Identification of mercury fractions in water, soil and sediment from typical alkaline mercury mining area and modelling their transport under different flow regimes

Dissertation for the Degree of PhD

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Table of Content

Abstract

Mercury (Hg) is regarded as a global pollutant due to the long residence time of elemental Hg in the atmosphere, with the potential for transport around at least the northern hemisphere following emission to the atmosphere. The Chinese environment in general has elevated contaminations of Hg. Elevated Hg concentrations are found in most environmental compartments, including air, water, soil, sediment and biota. Despite the high total Hg contamination, the MeHg concentrations in fish are in most cases below the levels for consumption advice. Rice in contaminated areas was instead found to be a more important pathway for MeHg exposure than fish due to the fact that rice is the main staple food in large part of China. The estimated MeHg intake level of Chinese people is generally lower than FAO/WHO's 1.6 µg kg^{-1} bw week^{-1}, except for populations with special occupations (e.g. Hg miner, fisherman).

China is currently the largest emitter of Hg to air and the demand for industrial use of Hg is predicted to increase. Due to great demand for Hg, the mining and smelting of Hg boomed in the 1970s to 1990s. Mining and smelting residues caused serious environmental problem for the local environment and continue to release Hg to the nearby environment after closure of mines or smelters. Several orders of magnitude higher Hg levels were found in soil, sediment and water in mining areas. After the mining activities were stopped the contaminated soils and sediments continue to release Hg, causing long-term impacts to the local environment. It is necessary to understand the transport mechanism of Hg, so that appropriate abatement measures can be taken in order to minimize the impact of Hg contamination.

Water, sediment and soil in a region with previous Hg mining and retorting continue to receive Hg inputs from gangue tailings and calcine waste piles. In this study a refined sequential extraction technique was used to determine Hg pools in soil and sediment in order to assess its potential mobility in contaminated areas, allowing identification of the following conceptual Hg fractions: elemental Hg, exchangeable Hg, strongly-bound Hg, organically-bound Hg and total Hg (THg). This fractionation scheme was used on stream sediments and rice paddy soils, collected from the Wanshan Hg mining area in China.

The THg concentrations were as high as 480 mg kg^{-1} in stream sediment samples and reached 130 mg kg^{-1} in paddy soil samples. Exchangeable- and strongly-bound Hg constitute 10 - 30% and 20 - 40% of the THg, respectively, for most sediment and soil samples. The residual fraction (probably mostly cinnabar, HgS) varies considerably (4 - 82%), with higher residual

levels in the sediment samples than in soil samples. Rice paddy soils, which are richer in soil organic matter, also contain a small but significant amount of organically-bound Hg. Exchangeable-, strongly-bound- and organically-bound Hg fractions are mainly sorbed to fine particles, which have enhanced mobility due to particle transport in the streams. Elemental Hg is only found in significant proportions close to a few active artisanal retort sites.

Seepage runoff from Hg mine gangue tailings and waste dumps of calcines from the smelters contains high content of Hg. The hydrological, physical and chemical variables governing temporal and spatial variation in levels and form of Hg in streams impacted by Hg contaminated runoff were evaluated. Water samples were analyzed for different Hg fractions: total Hg (THg), dissolved Hg (DHg), methylmercury (MeHg) and reactive Hg (RHg). Samples collected during different flow regimes in the Wanshan Hg mining area showed significant temporal variations in Hg concentrations and fractions. Periods of relatively high flow had high concentrations of THg in water due to more particles being re-suspended and transported. The concentrations of major anions (Cl^-, F^-, NO_3^- and SO_4^{2-}) were lower during higher flow due to dilution. Due mainly to sedimentation of particles in addition to some dilution from tributaries the concentration of THg decreased from 2 100 ng L^{-1} to background levels (< 50 ng L^{-1}) within 10 km distance downstream of the point source. Sedimentation accounts for 69% and 60% of the decrease in THg during high flow and low flow regimes, respectively, in the upper part of the stream. Speciation calculation of the DHg fraction, using speciation software Visual MINTEQ, showed that $Hg(OH)_2$ associated with dissolved organic matter (DOM) constitute over 95% of DHg in surface waters in Wanshan.

