generated in the treatment process.

Table 7
Thallium contents in minerals and rocks from typical Tl/Tl-bearing deposit in China.

Deposit	Mineral/rock	Tl content (mg/kg)	References	
Lanmuchang Hg-As-Tl deposit, Guizhou Province	As-Tl ore	300–42,500	Tu et al., 2004	
	Tl ore	126–21,200	Tu et al., 2004	
	Tl-Hg ore	102–51,000	Tu et al., 2004	
	Argillaceous limestone	2	Tu et al., 2004	
	Siltstone	1.3–5	Tu et al., 2004	
	Sandstone	5300	Zhang et al., 1997	
	Calcareous siltstone	300	Zhang et al., 1997	
	Calcareous mudstone	410	Zhang et al., 1997	
	Sandy shale	400	Zhang et al., 1997	
	Argillaceous limestone	2	Zhang et al., 1997	
	Argillaceous siltstone	1.3–2	Zhang et al., 1997	
	Dolomite	0.2	Zhang et al., 1997	
	Siltstone	0.5	Zhang et al., 1997	
	Calcareous siltstone	300	Zhang et al., 1997	
	Calcareous mudstone	410	Zhang et al., 1997	
	Argillaceous dolomite	410	Zhang et al., 1997	
	Tl mineralized rock	65–84	Zhang et al., 1997	
	Tl ore	126–201	Zhang et al., 1997	
	Realgar ore	240	Zhang et al., 1997	
	Orpiment ore	370	Zhang et al., 1997	
	Quartz	0.91–1	Zhang et al., 1997	
	Calcite	0.64–1.35	Zhang et al., 1997	
	Tl mineralized rock	65–84	Zhang et al., 1997	
	Nanhua As-Tl deposit, Yunnan, South China	Silt dolomite	1.26–1.30	Zhang et al., 2005
		Laminated argillaceous dolomite	0.33–0.79	Zhang et al., 2005
		Fuchsia argillaceous siltstone	0.43	Zhang et al., 2005
		Tl mineralized rock	25–90	Zhang et al., 2005
Argillaceous limestone		2–5	Zhang et al., 2005	
As-Tl ore		964–1900	Zhang et al., 2005	
Mineralized dolomite		33.8	Zhang et al., 2005	
Diabase		21.4	Zhang et al., 2005	
Mineralized silt		36.1	Zhang et al., 2005	
Lanping Jinding lead-zinc ore, Yunnan, South China		Limestone	0.67–15	Tu et al., 2004
	Dolomite	0.13–11	Tu et al., 2004	
	Shale	0.76–8	Tu et al., 2004	
	Clay rock	0.8–4	Tu et al., 2004	
	Sandstone	0.4–5.1	Tu et al., 2004	
	Siliceous rock	0.3	Tu et al., 2004	
	Anthracite	0.1–0.4	Tu et al., 2004	
	Quartz porphyry	2.8	Tu et al., 2004	
	Granite	0.18–3.8	Tu et al., 2004	
	Basalt	1	Tu et al., 2004	
	Diabase	0.3–1.3	Tu et al., 2004	
	Quartz vein	0.3	Tu et al., 2004	
	Zinc oxide ore	4–30	Jiang et al., 2014	
Lead-zinc ore	110	Jiang et al., 2014		

3.4. Adsorption

Adsorption is based on mass transfer between liquid and solid phases (*i.e.*, adsorbent) (Kurniawan and Babel, 2003). In the case of sorption of a pollutant onto an adsorbent, three key stages are involved: (i) pollutant penetration from bulk solution to the adsorbent surface; (ii) pollutant adsorption on the adsorbent surface; and (iii) pollutant penetration into the adsorbent structure (Barakat, 2011). Adsorbents can be derived from agricultural waste, industrial by-products, and natural materials.

Adsorbent materials currently in use on an industrial or pilot scale are activated carbon and zeolites. Activated carbon has been shown to adsorb > 98% of Tl from simulated wastewater, involving oxidation of Tl(I) to Tl(III) (Rivera-Utrilla et al., 1984). Eyde et al. (1993) developed the CABSORB ZS500RW zeolite adsorption technology and successfully applied it to remove Tl from mine wastewater, reducing the Tl concentration from 50 to 1000 µg/L to 1.7 µg/L.

