Science of the Total Environment 421-422 (2012) 51–58

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Review

Thallium pollution in China: A geo-environmental perspective

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ARTICLE INFO

Article history:
Received 30 November 2010
Received in revised form 27 February 2011
Accepted 1 April 2011
Available online 22 April 2011

Keywords:
Thallium
Sulfide mineral
Pollution
Health impact
Geo-environment
China

ABSTRACT

It is well known that thallium (Tl) is a non-essential and toxic metal to human health, but less is known about the geo-environmentally-induced Tl pollution and its associated health impacts. High concentrations of Tl that are primarily associated with the epithermal metallogenesis of sulfide minerals have the potential of producing Tl pollution in the environment, which has been recognized as an emerging pollutant in China. This paper aims to review the research progress in China on Tl pollution in terms of the source, mobility, transportation pathway, and health exposure of Tl and to address the environmental concerns on Tl pollution in a geo-environmental perspective. Tl associated with the epithermal metallogenesis of sulfide minerals has been documented to disperse readily and accumulate through the geo-environmental processes of soil enrichment, water transportation and food crop growth beyond a mineralized zone. The enrichments of Tl in local soil, water, and crops may result in Tl pollution and consequent adverse health effects, e.g. chronic Tl poisoning. Investigation of the baseline Tl in the geo-environment, proper land use and health-related environmental planning and regulation are critical to prevent the Tl pollution. Examination of the human urinary Tl concentration is a quick approach to identify exposure of Tl pollution to humans. The experiences of Tl pollution in China can provide important lessons for many other regions in the world with similar geo-environmental contexts because of the high mobility and toxicity of Tl.

Contents

1. Introduction

Thallium (Tl) is one of the 13 priority pollutant metals (Keith and Telliard, 1979). It is more toxic to mammals than cadmium, lead, copper or zinc, and is known to have caused many accidental, occupational and therapeutic poisonings since its discovery in 1861 (Smith and Carson, 1977; Mulkey and Oehme, 1993). The triad of gastroenteritis, polyneuropathy and alopecia is regarded as the classic syndrome of Tl poisoning (Liu, 1983; Feldman and Levisohn, 1993; Tabandeh et al., 1994; WHO/IPCS, 1996). Historically, Tl poisoning was noticed from industrial emission of coal burning and smelting (Smith and Carson, 1977; Brockhaus et al., 1981; Wells, 2001), and from criminal purpose by using Tl chemicals (Zhou, 1998). However, less attention has been paid to geo-environmentally-induced Tl pollution and its associated human health impacts.

Tl is usually excluded from the list of metals to be analyzed despite its high toxicity, although Tl can be precisely measured by the inductively coupled plasma-mass spectrometry (ICP-MS) techniques. This is due to its low concentrations in the natural environment, although it is widely distributed in nature. The mean abundance of Tl in the Earth's upper

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doi:10.1016/j.scitotenv.2011.04.008

crust is 0.75 mg/kg (Taylor and McLennan, 1985), 0.001–0.25 μg/L in groundwater (Frengstad et al., 2000), 0.001–0.036 μg/L in lake water (Cheam et al., 1995; Lin and Nriagu, 1999), and 0.012–0.016 μg/L in seawater (Flegal and Patterson, 1985). Tl in soil is generally less than 1 mg/kg (Fergusson, 1990), and it is low to 0.03–0.3 mg/kg in the world edible plants (Kabata-Pendias and Pendias, 1992).

Recent studies on Tl pollution indicated that Tl was an emerging pollutant in the environment of China due to the increasing awareness of its high risk to human health (Zhang et al., 1997, 1999; Chen et al., 2001; Xiao et al., 2003a,b, 2004a, 2007; Yang et al., 2005; Zhou et al., 2008; Liu et al., 2010; Xinhua News Agency, 2010; Li et al., 2011). The first reported adverse health impact of Tl pollution in China was from a rural area at Lanmuchang (105°30′23″E, 25°31′28″N, Fig. 1) in Southwest China (APASSGP and EGLIGCAS, 1977). Thallotoxicosis-related symptoms, e.g., weakness, muscle and joint pain, disturbance of vision and hair loss, were rerecorded for 189 cases of Tl poisoning at this area in the 1960s and 1970s (Liu, 1983; Zhou and Liu, 1985). More than 10 cases of incidental Tl poisoning have occurred in China since 1997, which aroused more public concerns on the health risk of Tl pollution in the environment. In the recent two decades, increasing studies on Tl pollution in China showed the environmental impacts of Tl released from Tl-rich sulfide minerals through natural weathering processes and/or mining activities (Zhang et al., 1997, 1999; Chen et al., 2001; Xiao et al., 2003a,b, 2004a; Yang et al., 2005; Zhou et al., 2005; Liu et al., 2010) (Fig. 1), the accumulation of Tl in food chain (Xiao et al., 2004b,c; He, 2008), Tl exposure to humans and its associated health effects (Zhang et al., 1997; Xiao et al., 2004b, 2007; Li et al., 2011). With respect to Tl toxicity and pollution impacts in China, the maximum contaminant level in drinking water of China is fixed as 0.1 μg/L (CNS, 2006), much lower than that (2 μg/L) in the USA drinking water (USEPA, 1992). A recent incidental Tl pollution (0.18–1.03 Tl μg/L) from the waste water discharge of a lead/zinc smelting plant on drinking water source of northern branch of Pearl River in southern China was reported in 2010 (Xinhua News Agency, 2010), which further aroused public concerns on Tl pollution in China.