Many heavily polluted areas are located in remote regions that lack routine hydrologic monitoring. A modelling approach to produce scenarios of water chemistry trends for regions that lack hydrological data is therefore needed. To model Hg transport in a stream draining the Wanshan mining area, a GIS hydrologic model (HEC-HMS), providing hydrological data, was coupled with a simulation model for Hg fractions in water (WASP 7). Hydrological variations in the stream flow are thereby simulated based on readily available precipitation data. The produced hydrograph is then used as input to the WASP model which simulated variations in total suspended substances (TSS), THg, DHg and MeHg concentrations at different parts of the river under different flow regimes. Compared to measured values the model produced reasonable simulation results for TSS, THg, DHg and MeHg, with relative errors generally around 10%. High flow events are the main contributors for transport of both suspended particles and THg. Three high flow events captured during the field sampling

campaigns accounted for about 50% of annual transport of THg. The annual total transport of Hg was estimated to be 8.8 kg Hg in the upper reaches of the stream, while only 2.6 kg was found to be released out of the stream where the stream meets a large river 20 km downstream of the pollution source. Hence, about 70% of Hg is retained in the stream mainly through sedimentation.

Elevated Hg concentrations were found in all water, soil and sediment samples related to the studied stream draining the Wanshan mining area. Exchangeable Hg fraction is mainly sorbed to fine particles, which have enhanced mobility due to particle transport in the streams. The residual fraction varies considerably but is mainly found in coarse particles in the higher reaches of the stream. Ongoing artisanal retorting has a significant impact on the fraction of elemental Hg found in the environment. The transport of Hg is mostly controlled by the transport of suspended solids as most Hg exists as particulate form. Flow is a key factor in controlling the transport of suspended solids and thus THg. Most of Hg is retained in the stream through sedimentation.

List of Papers

Paper 1: *Identification of fractions of mercury in water, soil and sediment from a typical Hg mining area in Wanshan, Guizhou province, China*
Yan Lin, Thorjørn Larssen, Rolf D. Vogt and Xinbin Feng.
Applied Geochemistry. 2010:25;60-68

Paper 2: *Transport and fate of mercury under different hydrologic regimes in polluted stream in mining area*
Yan Lin, Thorjørn Larssen, Rolf D. Vogt, Xinbin Feng, Hua Zhang
Journal of Environmental Sciences. 2011:23(5);757-764

Paper 3: *Modelling transport and transformation of mercury fractions in heavily contaminated mountain streams by coupling a GIS-based hydrological model with a mercury chemistry model*
Yan Lin, Thorjørn Larssen, Rolf D. Vogt, Xinbin Feng and Hua Zhang.
Submitted to Science of Total Environment

Paper 4: *Mercury in the Chinese environment - a review*
Yan Lin, Rolf D. Vogt, Thorjørn Larssen

Abbreviations

Hg: mercury

Hg^0: elemental mercury

Hg^{2+}: divalent mercury

Hg^p: particulate bound mercury in atmosphere

DHg: dissolved mercury

GEM: Gaseous elemental Hg

MeHg: methyl mercury

PHg: particulate mercury

RGM: reactive gaseous mercury

THg: total mercury

TGM: total gaseous mercury

BAF: bioaccumulation factor

FAO: Food and Agriculture Organization of the United Nations

GIS: geographic information system

MOH: Ministry of Health of China

PTWI: provisional tolerable weekly intake

SEPA: State Environmental Protection Administration of China

SRB: sulfate reduction bacteria

SRR: sulfate reduction rate

UNEP: United Nations Environment Programme

US EPA: United States Environmental Protection Agency

USGS: United State Geological Survey

WHO: World Health Organization

1. Introduction

Mercury (Hg) is one of the most toxic heavy metals commonly found in all compartments of the global environment: atmosphere, lithosphere, hydrosphere, cryosphere and biosphere. Hg emitted to the environment may be transported in the atmosphere over long distances due to its existence as a gas under natural conditions, and it draws therefore much attention as a global pollutant.

Three oxidation states of Hg (0, I and II) exist in the environment (Barbosa et al., 2001). The most common species of Hg, and which are encountered in practically all environmental media except air, are $HgCl_2$, $Hg(OH)_2$, HgS and the organomercuric compound methylmercury (CH_3Hg^+), with other organomercurials (i.e., dimethylmercury and phenylmercury) existing in small fractions. In the atmosphere, the predominant form is elemental Hg (Hg^0) (USEPA, 1997).

Emission to air followed by atmospheric deposition is an important regional and global pathway for Hg contamination. The global anthropogenic annual Hg emission to the atmosphere was estimated to be approximately 2 000 tons per year (1 930 tons in 2005 by UNEP's emission inventory (UNEP, 2008) and 2 320 tons in 2009 by Pirrone et al. (2010)). The uncertainties in the calculations are large; UNEP reported a low-end estimate of 1 220 tons yr^{-1} and a high-end estimate of 2 900 tons yr^{-1} (UNEP, 2008). A major additional uncertainty in the global mass balance of Hg is the contribution from natural sources and the contribution from re-emission of previously deposited Hg from oceans, lakes and soils. UNEP (2008) estimated the sum of natural sources and re-emission to be in the range 1 800 – 4 800 tons yr^{-1}, while Pirrone et al. (2010) concluded that this number was 5 207 tons yr^{-1}. Globally, the major anthropogenic contributions of Hg to the atmosphere are from fossil-fuel (mainly coal) fired power plants (810 tons yr^{-1}), artisanal small scale gold mining (400 tons yr^{-1}), non-ferrous metals manufacturing (310 tons yr^{-1}), cement production (236 tons yr^{-1}), waste disposal (187 tons yr^{-1}) and caustic soda production (163 tons yr^{-1}) (Pirrone et al., 2010). Asian Hg sources account for approximately 2/3 of the global anthropogenic emissions (UNEP, 2008) and China is by far the country with the largest Hg emissions.