Metal oxides of Fe, Mn, and Al are effective in adsorbing Tl from wastewater at the laboratory scale. Adsorption of Tl(I) on MnO₂ is accompanied by rapid oxidation to Tl₂O₃ (Bidoglio et al., 1993; Jibiki, 1995; Lu et al., 2016; Koschinsky and Hein, 2003; Voegelin et al., 2015). Li et al. (2017b) synthesized Fe-Mn binary oxides with

particularly high oxidizing potential. The combined adsorption-oxidation mechanism enables rapid, selective and effective removal (over 95%) over a wide range of pH (3–12) and at elevated ionic strength (0.1–0.5 mol/L) (Nazari et al., 2017).

The increasing progress in nanotechnology offers opportunities for their utilization in wastewater treatment. Owing to their nanoscale size, nanoparticles show unique physical and chemical properties such as large surface area to volume ratios and high interfacial reactivity. Nanostructured titanium peroxide was found very effective in removing Tl⁺ from water, with a maximum adsorption capacity of 412 mg/g at pH 7.0 (Zhang et al., 2018). The presence of Ca²⁺, Mg²⁺, K⁺, Cu²⁺, Zn²⁺, fulvic acid and humic acid did not show a significant effect. Nano-scale MnO₂ and Al₂O₃ also exhibited satisfactory Tl(I) and Tl(III) removal capacity (Huangfu et al., 2015; Wan et al., 2014; Zhang et al., 2008). Highly efficient removal of trace Tl from contaminated waters was reported by Liu et al. (2017a, 2017b, 2017c), using ferric nanoparticles formed *in situ* from ferrate. Over 92% of Tl (1 µg/L) was removed within 5 min by applying 2.5 mg/L of K₂FeO₄ (pH 7.0, 20 °C). A FeOOH-loaded MnO₂ nano-composite material was found effective in Tl removal after a pollution accident, owing to its fast removal rate and high adsorption capacity (450 mg/g) for Tl⁺ (Chen et al., 2017). At present, titanium dioxide nanotubes and carbon nanotubes have been