However, the absence of detailed knowledge in the source, mobility, dispersion, and exposure to humans of Tl that have produced significant adverse consequences for human health, is still a matter of high concern in China. A full understanding of such knowledge is necessary to evaluate Tl's environmental impacts and to implement appropriate measures for Tl pollution remediation. This paper aims to review the research progress in China on Tl pollution and to address the environmental concerns on Tl pollution related to Tl-rich geo-environment in China. To learn from the experiences in Tl pollution in China is also important for many other regions in the world with similar geo-environmental contexts because of the high mobility and toxicity of Tl.

2. Occurrence of high Tl concentrations associated with epithermal metallogenesis of sulfide minerals

Tl of geological origin generally presents low concentrations in various rocks, i.e. 0.06–1.2 mg/kg in igneous rocks (De Albuquerque and Shaw, 1972), 0.65 mg/kg on average in metamorphic rocks, and 0.27–0.48 mg/kg in sedimentary rocks (Heinrichs et al., 1980). However, Tl usually occurs in high concentrations in sulfide minerals, although Tl minerals and mineralization are rare in nature (De Albuquerque and Shaw, 1972). For instance, Tl contents range from 4 to 1300 mg/kg in galena and sphalerite of the Truskavets deposit in Ukraine (Voskresenskaya, 1969), from 300 mg/kg to >1% in realgar of the Allcar deposit in Yugoslavia (Jankovic, 1989), and from 23 to 55 mg/kg in pyrite of Kuroko-type deposit in Japan (Murao and Itoh, 1992). According to Sobott (1995), the enrichment of Tl in specific sulfide minerals results from the epithermal (<200 °C) metallogenesis.

It is interesting that high concentrations of Tl that are associated with the low-temperature metallogenesis were also observed in China. Particularly, the large-scale epithermal metallogenesis in Southwest China results in high geochemical baselines of Tl. This domain is mainly composed of Paleozoic and early Mesozoic sedimentary rocks (impure carbonate rocks and siliciclastic sedimentary rock) and is characterized by the occurrence of metal mineralization of Au, Hg, Sb, As, Tl, Pb, Zn, Ni

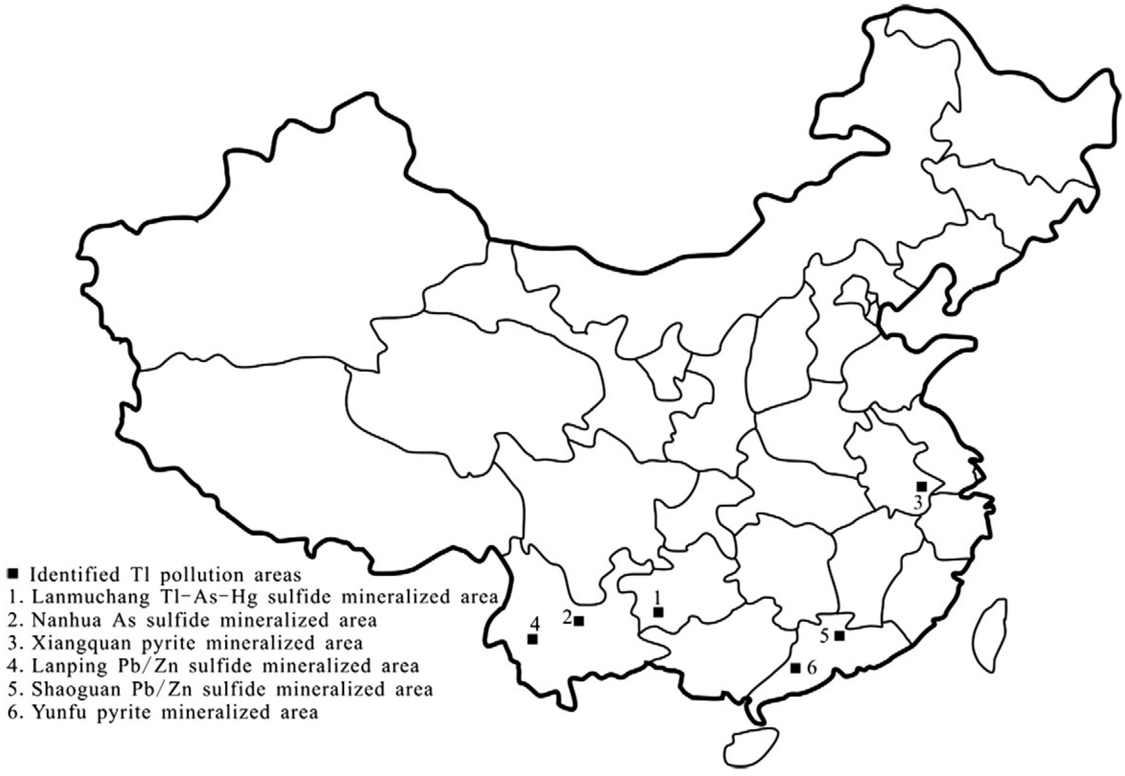

Fig. 1. Map showing the Tl pollution areas in China.