Direct release of Hg to water can cause serious damage to local environment and impacts on human health for local population. There have been reports on serious Hg pollution incidents caused by discharge from industrial sources. Minamata disease was one of the most known cases (Mahaffey, 2004). Substantial amount of MeHg was released to the Minamata Bay from a chemical plant. The MeHg was bioaccumulated in fish which were consumed by people causing serious damage to especially fetus. Another type of direct release is the drainage from Hg mines. Cinnabar (HgS) is the most common Hg ore and it is commonly found in limestone bedrock. Hg is usually extracted from cinnabar by calcinations. In this process the ore is crushed and pyrolyzed at more than 600 °C, reducing Hg(II) in the cinnabar to volatile Hg^0 which is captured by distillation. The main products of this roasting process are elemental Hg and calcine waste. Because this procedure was not 100% efficient some Hg inevitably remained in the calcine. Parts of this residual Hg occur in more soluble forms of Hg which thereby are more readily mobilized (Biester et al., 1999). The roasting process and Hg residues in calcines are also important sources of Hg emission to the atmosphere. Hg escaping the distillation process as well as evaporation of elemental Hg in the calcine waste caused and continues to cause elevated Hg concentrations in the ambient air, with subsequent deposition in surrounding areas as well as long range atmospheric transport.

Hg continues to attract significant scientific attention as a widespread pollutant and a serious threat to human health. The research is spurred by the need for enhanced knowledge to facilitate more effective knowledge based abatement actions and international conventions to reduce Hg emissions (Selin and Selin, 2006). China, which collectively is the largest source of Hg emission, plays a key role in dealing with Hg pollution control. During the past few years China has implemented stricter environmental regulations on industries. China has set total emission control target for heavy metals, which includes Hg, in its 12th five-year plan. The total emission of heavy metals in 2015 in heavily polluted areas has to be reduced by 15% compared to 2007, while other areas have to maintain their emissions level as in 2007[1].

2. Objectives of this thesis

The main objective of this PhD study was to identify the environmental factors affecting the Hg transport in a heavily polluted area and develop a method for modeling Hg transport. Sustainable long-term management of the Hg contamination problem requires knowledge regarding the main factors controlling the Hg transport and dispersion. A necessary prerequisite for an assessment of these factors are an understanding of to what extend Hg is mobilized and transported and how Hg is transported downstream. A comprehensive analysis of Hg amount and form in all environmental media including water, soil and sediment is

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[1] See http://www.china.com.cn/policy/txt/2011-02/19/content_21956713.htm

required, and a proper modeling tool needs to be developed in order to assess and predict the Hg transport.

Fig. 1, Map of China and the approximate location of Wanshan

This thesis focuses on the Hg transport mechanism in the Wanshan mining area (Fig. 1) and develops an applicable method to model Hg transport. As the research is conducted in China, a general overview of the environmental Hg pollution levels in China is given in the literature review as background information, putting the results from the present studies in a broader national context. As a mining area is the focus of this thesis, a more detailed overview of research conducted at important mining areas in the world is also presented in the thesis. This allows for comparison of the results generated in this study with other studies.

3. Hg pollution in China

3.1 Release and intentional use of Hg in China

China is currently the world's biggest emitter of Hg. Furthermore, Hg emissions are increasing most rapidly in Asia (including China). The demand for Hg in China is predicted to increase due to fast expansion of PVC production where Hg is used as catalyst. Direct release of Hg from industrial sources and mines causes serious pollution to its local environment. There have been reports on serious Hg pollution incidents caused by discharge from industrial sources. The earliest Hg pollution reported in China was in Second Songhua River (Yu et al., 1983). The river was seriously contaminated by Hg containing wastewater discharged by Jilin Petro Chemical Plant. The polluted sediment is still releasing Hg to the river. Guizhou Province has also had seriously incidents. Baihua Reservoir was reported to be heavily polluted by Hg released from Guizhou Organic Chemical Plant (Hou et al., 2004).