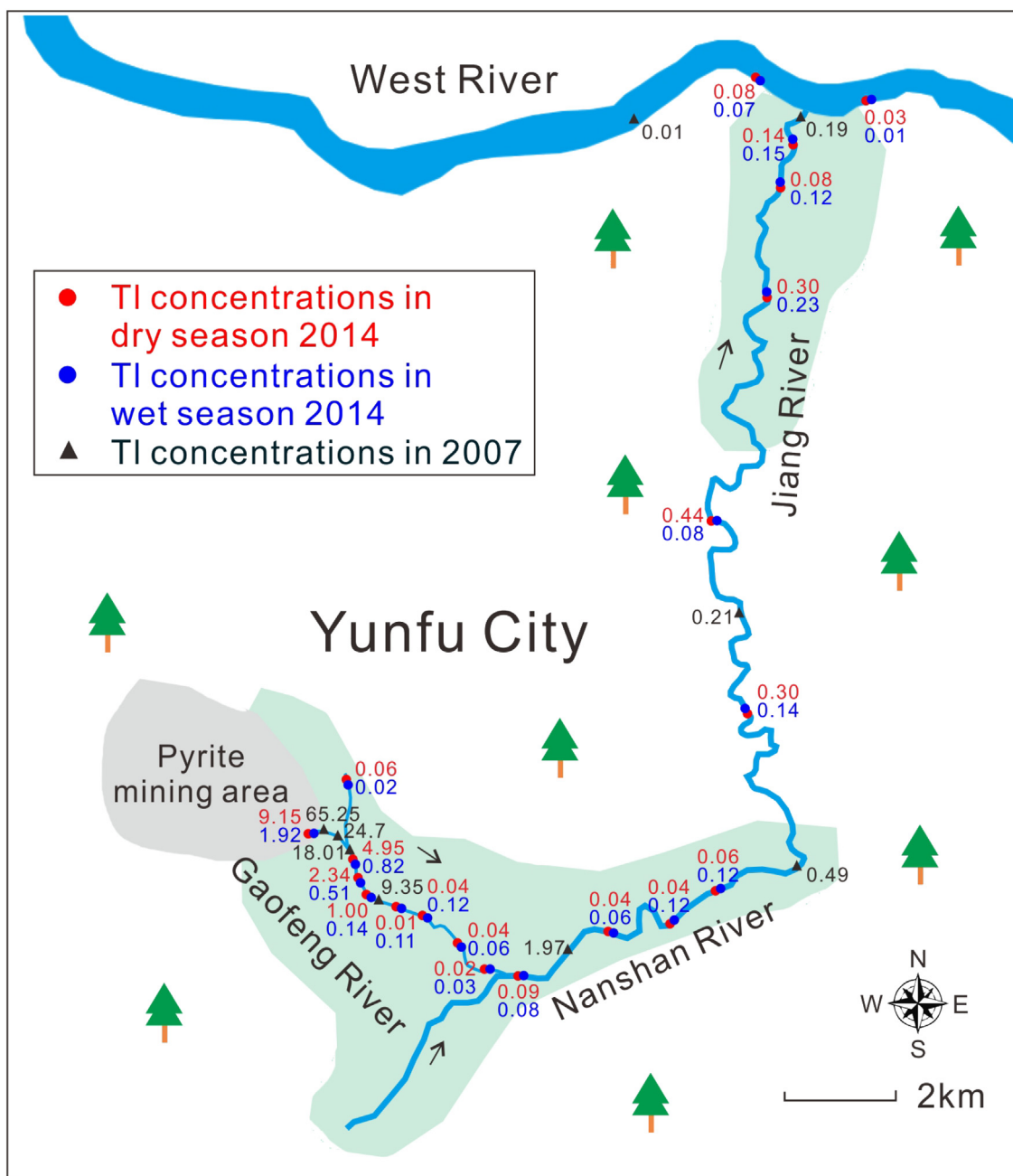


Fig. 6. Map showing Tl concentrations ($\mu\text{g/L}$) in the water system of a Tl-bearing pyrite mining area (→ rivulet; 🌲 forest; 🏠 residential area). Data based on Liu et al. (2016) and Qi (2009).

tested at the laboratory scale for treating Tl-containing wastewater. Liu et al. (2014) showed that titanate nanotubes can adsorb Tl^+ and Tl^{3+} through ion-exchange and coprecipitation mechanisms. Pu et al. (2013) studied adsorption of Tl^+ by multi-walled carbon nanotubes. Nanotubes pretreated by $\text{Na}_2\text{S}_2\text{O}_8$ showed the best removal efficiency (> 90% at $\text{pH} > 8.5$). Adsorption of Tl^{3+} by multi-walled carbon nanotubes was investigated by Rehman et al. (2013). Carbon nanotubes oxidized by HNO_3 exhibited the strongest adsorption capacity for Tl^{3+} . The best removal efficiency was observed at $\text{pH} 7$.

The bio-sorption process using agricultural waste or plant material is an eco-friendly method, which can substitute for conventional adsorbents. Various functional groups (e.g., hydroxyl, amido, amino, carboxyl, acetamido, phenolic, alcohols, and esters groups) present in the cellulose, hemicellulose, and lignin are substantially available in the waste agricultural biomass, which will contribute to the highly affinity

towards the metal ions via hydrogen replacement and complexation with the metal ions (Carolin et al., 2017; Yan et al., 2010). Memon et al. (2008) developed a simple and low-cost alkaline modification of sawdust resulting in increased sorption capacity from 2.71 to 13.2 $\text{mg}(\text{Tl}^+) \text{g}^{-1}$ within 8 min. Sugar beet pulp, a waste-product of sugar-refining factories, was suggested as sorbent after NaOH modification with a maximum Tl(I) removal capacity of 246.3 mg/g .