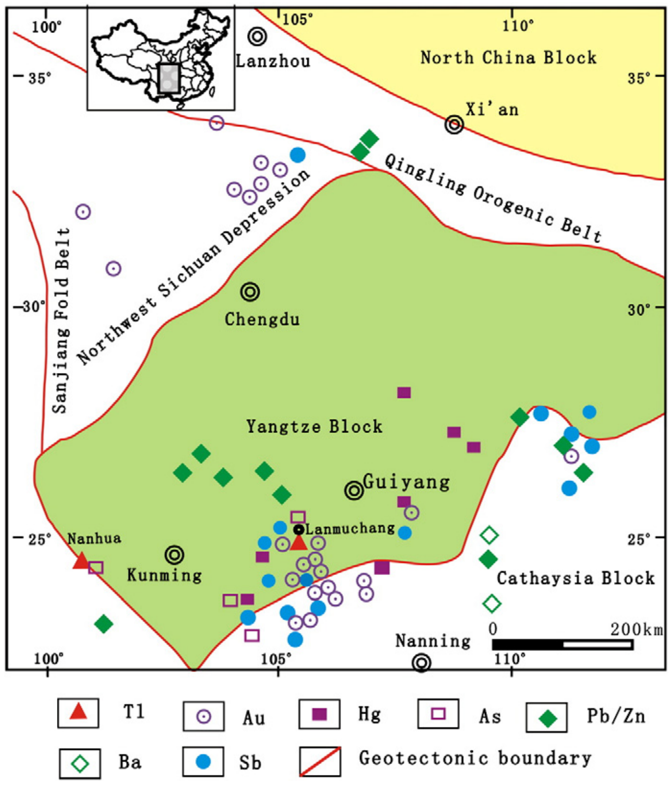

Fig. 2. Map showing the distribution of epithermal ore deposits in Southwest China. Modified after Hu et al., 2007.

and Mo and deposits of associated ores within a large area of 900,000 km^2 (Fig. 2). Minerals in this epithermal metallogenesis domain include pyrite, marcasite, arsenopyrite, stibnite, realgar, orpiment, cinnabar, Tl-sulfide minerals, some base-metal sulfide minerals (chalcopyrite, sphalerite, and galena), rare Ag–Sb and Pb–Sb sulphosalts, Hg-bearing minerals, sphalerite, and Ni-sulfide minerals (Peters et al., 2007). It is showed that Tl is an indicator of the above sulfide mineralization occurring at low temperature (<200 °C) (Tu, 1998). The associations of Tl with other low-temperature ore forming metals are listed in Table 1. Tl minerals are rare in nature, however, 8 Tl minerals were identified in this epithermal metallogenic domain. These Tl minerals are hutchinsonite ($PbTlAs_5S_9$), picotpaulite ($TlFe_2S_3$), ellisite (Tl_3AsS_3), thallium pyrite ($(Fe,Tl)(S,As)_2$), lorandite ($TlAsS_2$), christite ($TlHgAsS_3$), lanmuchangite ($TlAl(SO_4)_2 \cdot 12H_2O$), raguinite ($TlFeS_2$), and avicennite ($Tl_2O_3$) (He et al., 2005). In general, pyrite and sphalerite are the two major carriers of Tl in the mineral ores in China. Remarkably, two Tl ore deposits (Lanmuchang deposit and Nanhua deposit) were discovered within this domain (Fig. 2).

Table 1
Thallium concentrations in various epithermal ore deposits in Southwest China.

Epithermal ore deposits	Metal associations	Tl (mg/kg)	Reference
Thallium deposit	Tl–As–Hg	1800–3500	Xiao et al. (2004a)
Carlin-type gold deposit	Au–As–Hg–Tl	2.7–62.5	Zhang and Long (1994)
Mercury deposit	Hg–As–Tl	4.8–189	Zhang and Long (1994)
Antimony deposit	Sb–As–Tl	1.5–4.6	Zhang and Long (1994) and Ning (2009)
Arsenic deposit	As–Hg–Tl	1.5–1900	Zhang and Long (1994) and Zhang et al. (1997)
Molybdenum deposit	Mo–Ni–Tl	246–293	Ruo et al. (2003)
Lead/zinc deposit	Pb–Zn–Cd–Tl	6.5–485	Li (2007) and Xiao (2009)
Coal deposit	Ge–Tl; As–Tl	2.77–46	Xiao et al. (2004a) and Qi et al. (2007)

Beyond the epithermal metallogenic domain in Southwest China, a recently discovered Tl ore deposit in Xiangquan of Eastern China was also found to be associated with epithermal metallogenesis (Zhou et al., 2005) (Fig. 1). Tl mainly occurs in pyrite (up to 5000 mg/kg Tl) of the ore deposit, which may pose potential environmental impacts on the local environment (Zhou et al., 2008). However, a similar context of high Tl (46 mg/kg on average) in pyrite (Xie et al., 2001) associated with epithermal metallogenesis from Yunfu pyrite deposit of Guangdong Province (Fig. 1) has resulted in serious Tl pollution, through mining and sulfuric acid producing by using the ores of Tl-rich pyrite, and posed high risk to the soil and water safety in the catchment of Pearl River (Yang et al., 2005; Liu et al., 2010).