UNEP (2008) estimated China's Hg emission to air to be 825 tons in 2005 and Wu et al. (2006) estimated the amount to be 696 tons in 2003. Pirrone et al. (2010) estimated China's Hg emission to be 609 tons. All studies have fossil fuel combustion as the largest single source (Fig. 2; note that Wu et al. (2006) split the fossil fuel into several sectors and that the power plant contributes less than half of the total coal related emissions). There are however also important differences in source distribution between the two studies, illustrating the large uncertainties in the input data for the emission estimates: Wu et al. (2006) and Pirrone et al. (2010) reported the non-ferrous metals smelting sector to be the second largest sector in China, while UNEP (2008) had artisanal gold production as the second largest sector (Fig. 2).

During the next few decades there is forecasted a significant increase in anthropogenic Hg emissions in Asia, especially in China (Wong et al., 2006). This is manly due to that China's coal consumption is projected to rise from 2.6 billion tons in 2007 (NBS, 2010) to 3.8 billion tons in 2015 (PDO, 2010). Zinc production in China, the largest contributor to Hg emissions in the non-ferrous metals production sector, is also projected to rise from 1 million tons in 2005 to 3.6 million tons in 2030 (Maxson, 2009). However, these increases in industrial activity will not give a similar increased release of Hg to the environment, as larger and more modern plants typically have considerably lower Hg emissions (Li et al., 2010a).

The estimated industrial use of Hg in China in 2005 was 1 425 - 1 845 tons (Maxson, 2009). The by far most important application is the use of Hg as catalyst in the production of vinyl chloride monomer, consuming around 800 tons in 2005 and projected to increase (Maxson, 2009). The other major Hg consuming sectors are batteries, medical equipment and fluorescent lamps (Maxson, 2009). To what extent the Hg used in these industries are recycled and to what extent they are released in the environment is uncertain.