The adsorption process is an alternate and assuring method in contrast with the traditional process due to the advantages of low operating cost, low fouling problems, and high economic feasibility for heavy metal removal from wastewater (Carolin et al., 2017; Ai et al., 2018; Zhao et al., 2018). The reversible adsorbents can be recreated by the desorption process and the regenerated adsorbent can be reused for several time with uncompromised performance. In view of the high efficiency due to high specific area and chemical reactivity, super

Table 8
Physical and chemical properties of selected thallium compounds (based on Stokinger (1987), Lide (1990), O’Neil (2007) and Cvjetko et al. (2010)).

Compound	Chemical formula	Melting point (°C)	Boiling point (°C)
Thallium(I) oxide	Tl ₂ O	300	1080 (decomposes)
Thallium(III) oxide	Tl ₂ O ₃	717	875 (decomposes)
Thallium(I) sulfate	Tl ₂ SO ₄	632	Decomposes
Thallium(I) sulfide	Tl ₂ S	448.5	–
Thallium(I) carbonate	Tl ₂ CO ₃	273	–
Thallium aluminium sulfate	TlAl(SO ₄) ₂ ·12H ₂ O	91	–
Thallium hydroxide	TlOH	139 (decomposes)	–
Thallium(I) nitrate	TlNO ₃	206	430
Thallium(III) nitrate trihydrate	Tl(NO ₃) ₃ ·3H ₂ O	105–107 (decomposes)	–
Thallium(I) acetate	CH ₃ COOTl	131	–
Thallium ethylate	TlOC ₂ H ₅	-3	130 (decomposes)
Thallium(I) bromide	TlBr	480	815
Thallium(I) chloride	TlCl	430	720
Thallium(III) trichloride	TlCl ₃	25	Decomposes
Thallium(I) fluoride	TlF	327	655
Thallium(III) trifluoride	TlF ₃	550 (decomposes)	–
Thallium(I) iodide	TlI	440	823