The average concentrations of Tl in rocks of the epithermal metallogenic domain in Southwest China ranged from 1.63 to 3.81 mg/kg (Tu, 1998), which was much higher than Tl's abundance in Earth's upper crust (0.75 mg/kg) (Taylor and McLennan, 1985). In the Lanmuchang Tl mineralized area within this epithermal metallogenic domain (Fig. 2), the concentrations of Tl are 6–490 mg/kg in the host rocks, and 100–35,000 mg/kg in the sulfide minerals (Xiao et al., 2004a). The geochemical simulation of Tl metallogenesis illustrated that lower pH value and higher temperature of the thermal fluids facilitated the mobility of Tl in the stratum, but high solubility of Tl was also observed even in lower temperature (<200 °C) (Long, 1995). Iron abundance in the stratum of the regional epithermal metallogenic domain in Southwest China played a catalyzing role in promoting mobility of Tl, and the clay minerals also aided the enrichment of Tl in rocks (Long, 1995). Positive correlations between Tl and iron, sulfur, potassium and rubidium in rocks and sulfide mineral ores were observed, which implied a lithophile and chalcophile behavior of Tl (Xiao et al., 2004a). These correlations reflect the redox properties of Tl that Tl generally exists in sulfide minerals in the reducing environment, but only in the strong oxidized environment it exits in oxidized minerals (Vink, 1993). Therefore, Tl is a quite mobile metal during the weathering processes, by which Tl is readily mobilized and transported together with alkaline metals and sulfates to the surface environment (Xiao et al., 2004a).

The occurrence of Tl associated with the epithermal metallogenesis is also a well-established fact in the world. For instance, hydrothermal precipitates in the Rotokawa geothermal system of New Zealand have Tl levels as high as 5000 mg/kg (Krupp and Seward, 1987). The Allchar Sb–As–Tl deposit in the former Yugoslavia also boasts an extremely high natural Tl contents (Percival and Radtke, 1994), as does the Lengenbach Pb–Zn–As–Ba–Tl in Switzerland (Hofmann and Knill, 1996). Similarly, the local environments of the above sulfide mineralized areas may exit enrichments of Tl.

3. Tl pollution related to geo-environmental processes

The geo-environmental processes that are involved in the environmental media of water, soil, and plant (Guha, 2003) may facilitate the release, transportation and secondary enrichment of metals into the soil, water, and even food crops. The enrichments of Tl that are involved with the geo-environmental processes have high potential of producing Tl pollution.

Tl in soil is generally less than 1 mg/kg (Fergusson, 1990), however, high concentrations of Tl were observed in many areas of the world. For instance, high concentrations of Tl (1.54–55 mg/kg) in the arable soils of France were reported by Tremel et al. (1997a). Relatively high Tl levels (1.5–3.0 mg/kg) were also found in the soils of Southwest Siberia (Il'in and Konarbaeva, 2000). Elevated levels of Tl (8.8–35 mg/kg) in soils from the Silesian–Cracowian zinc–lead mine areas were recorded (Lis et al., 2003). These high Tl contents in the soils are of pedogeochemical origin (Tremel et al., 1997a; Il'in and Konarbaeva, 2000) or anthropogenic (mining, processing and smelting) origin (Lis et al., 2003).

Tl generally presents low concentrations (0.29–1.2 mg/kg) in the soils in China (Qi et al., 1992). However, the levels were remarkably elevated in soils impacted by natural mineralization of sulfide minerals and/or mining activities. Relatively higher Tl contents (0.94–1.4 mg/kg) were recorded in soils surrounding a pre-mined Carlin-type gold deposit and elevated levels (40–124 mg/kg) in soils from the Tl-rich sulfide mineralized area of Lanmuchang in Southwest China were recorded (Xiao et al., 2004b). High contents of Tl (3.17–4.47 mg/kg) were recorded in the soils from a Tl-rich pyrite mineralized zone in Eastern China (Zhou et al., 2008). Tl in the soils from a Tl-rich pyrite processing area of South China was also recorded at 5–15 mg/kg (Yang et al., 2005). In similar, the high Tl contents in soil in China are also of pedogeochemical origin or anthropogenic origin.

The mobile fractions of Tl in Tl-polluted soils are essential in causing environmental impacts. The sequential extraction on the Tl-polluted soils in China showed that the water-soluble fraction of Tl accounted for approximately 0.1% of the total Tl content in soil, the weak acid (CH_3COONH_4) extracted fraction accounted for 0.6%–4%, and the strong acid (HNO_3) extracted fraction accounted for 60%–70% (Xiao et al., 2003b). This implied a high portion of Tl that exit in the environmentally mobile fraction in the polluted soils. This finding is significant for the mobility of Tl in the polluted soils. In many cases, the Tl-polluted soils are acidic due to the acid production from the weathering of Tl-rich sulfide minerals or the sulfide ore mining, processing and smelting. For instance, 70% of the determined pH ranges from 3.3 to 6.0 from the Tl-polluted soils of Lanmuchang in Southwest China (Xiao et al., 2004b). Low pH (3.66–5.33) was also recorded from the soil profile from a pyrite processing site in South China (Yang et al., 2005). These determined low pH values in the polluted soils implied the contribution of the weathering, mining, processing or smelting of Tl-rich sulfide minerals.