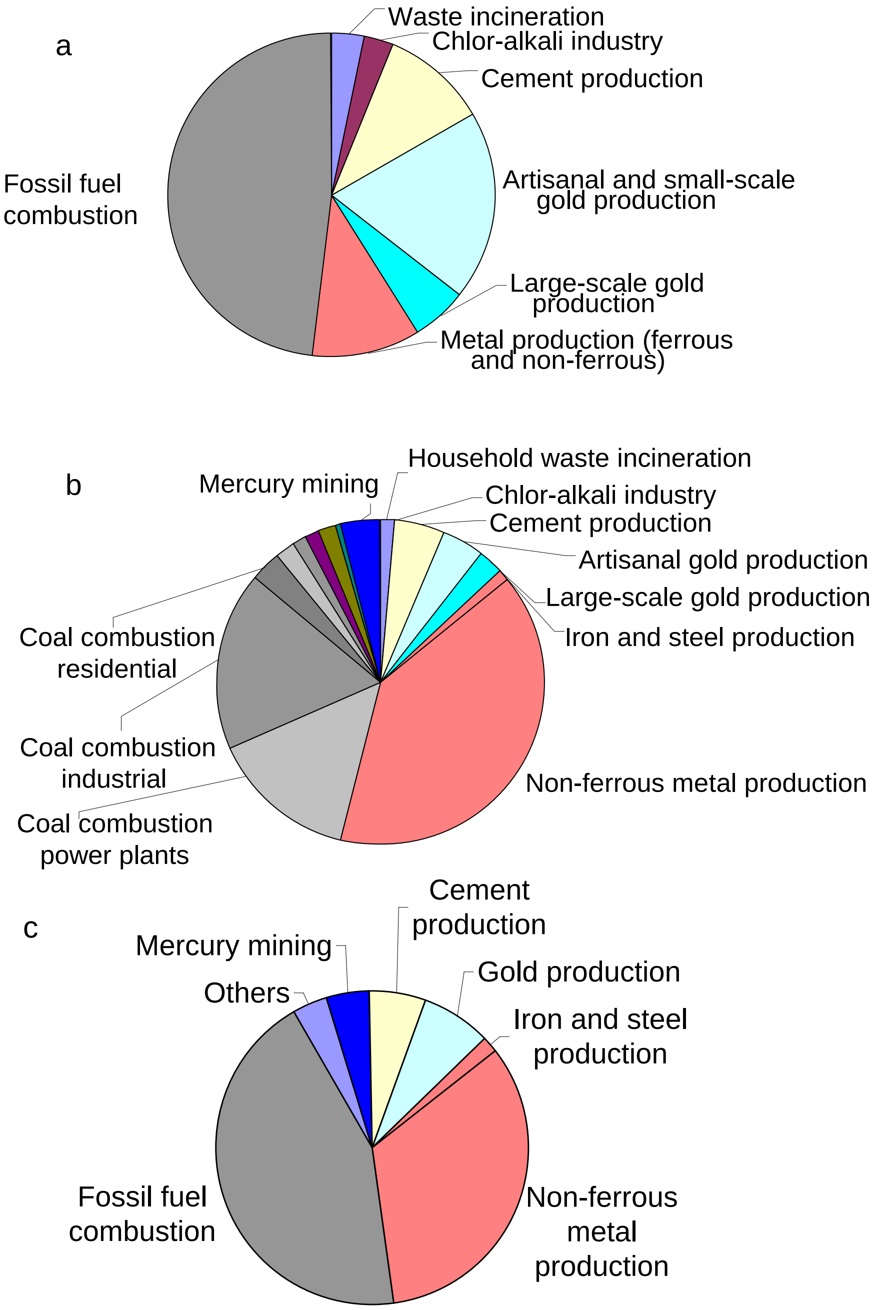

Fig. 2, Source distribution of China’s anthropogenic Hg emission to air from two different emission inventory studies: a (825 tons in 2006) by UNEP, 2008, b (696 tons in 2005) by Wu et al., 2006, c (609 tons in 2003) by Pirrone et al., 2010.

3.2 Hg in atmosphere in China

Atmospheric Hg concentrations in China are generally elevated. The atmospheric Hg concentrations usually range from 2 to 35 ng m^{-3} in summer (non-heating season) and 3 to 80 ng m^{-3} in winter (heating season) (Paper 3). The cause for this seasonal difference is that atmospheric Hg concentrations are significantly affected by the combustion of coal as this is the main source for power generation and heating. The levels of atmospheric Hg in large Chinese cities are as expected significantly higher than concentrations in remote areas but similar to what is found in other big cities in Japan and South Korea (Fang et al., 2009). Remote areas in China have elevated Hg concentrations in the air compared with average background value in Northern Hemisphere and Arctic Ocean. The average background atmospheric Hg concentrations measured in remote mountain areas are found to lie between 2 - 5 ng m^{-3}. In the coastal regions concentrations from 2 to 7 ng m^{-3} have been reported (Paper 3). These values were higher than the reported background values for the Northern Hemisphere (1.5-1.7 ng m^{-3}, Temme et al., 2004) and different remote areas in Europe and North America (usually lower than 2.0 ng m^{-3}, Travnikov, 2005; Kim et al., 2005; Valente et al., 2007). The atmospheric Hg concentrations over the South China Sea are also higher than that of Arctic Ocean (1.6 ng m^{-3}, Steffen et al., 2005).

3.3 Hg in water in China

Studies of 1st order forest streams draining catchments with no direct industrial impact (Mt Leigong, Tieshanping and Luchongguan) inherently hold lower Hg concentrations compared to the large Chinese rivers receiving multiple anthropogenic discharge sources. The Hg concentrations values in these small streams are comparable to similar headwater streams in some European studies (Larssen et al., 2008; Lee et al., 1995; Porvari and Verta, 2003). The annual total atmospheric input fluxes of Hg were 119.5 μg m^{-2} a^{-1} for Mt. Leigong and 291.2 μg m^{-2} a^{-1} for Tieshanping (Wang et al., 2009) were much higher than the European studies mentioned above. Comparable concentrations in runoff despite higher loading indicate a strong retention of atmospheric Hg deposition in these catchments in southwest China.

High order rivers in China are usually heavily polluted by Hg. THg concentrations in the larger Chinese rivers generally exceeds 100 ng L^{-1} (Paper 3) (Class IV in Chinese Surface Water Quality Standard, SEPA 2002). This picture may be somewhat biased due to that the Chinese river that are studied for their Hg content have known large Hg contamination sources, including metal smelting plants, chemical plants and Hg mining and smelting. There may therefore be a tendency that researches focus too much on rivers with particular contaminant issues. No synoptic survey of Hg in the large river basins of China exists till now.

Nevertheless, practically all big rivers in China pass through several major cities with considerable industrial activities and hence receive large amounts of sewage and industrial wastewater which may be contaminated with Hg. Due to pollution in rivers, the Chinese river estuaries and even coastal seawaters are also heavily polluted. Large river estuaries, e.g. Pearl River Delta, Yangtze River Delta and Wuli Estuary, are heavily impacted by upstream industrial sources. The contaminated rivers further cause the Hg concentrations in coastal seas to be highly elevated.

3.4 Hg in soil and sediment in China

Many of the reported Hg levels found in urban and agricultural soils (0.02-0.22 mg kg^{-1}) exceed background level for Hg in China (0.15 mg kg^{-1}) (NEPA, 1994). In general the urban and agricultural topsoil are a classified as class II by the Chinese environmental standard for soils (THg below 1 mg kg^{-1}, SEPA, 1995). The sediments in Chinese lakes, rivers and estuaries all showed highly elevated Hg concentrations. The Hg levels were comparable to contaminated sites in other areas in the world, such as Gulf of Trieste, Italy (0.2–5 ng L-1) which receives outflow from Idrija Mine, Slovenia (Faganeli et al., 2003).