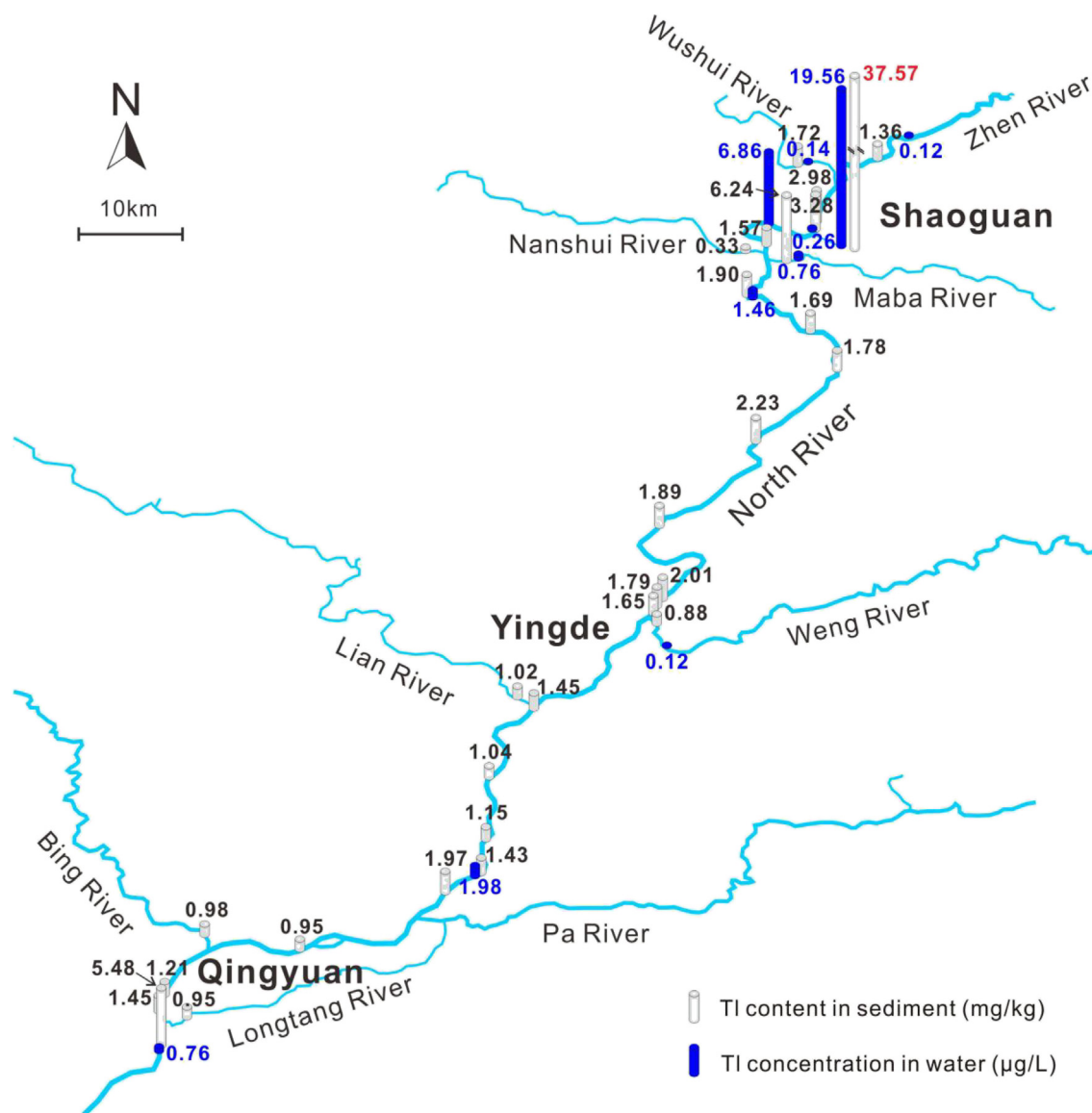


Fig. 7. Distribution of Tl in surface waters and sediments of the North River. Data based on Gao et al. (2008) and Qi (2009).

Table 9
Comparison of various treatment techniques for thallium removal from wastewater.

Techniques	Case study			Efficiency	Advantages	Disadvantages	References
	Agents	Dosages	Water quality				
Chemical precipitation/coagulation	Na ₂ S + Fe ⁰	Na ₂ S 11.4 mg/L Fe ⁰ 100 g/L	Ca 42,000 µg/L Cu 40 µg/L Fe 260 µg/L Sb 300 µg/L Tl 300 µg/L Sulfate 1,400,000 µg/L pH = 5	Tl 100% (1 h)	Effective for industrial wastewater with high salinity	Generation of acid gas as secondary pollution	Williams-Beam and Twidwell, 2003
	Fe ⁰ + H ₂ O ₂ + NaOH/Ca(OH) ₂	Fe ⁰ 12.5 g/L (30 wt%) H ₂ O ₂ 75 mL/L	Tl 500 mg/L Zn 500 mg/L Pyridine Quinone pH = 3–4 (Fenton) and 10–11	Tl 96% (20 min)	Simple procedure, wide range of applications, additional removal of various heavy metals besides Tl, suitable for large-scale treatment of industrial wastewater	Increased sludge generation, high costs of sludge disposal, high consumption of low-reusable and toxic chemicals, poor settling, slow metal precipitation	Kikuchi et al., 1990
	KMnO ₄ + CaO	KMnO ₄ 4 g/L CaO 9.2 g/L	Tl 1406.5 µg/L pH = 2.7 (oxidation)	Tl 100% (1 h)			Chen, 2013; Zhang et al., 2013b
	H ₂ O ₂ + CaO	(30 wt%) H ₂ O ₂ 8.8 mL/L CaO 12.9 g/L	pH = 8–9 (coagulation)	Tl 100% (1 h)			Chen, 2013; Zhang et al., 2013b
	Ca(ClO) ₂ + CaO	Ca(ClO) ₂ 7.4 g/L CaO 9.2 g/L		Tl 100% (1 h)			Chen, 2013; Zhang et al., 2013b

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Table 9 (continued)