Water is an important media to transport and disperse Tl in the environment. Tl generally presents quite low contents in water (Flegal and Patterson, 1985; Cheam et al., 1995; Lin and Nriagu, 1999; Frengstad et al., 2000). However, in the Tl-rich geo-environment in Southwest China, Tl presents elevated levels in waters. For instance, the concentration of Tl is 13–1966 μg/L in groundwater and 1.9–8.1 μg/L in stream water from a Tl–As–Hg–Au mineralized zone (Xiao et al., 2000, 2003a). The Tl levels are 13.2–193 μg/L in groundwater and 0.92–45.9 μg/L in stream water from a Pb–Zn mine area in Lanping (Li et al., 2007) (Fig. 1). Similarly, high concentrations of Tl (2.5–80.3 μg/L) were detected in river waters surrounding the base-metal sulfide mine areas in northeastern New Brunswick, Canada (Zitko et al., 1975). The above high levels of Tl in waters indicated that both weathering processes and mining activities can accelerate the release of Tl (high mobility in low pH condition by acid production of sulfide weathering) from the Tl-rich rocks and sulfide minerals into water.

The enrichment of Tl in soil and water may result in Tl transfer to food crops. Previous studies have demonstrated that Tl tends to accumulate in the food crops grown in Tl-polluted soils (Tremel et al., 1997b; Zhang et al., 1999; LaCoste et al., 2001; Xiao et al., 2004b; Pavlickova et al., 2006; He, 2008; Vaneka et al., 2010). For instance, high contents of Tl were recorded in the French rape seeds (33 mg/kg) and shoots (20 mg/kg) (Tremel et al., 1997b), and in mustard shoots (65 mg/kg), leaves (47.8 mg/kg), and roots (34.8 mg/kg) (Vaneka et al., 2010). High Tl levels were also detected in crops cultivated in soils that are polluted by dust emission of a cement plant in Germany, i.e. 9.5 mg/kg in cereal grains and 45 mg/kg in green cabbage (Dolgner et al., 1983). The original source of Tl in the dust was likely from the minerals of pyrite (FeS_2) or troilite (FeS) or coals (containing pyrite) or tailings of base-metal processing or smelting slag, which are all the raw materials together with limestone and clays for cement producing. In China, similar Tl accumulation in crop plants grown in the Tl-polluted soils was also recorded. In the Lanmuchang Tl-polluted area, Tl showed the highest concentration in green cabbage, ranging from 120 to 495 mg/kg with an average of 338 mg/kg (Xiao et al., 2004b). For other local crops, Tl presented at 0.87–5.3 mg/kg in Chinese cabbage, 0.8–5.3 mg/kg in chili, 1–5.2 mg/kg in shelled rice, and 0.78–3.1 mg/kg in granular corns (Table 2) (Xiao et al., 2004b). These findings clearly demonstrate that Tl pollution in soil and water may result in the Tl pollution in food crops. The potential health risk of Tl pollution in food chain should be highly concerned.

4. Pathways of Tl transfer in the environment

Previous studies have demonstrated that Tl is a quite mobile metal (rather than being locked-up into solid oxides) in most aqueous environments, and can disperse easily during oxidation of Tl-bearing sulfides (Vink, 1993; Xiao et al., 2000, 2003a). High levels of Tl in the geo-environment of the regional epithermal metallogenic domain in Southwest China are mainly associated with sulfide minerals. Regional climate, e.g. high rainfall precipitation (around 1000 mm per year) and warm temperature, is the main factor that facilitates the release of Tl from the sulfide minerals and rocks through weathering process. Lower pH (around 4–6) in rainfall of the region also facilitates the oxidation of Tl-rich mineral and rocks. Regional physiognomy (steep landscape) and hydrology (development of underground rivers) would also aid Tl dispersion from the source points to the downstream areas.

Mining and agricultural activities are the main human factors affecting the transfer of Tl in the environment. Tl in the sulfide minerals is normally not recycled in China but left in waste rocks and tailings exposed to surface oxidation. The mine wastes containing high contents of sulfide minerals have higher potential of acid production. The produced acid mine drainage can easily extract Tl from the solid wastes into the water system. Therefore, Tl may easily enter the farmland through irrigation in the surrounding and downstream areas of the mining and smelting sites.

Much attention has been paid to the transfer of Tl to the drinking water supply and agricultural irrigation systems. The case studies from

Table 2

Concentrations of Tl, Hg and As in crop materials (mg/kg, DW).

Crop samples	Tl		Hg		As	
	Range	Mean ± SD[a]	Range	Mean ± SD	Range	Mean ± SD
Green cabbage (n = 3)[b,c]	120–495	338 ± 195	0.45–0.72	0.63 ± 0.15	0.38–0.89	0.7 ± 0.28
Green cabbage (n = 6)[d]	95.8–187.9	139.9 ± 39				
Green cabbage (n = 6)[e]	41.4–121.1	78.1 ± 33				
Chinese cabbage (n = 8)[c]	0.87–5.3	2.5 ± 2.0	0.1–0.7	0.4 ± 0.23	0.17–1.3	0.8 ± 0.32
Chili (n = 3)[c]	0.8–5.3	3 ± 2.3	0.01–0.04	0.02 ± 0.02	0.15–0.29	0.23 ± 0.07
Corn (n = 8)[c]	0.78–3.1	1.4 ± 0.74	nd		0.01–0.02	0.02 ± 0.01
Rice (n = 4)[c]	1.0–5.2	2.4 ± 2.0	0.02–0.03	0.03 ± 0.03	0.1–0.18	0.15 ± 0.01
World edible plant[f]	0.03–0.3		0.013–0.17		0.01–1.5	

[a] SD refers to standard deviation.