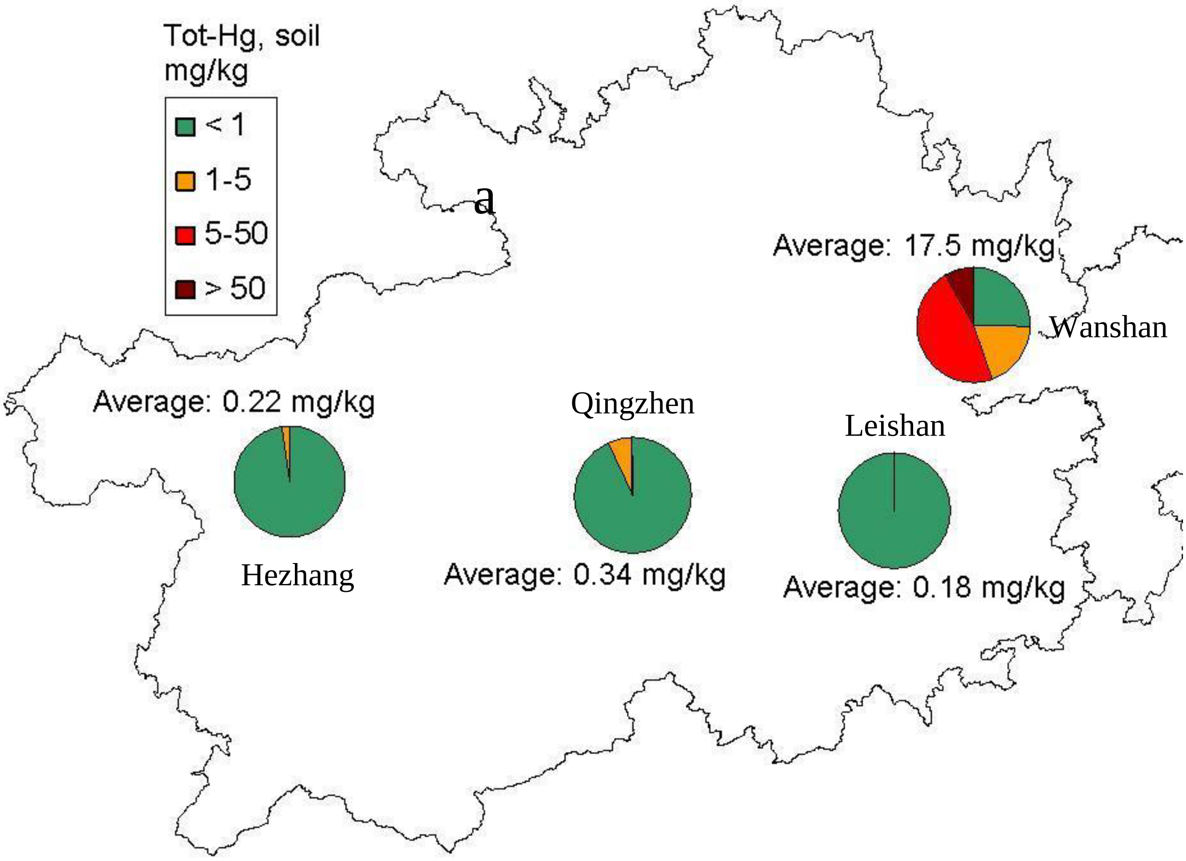

Fig. 3a, THg concentrations in soil in Guizhou Province.