Techniques	Case study	Agents	Dosages	Water quality	Efficiency	Advantages	Disadvantages	References
Adsorption	MnO ₂ sludge		7 g/L	Ti 350 mg/L Cd 6.3 g/L Zn 3.37 g/L	Ti 99.1% (40 min)	Easy operation, low fouling problems, high efficiency, low-cost sorbents derived from agricultural waste, industrial by-products, or natural materials; reusable sorbents after regeneration by desorption.	Sludge production; increased risk of nano-pollutants	Jibiki, 1995
	Fe-Mn binary oxides (0.24–6.6 μm)		0.5 g/L	pH = 4.8 Ti(O) 10–500 mg/L	Langmuir q _{max} = 197.6 mg/g (24 h)			Li et al., 2017b
	Prussian blue-alginate composite capsules (100–700 μm)		1 g/L	pH = 10 Ti(O) 10–500 mg/L	Langmuir q _{max} = 103 mg/g (72 h)			Vincent et al., 2014
	Polyacrylamide zeolite (2 mm)		10 g/L	pH = 4 Ti(O) 10–2000 mg/L	Langmuir q _{max} = 378.1 mg/g (25 h)			Senol and Ulusoy, 2010
	TiO ₂ (110 μm)		0.2 g/L	pH = 5 Ti(O) 5–130 mg/L	Langmuir q _{max} = 412 mg/g (24 h)			Zhang et al., 2018
	Nano-Al ₂ O ₃		3 g/L	pH = 7.0 Ti (III) 1–35 mg/L	Langmuir q _{max} = 5.78 mg/g (10 min)			Zhang et al., 2008
	Nano-MnO ₂		4.35 mg/L	pH = 4.5 Ti(O) 0–10 mg/L	Langmuir q _{max} = 672 mg/g (2 h)			Huangfu et al., 2015
	Amorphous hydrous MnO ₂		0.5 g/L	Ti(O) 0–100 mg/L pH = 5.0	Langmuir q _{max} = 353.6 mg/g (24 h)			Wan et al., 2014
	K ₂ FeO ₄ nanoparticle		5 mg/L	Ti 0.531 μg/L N-NH ₃ 0.89 mg/L Ca ²⁺ 27.22 mg/L Mg ²⁺ 10.96 mg/L COD 8.45 mg/L pH = 6.23	Ti 85% (30 min)			Liu et al., 2017c
	Nano FeOOH-loaded MnO ₂		0.4 g/L	Ti 10–150 mg/L pH = 7.0	Langmuir q _{max} = 450 mg/g (24 h)			Chen et al., 2017
	Na ₂ S ₂ O ₈ -modified MWCNTs		0.1 g/L	Ti(O) 12.5–150 μg/L pH = 6.0	D-R model q _{max} = 1091 mg/g (24 h)			Pu et al., 2013
	HNO ₃ -oxidized MWCNTs		0.5 g/L	Ti (III) 10–80 mg/L pH = 7.0	Langmuir q _{max} = 31.5 mg/g (6 h)			Rehman et al., 2013
	Titanate nanotubes		0.2 g/L	Ti (I) 10–150 mg/L pH = 5.0 Ti (III) 10–150 mg/L pH = 2.0	Langmuir Ti(O)q _{max} = 709.2 mg/g (3 h) Ti(III)q _{max} = 847.5 mg/g (3 h)			Liu et al., 2014
	NaOH-treated sawdust		2 g/L	Ti(O) 0–1000 mg/L pH = 6.0	D-R model q _{max} = 13.18 mg/g (8 min)			Memon et al., 2008
	NaOH-treated sugar beet pulp		7 g/L	Ti(O) 20 to 20,000 mg/L pH = 5.0 NG	D-R model q _{max} = 246.3 mg/g (15 min)			Zolgharnein et al., 2011
Solvent extraction	TBP, DEHPA, DEHDTPA	NG ^a	NG	NG	NG	High efficiency, high selectivity	High consumption of chemicals, generation of organic waste	Yang et al., 2017

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Table 9 (continued)