[b] n = number of sample.

[c] Xiao et al. (2004b).

[d] Pot trials spiked with Tl (4.1 mg/kg) from He (2008).

[e] Pot trials spiked with Tl (8.1 mg/kg) from He (2008).

[f] Kabata-Pendias and Pendias (1992).

the Lanmuchang Tl-polluted area in Southwest China clearly illustrated the presence of such transfer processes in the local geo-environment (Zhou and Liu, 1985; Xiao et al., 2003a). In the Lanmuchang area, the local domestic wells were contaminated by the recharge of Tl-rich groundwater. High concentrations (17–40 μg/L) of Tl were detected in 1977 (Zhou and Liu, 1985). After 1998, some of the wells have been abandoned, while other wells that were still supplying drinking water showed lower levels of Tl (0.12–0.38 μg/L) (Xiao et al., 2003a). The lower Tl contents in the well water may be attributed to the fact that the oxidation process for Tl-bearing sulfides or host rocks actually tends to deplete Tl over the years and less Tl was released into the groundwater recharging to the wells (Xiao et al., 2003a). The local stream water receiving the acid mine drainage and groundwater discharge was used for local irrigation. The averaged concentrations of Tl in the stream water were 8.1 μg/L in dry season and 1.9 μg/L in rainy season (Xiao et al., 2003a). It has been demonstrated that irrigation water containing 1 μg/L of Tl would contribute to Tl accumulation ranging from 0.26 to 1 mg/kg (dry weight, D.W.) in plant materials, which can be regarded as the upper limit for human and farm animal consumption (Sager, 1998).

Tl transfer from soil to food crops is also highly concerned in China. The study by Xiao et al. (2004b) illustrated that Tl in soils was preferentially transferred to locally planted food crops compared to other metals (metalloids) (e.g., arsenic and mercury) (Table 2). The accumulation of Tl in the edible parts of the local crop species is decreased in the following order with respect to mean values (D.W.): green cabbage (338 mg/kg) > chili (3 mg/kg) > Chinese cabbage (2.5 mg/kg) > rice (2.4 mg/kg) > corn (1.4 mg/kg) (Xiao et al., 2004b). The highest level of Tl in green cabbage is up to 500 mg/kg, surpassing the levels of Tl (40–124 mg/kg) in the root soils (Xiao et al., 2004b). Recent studies have recorded that Tl may accumulate in green cabbage up to 1180 mg/kg (D.W.) from the Lanmuchang area (Xiao, T.F., unpublished data). Tl concentrations may present 10–29 times the levels of Tl spiked in the pot experiments (Table 2) (He, 2008).

In addition, other potential pathways for Tl entering the human body may include consumption of domestic birds and animals, air inhalation, and inadvertent soil ingestion in China (Xiao et al., 2007). Appreciable amounts of Tl were recorded in the local domestic poultry and animals of Lanmuchang Tl-polluted area, i.e. 7.2 to 10.3 mg/kg (fresh weight, F.W.) in chickens, 3 to 12.7 mg/kg (F.W.) in eggs and 0.1 to 0.38 mg/kg (F.W.) in pork (Feng et al., 2001). Although averaged concentration of Tl in Chinese coals (0.47 mg/kg) is similar with that (0.63 mg/kg) in the world coals (Dai et al., 2011), but concentrated Tl levels were recorded in coals of certain areas. For instance, high Tl contents were recorded in coals from a sulfide mineralized zone in Southwest China (5.7–46 mg/kg) (Xiao et al., 2004a), and from the germanium-bearing coals in Northern China (2.77–31.7 mg/kg) (Qi et al., 2007). Thus, the air inhalation of Tl-bearing particles outdoor from power plants and indoor from cooking and heating in rural areas may be a potential pathway of transferring Tl into human body in China. However, the data for Tl levels in the air around the polluted areas in China or in the world are not available. Finally, the inadvertent ingestion of Tl-bearing soils by so-called hand-to-mouth behavior may also transfer Tl to human body. It has also been shown that soil ingestion is a health concern for children (Lambert and Lane, 2004), however, there have been no studies on this specific pathway for Tl transfer either in China or in the world.