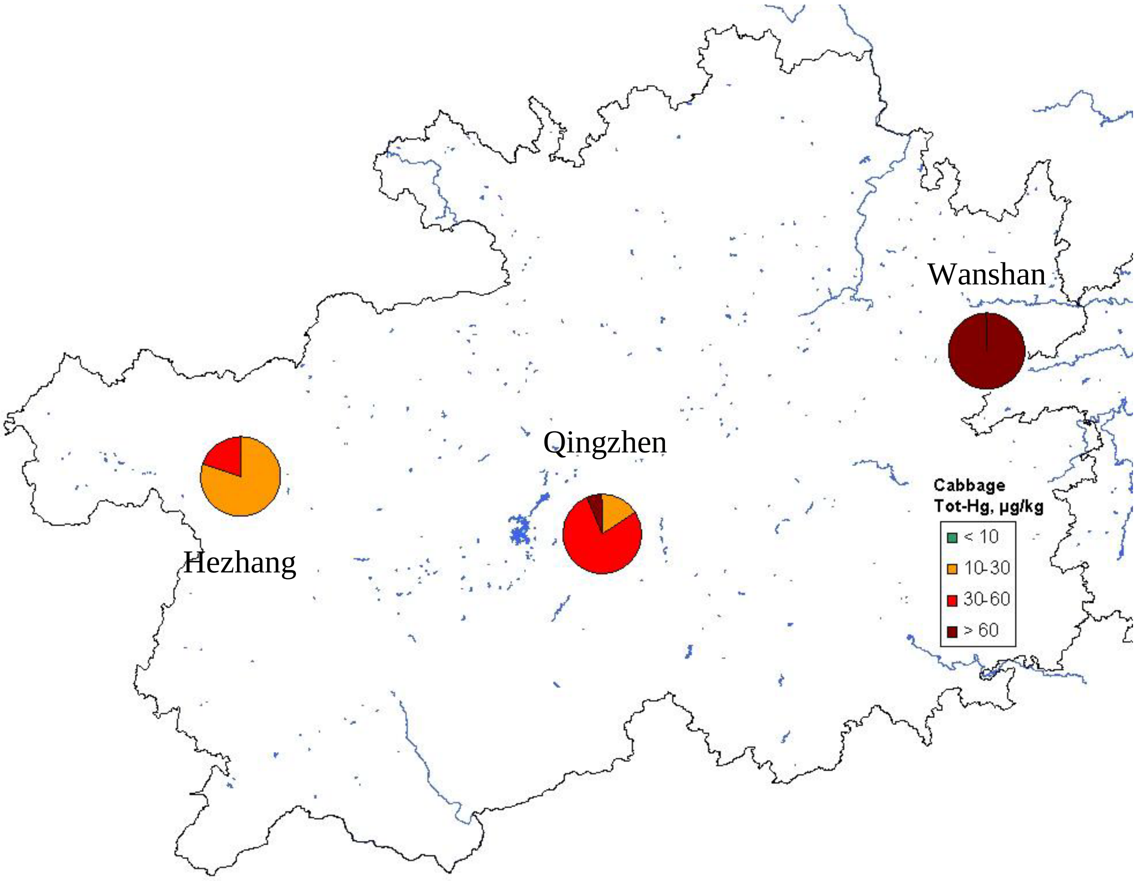

Fig. 3b, THg concentrations in cabbage in Guizhou Province.