Techniques	Case study	Dosages	Water quality	Efficiency	Advantages	Disadvantages	References
Ion exchange	IMAC GT 73 resin	200 mL/L	Tl 0.34 g/L Cd 6.3 g/L As 0.82 g/L Zn 2.1 g/L Fe 0.022 g/L Anions (bisulfite, sulfate, bisulfate, and chloride) 5 g/L pH = 2.07	Tl 83.2% Cd 45.7% As 100%	Simple and convenient operation, high metal removal efficiency, recovery of valuable metals, low sludge production, high selectivity	Affected by other metal ions in wastewater, high operational costs, resin fouling due to high concentrated metal solution, secondary pollutant caused by resin regeneration, cannot be utilized in large scale	Albert and Masson, 1994
	H ₂ O ₂ + Sulfate modified anion exchange resins (pH = 1.6)	Sulfate modified anion exchange resins 500 g/L H ₂ O ₂ (30 wt%) 5 mL/L	Tl 6.3 mg/L Na 1686 mg/L Mg 22 mg/L Mn 32 mg/L K 8367 mg/L Fe 5.2 mg/L Ni 0.24 mg/L Pb 8.3 mg/L Cu 0.24 mg/L Cd 430 mg/L Ca 682 mg/L Al 1.5 mg/L Zn 7267 mg/L Cl 47,333 mg/L pH = 5.8	Tl 84.8% K 7.6% Pb 95.7% Cd 94.7% Ca 54.7% Zn 42.4% Cl 98.5%			Li et al., 2017a
Biotechnology	Microorganisms inoculated from anaerobic sludge in microbial fuel cells	Cubic single-chamber air cathode MFCs, 125 mL Aerated electrochemical reactor	Tl(O) 100 µg/L pH = 5.8	Tl 67.2% (72 h)	Coupling with electricity generation	Not suitable for high Tl concentrations, need further development	Wang et al., 2017 Tian et al., 2017
			Tl(O) 5 mg/L pH = 2.0	Tl 80.5% (4 h)			

magnetism properties, and short intraparticle diffusion distance as well as easy regeneration, adsorption to metal oxides is a very promising method for Tl removal from wastewater (Azimi et al., 2017). However, problems like high fluid resistance and large-scale solid-liquid separation need to be solved for routine application. Application of nanoparticles can be combined with traditional chemical and physical treatment processes to achieve more efficient removal. The unique and versatile properties of nanomaterials are trendsetting in environmental technology (Masciangioli and Zhang, 2003; Gu et al., 2018). Using nanotechnology for the preparation of metal oxide-modified polymer composites is another promising approach (Zhang et al., 2018; Li et al., 2018). Moreover, based on the low cost and wide availability, the application of agricultural waste should be comprehensively explored, and their advantages towards the treatment of Tl-contaminated wastewater should be specifically described in future studies.

3.5. Biotechnology

Microbial fuel cells (MFCs), as a new and efficient biotechnology of utilizing biomass energy, can directly convert chemical energy of waste components into electrical energy, providing a dual function of decontamination and electricity generation. MFCs can be operated with bacteria that act as catalysts to oxidize organic and inorganic substances in wastewater.

Wang et al. (2017) investigated the oxidative capacity of MFCs for Tl(I). The removal efficiency by coagulation of generated Tl(III) reached $67.2 \pm 2.3\%$, accompanied with a maximum electrical power density of $457.8 \pm 15.2 \text{ mW/m}^2$ after 72 h reaction time for wastewater with an initial Tl(I) concentration of $100 \mu\text{g/L}$. High-throughput 16S rRNA gene sequencing showed that *Rhodococcus erythropolis* and emerging acidophilus bacteria were active in the catalysis of Tl(I) oxidation, and that *Aspergillus ochraceus* and *Amicobacterium* increased the conversion of chemical energy, the key factor for power. Tian et al. (2017) proposed removal of Tl(I) from groundwater using an aerated electrochemical reactor (AER) with single-chamber MFCs as a renewable energy source. Experiments showed that 80.5% of Tl(I) could be removed in 4 h. Tl(I) oxidation was mainly attributed to indirect electrochemical oxidation.