5. Adverse health impacts of Tl pollution

The evidences of adverse environmental impacts of Tl pollution in China have been well illustrated in the Lanmuchang area in Southwest China (Zhou and Liu, 1985; Zhang et al., 1997, 1999; Xiao et al., 2007). Lanmuchang, a rural area with approximately 1000 inhabitants, presents a specific geo-environmental context with Tl pollution in local soils, waters and food crops. The adverse environmental impacts of Tl pollution in this area were revealed by chronic Tl poisoning with symptoms of weakness, muscle and joint pains, disturbance of vision and hair loss (APASSGP and EGLIGCAS, 1977; Liu, 1983; Zhou and Liu, 1985). Previous epidemiological investigations showed that high concentration of Tl existed in the urines of the local villagers, ranging from 600 to 3000 μg/L in the 1970s (Zhou and Liu, 1985), 77.7 to 2660 μg/L in the 1990s (Zhang et al., 1999), and 2.51 to 2668 μg/L (Mean = 521.9 μg/L, Fig. 3) in 2003 (Xiao et al., 2007). These high urinary Tl levels were 1–4 orders of magnitude higher than the accepted maximum urinary Tl concentration (<1 μg/L) for “non-exposed” humans in the world (CDC, 2003). In accordance with the health guidelines for Tl by the World Health Organization (WHO) (WHO/IPCS, 1996), the majority of the local population with urinary Tl concentrations above 4.5–6 μg/L in the Lanmuchang area might suffer from the early adverse health effects. Some of the villagers with urinary Tl concentrations (>500 μg/L) could be considered as approaching clinical intoxication (Xiao et al., 2007). It is surprising to note that the high Tl levels in urine of the local villagers are nearly constant within the past four decades. This likely reflects a long-term exposure to Tl in the local environment, which was probably caused by the continuous consumption of Tl-containing foods grown in the local Tl-polluted soils over the years (Xiao et al., 2004b, 2007). In contrast, exposure to the Tl in the well water still supplying drinking water has been remarkably reduced from 17–40 μg/L (Zhou and Liu, 1985) to 0.12–0.38 μg/L (Xiao et al., 2003a). However, Tl content (0.12–0.38 μg/L) in the local well waters is still over the maximum contaminant level (0.1 μg/L) in China (CNS, 2006). Therefore, the potential risk of Tl poisoning from the drinking water in the Lanmuchang area should be constantly monitored.

The local villagers commonly consume vegetables grown in local Tl-contaminated soils of Lanmuchang throughout the entire year. The average daily dietary intake of Tl through locally planted crops was estimated to be 1.9 mg per person, as compared to 0.01 mg for Hg and 0.03 mg for arsenic (Xiao et al., 2004b). This was approximately 1000 times higher than the world average daily intake (2 μg/day, Sabbioni et al., 1984). It was also far above the ‘oral reference Tl dose’ of 0.056 mg/day (RAIS, 1994) and the Tl intake of 3.8 μg/day for an average adult from vegetables in the USA (USEPA, 1980). Xiao et al. (2007) showed that the urinary Tl concentrations of the local population in the Tl-impacted Lanmuchang area had positive correlations with the crop Tl contents ($r = 0.990$, $p < 0.0001$) and with the soil Tl contents ($r = 0.952$, $p < 0.0001$). These results clearly imply that Tl contents of the crops from Tl-polluted soils have significant effect on Tl concentrations in urine of the local population (Fig. 3). Significant differences of urinary Tl concentrations between male and female groups ($p = 0.6452$) or among different age groups ($p = 0.9353$) were not observed, suggesting that the health impact of Tl was independent of sex and age of the locally exposed population (Xiao et al., 2007). The above findings strongly demonstrated that Tl in soil is likely to be transferred to the human body through the consumption of local food crops with high biological ability to accumulate Tl, which ultimately produces adverse health effects.

In addition, consumption of domestic birds and animals bred in Tl-polluted areas, air inhalation of Tl-bearing particles, and inadvertent Tl-polluted soil ingestion may also increase the amounts of Tl into human body and produce adverse health effects.

6. Geo-environmental management on Tl pollution

The multidisciplinary environmental studies by lithogeochemistry, soil geochemistry, hydrogeochemistry and biogeochemistry of Tl and its impact on human health in China have documented a real geo-environmental concern. The Tl-rich epithermal metallogenic domain in Southwest China is located in the upper reach catchments of both Yangtze River and Pearl River (China's first and third longest rivers, respectively). Tl in soils and waters from natural weathering or mining, coupled with the favorable hydrological regimes, could result in wide dispersion of Tl pollution into the rivers.

With respect to Tl toxicity and pollution impacts in China, the safe limit of Tl was set at 0.1 μg/L for the Chinese drinking water quality (CNS,

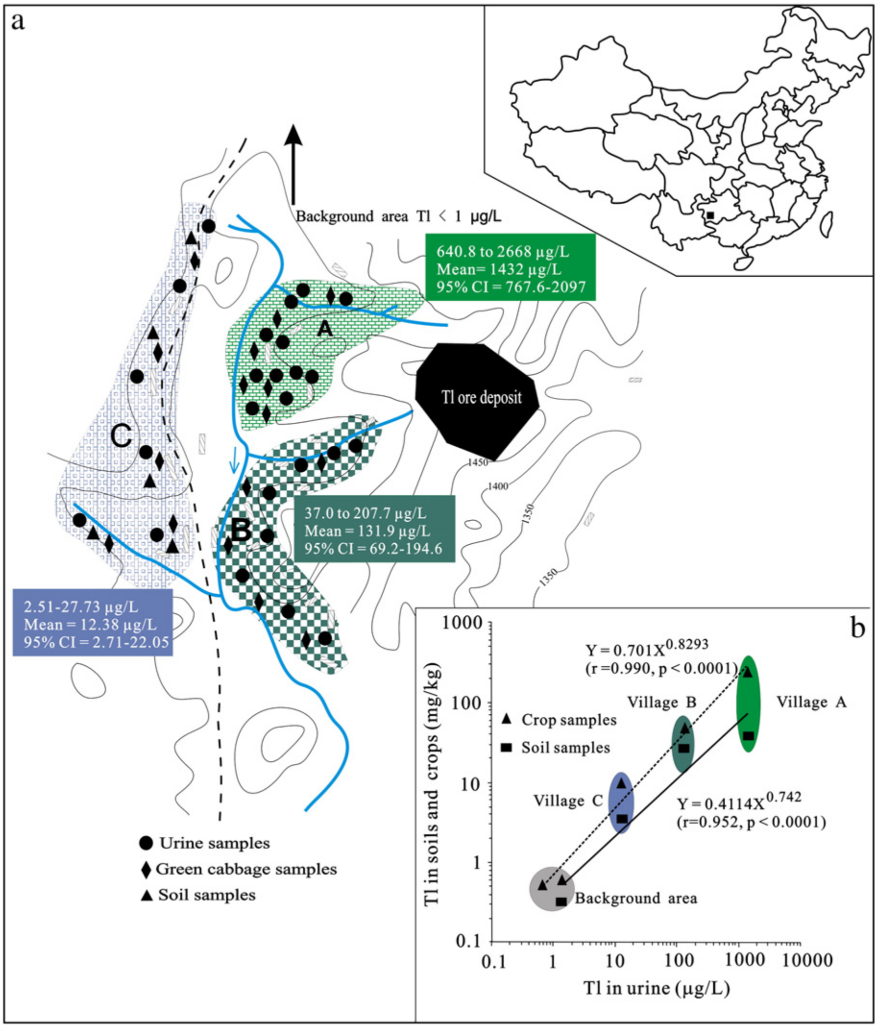

Fig. 3. (a) Map showing human exposure to Tl in terms of urinary Tl levels in the Lanmuchang Tl mineralized area, and (b) plot of Tl concentrations in soil and crop vs. Tl in urine (mean values).
Modified after Xiao et al., 2007.

2006), and the Tl-bearing mine wastes were also listed in the China National Hazardous Waste Inventory in 2008. However, there have been no threshold limits of Tl in soil and foodstuffs in China. According to the world experiences and the pollution situations in China, the authors suggest that the maximum contaminant levels of Tl be regulated at 1 mg/kg in the arable soils and 1 mg/kg (DW) in foodstuffs. Accordingly, Tl level at 1 μg/L in irrigation water would be the acceptable maximum contaminant levels for guaranteeing safe soil and foodstuff quality in China. These regulations will provide guidelines for the appropriate management of Tl pollution in China.

Tl dispersion and pollution in soils and waters should be regarded as critical parameters for proper land use and health-related environmental planning and regulation. The researches on Tl pollution and health impacts in China have identified certain plants (e.g., green cabbage and rape) that are able to highly accumulate Tl from arable soils with slightly higher content of Tl (1 mg/kg). These plants can be a health risk for human consumption. Therefore, proper land management practice surrounding the areas impacted by metal sulfide mineralization/mining should be carefully regulated. Simple solutions for immediate implementation include elimination of the planting of certain crops, particularly the high Tl accumulation crops, in Tl polluted soils. The practices for water quality monitoring, mine water treatment and mine waste site remediation should not neglect Tl. Testing the urinary Tl concentration of the population inhabiting the Tl-impacted areas represents a quick and easy method to detect Tl exposure since Tl poisoning symptoms may take years to manifest themselves in an unambiguous manner (Xiao et al., 2007).

7. Conclusions

Tl occurs at high concentrations in the environment associated with the epithermal metallogenesis of sulfide minerals in China. The natural mineralization and/or mining for the Tl-rich metal sulfide minerals have high potential of producing Tl pollution in the environment, which have raised a specific environmental concern in China and other parts of the world. The evidences of Tl pollution and environmental impacts in China reveal that Tl associated with epithermal metallogenesis can be dispersed beyond a mineralized zone. Its high abundances in local water, soil, and crops may rise above permissible levels and result in adverse health effects to local residents. The geo-environmental processes of water transportation and food crop accumulation of Tl are the main factors resulting in Tl pollution. In terms of geo-environmental concern, it is essential to understand the baseline and, dispersion pattern of Tl in the environment in order to provide guidelines for safe land use and minimize or prevent cases of adverse health impacts of Tl pollution. The practices for water quality monitoring, mine water treatment and mine waste site remediation should no longer neglect Tl, and testing the urinary Tl concentration of Tl-affected population represents a quick and easy method to evaluate Tl exposure. The experiences of Tl pollution in China can provide important lessons for many other regions in the world with similar geo-environmental contexts.

Acknowledgments

This research was funded by the Key Knowledge Innovation Project of Chinese Academy of Sciences (KZCX2-YW-135), the National Basic Research Program of China (2009CB426307), and the National Natural Science Foundation of China (40773072 and 40721002). The authors appreciate Prof. Xiangdong Li at the Hong Kong Polytechnic University for the helpful comments on early drafts of this manuscript. Four anonymous reviewers are acknowledged for their critical comments and suggestions which have considerably improved the manuscript.

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