At present, the microbial fuel cell technology has been evaluated using wastewater with low concentrations of Tl at the laboratory scale. Nevertheless, as an environmentally friendly technology that offers electricity generation in addition, it is a worthwhile and promising innovation with potentially significant environmental benefits.

3.6. Summary and future outlook

This paper reviewed the available treatment technologies for the removal of Tl from waters by illustrating the performance and highlighting the advantages, disadvantages, and limitations of different Tl removal methods. Chemical precipitation/coagulation removes the Tl pollutants with high efficiency, and is widely used by industry. However, this method may generate toxic sludge and is inappropriate for use at low Tl concentrations. Ion exchange methods are the most widely used for wastewater treatment due to low maintenance cost and good performance, but large-scale applications are limited by fouling problems. Adsorption methods using nanomaterials and metal oxide modified polymer materials represent a promising alternative to conventional techniques for sequestering Tl at the lab-scale. Nevertheless, availability and cost effectiveness are the two primary factors determining the most applicable sorbent for Tl abatement from waters.

Apart from the current available Tl treatment technologies described in this paper, other processes commonly used in removal of other metals can be potentially developed for the elimination of Tl from waters. Flotation is a most probable method for wastewater treatment with lower sludge formation compared with coagulation/precipitation (Patil et al., 2016). Membrane separation/filtration has lower space

requirement than conventional treatment for various heavy metals, which simultaneously expel pathogenic organisms from the effluent under the circumstances of regular membrane backwashing to guarantee performance (Fu and Wang, 2011). Electrochemical treatment allows water reuse via chemical-free pollutant eradication, but has limited application due to the short lifetime of electrode materials (Zhang et al., 2013a). The bioelectrochemical system (BES) shows great potentials in recovering different metals with various redox potentials due to its great flexibility, but much more needs to be done to further understand the mechanisms and investigate the feasibility of engineering applications (Wang and Ren, 2014). Effective phytoremediation of metals can be achieved within a reasonable time frame by increasing plant yield and contaminant accumulation (Rezania et al., 2016). Thus, it is essential to choose the most applicable method based on Tl concentration, operational cost, and water characteristics, etc.

From the perspective of more frequent Tl contamination in the environment under accelerated industrialization, researches based on lab-scale implementation of all the aforementioned treatment technologies should be evaluated at the pilot and industrial scale, to ensure the sustainable water security and human health.

4. Conclusions and perspectives

Thallium, closely associated with various types of sulfide minerals and rocks, is a prevalent pollutant in wastewater from industries utilizing Tl-containing minerals (e.g., mining, smelting, coal-combustion, steel-making, cement production, and electronic industry). With unprecedented economic growth, China is now facing an escalating level of Tl pollution and environmental risks from various industries. Thallium pollution in wastewater from industries utilizing sulfide minerals bearing high Tl contents (such as sulfide ore mining and smelting) has gradually gained greater stakeholder attention. Meanwhile other significant hidden sources like steel production, coal-burning and cement production, and e-industries, wherein Tl occurs as impurities with relatively low abundance in raw materials and/or additives, need further comprehensive investigations. Effective management and control measures for Tl-containing wastewater are still at the infancy stage, as compared to other metal contaminants (such as Pb, Zn, Cd, Cr, Hg, and As). With increasing Tl pollution in China, cost-effective Tl pollution control is in an urgent demand. Due to the high toxicity of Tl, existing standards require that the concentration of total Tl in industrial effluents should be lower than $5 \mu\text{g/L}$ and in drinking water $< 0.1 \mu\text{g/L}$. Traditional treatment techniques like chemical oxidation precipitation, ion exchange and solvent extraction are comparatively cost-intensive. Frontier new technologies using adsorption by nanomaterials, metal oxide modified polymer materials and microbial fuel cells which have become the alternative to the conventional techniques in sequestering Tl based on lab-scale implementation may pave the way to cost-effective and ecologically sound technologies for Tl pollution control. Such promising treatment technologies should be further expanded to the pilot and industrial scale, which will raise some unknown issues during scale-up trials. Thus, further in-depth relevant studies are critical to provide theoretical foundations for industrial applications at the commercial level.

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