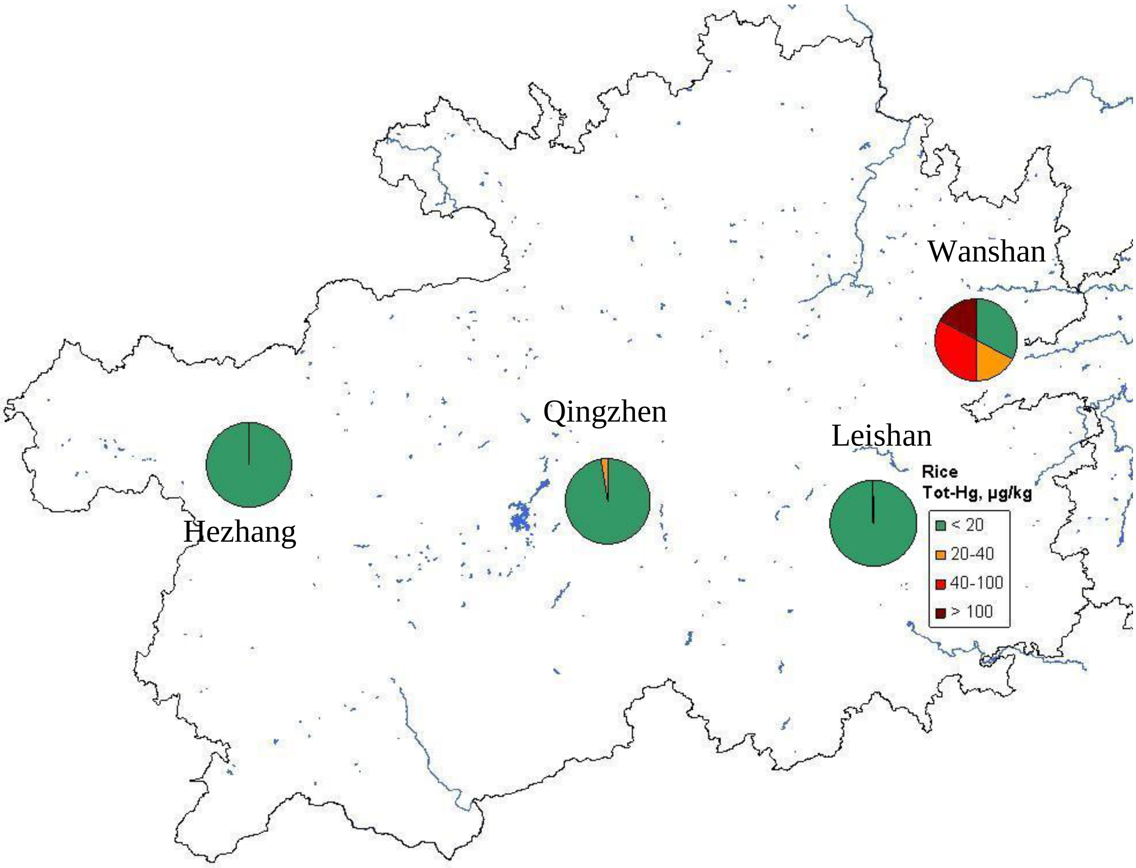

Fig. 3c, THg concentrations in rice in Guizhou Province.

A survey on the Hg levels in soils in Guizhou was conducted by the Sino-Norwegian Cooperation Project – capacity building for reducing Hg pollution in China (SINOMER). The project selected 4 representative sites (Hezhang, Qingzhen, Wanshan and Leishan, Fig. 3a); Hezhang used to host many small scale artisanal Zn smelters. Qingzhen is a county with a large power plant. Leishan is a remote natural reserve which is considered to be background site. Wanshan, which is well known for its long historic mining activities, is a study site for impact of mining and artisanal Hg smelting. Wanshan is also the research site for the present study. The results showed significant difference between the Wanshan and the other three areas. Soil in Wanshan is seriously polluted by Hg, while only a few soils in Hezhang and Qingzhen had Hg levels that exceeded 1 mg kg^{-1}. Leishan as a background site showed almost no signs of Hg contamination.

3.5 Hg in important food stuff in China

MeHg is usually considered the most toxic form of Hg and is the dominant form of Hg in fish. The percentage of MeHg to THg in fish is reported to be in the range 72–100% (Gray et al., 2000; Storelli et al., 2002). Since MeHg bioaccumulates, the level of MeHg in fish is mainly determined by its trophic level (Dietz et al., 1996). It is also influenced by the age and size of fish (Weech et al., 2004).

Fish that are used for human consumption in China usually have low trophic levels as the fish are usually farmed. Current available data show that most fish in China contain low THg and MeHg concentrations. In general, the THg concentrations in most fish samples in China were found to be lower than the FAO/WHO guideline of 0.5 mg MeHg kg^{-1} (FAO/WHO, 2009), except for a few hotspot areas with large local Hg contamination sources, such as Hg mines and Zn smelters. There are limited data on Hg levels in wild and older fish in China. The fish collected in sea have usually lower THg levels than those collected in freshwater rivers and lakes. Rice is important in Chinese diet. Studies showed that rice is another important source of MeHg exposure to the Chinese population (Feng et al., 2008; Zhang et al., 2010c). Hg levels in most Chinese rice samples are well below the health limit, except for a few heavily polluted sites such as in mining areas. Leaf vegetables (e.g. lettuce) may contain highly elevated levels of THg, but MeHg levels are usually low.

The majority of the Chinese population has low exposure of Hg based on hair concentration data. But people from areas which have a heavy fish diet (Zhoushan fishermen, Cheng et al.,

2009) and Hg mine workers (Li et al., 2008a; Li et al., 2009) showed dangerously high exposure of MeHg. In these areas the MeHg exposure levels are higher than the FAO/WHO's advisory limit, 1.6 µg kg^{-1} bw $week^{-1}$ (FAO/WHO, 2003).

The survey conducted by SINOMER project also studied the Hg levels in rice and vegetables in the previously mentioned 4 representative sites (Fig. 3b, c). This study showed that the Wanshan area is generally seriously polluted by Hg, but that most areas in Guizhou Province have no big problem in terms of Hg pollution. The concentrations in rice showed similar trend with that in soil (Fig. 3a, c). This indicates that Wanshan residents may pose health concern through consumption of local rice. It has to be noted that leaf vegetables, such as cabbage, usually contain high levels of THg.

Similar to the research on bioaccumulation in fish in other countries, MeHg accumulation in rice has become an important research topic in recent years in China. The bioaccumulation of MeHg in rice has been confirmed (Zhang et al., 2010c, d) and the accumulation process has been studied. Soil was found to be the potential source of MeHg in the tissues of rice plants and newly deposited Hg is found to be more readily transformed to MeHg in soil. Most of MeHg was transferred to rice seed during the ripening period (Meng et al., 2011).

4. Literature review of study area and other important mining areas in the world

This chapter gives an overview of Hg related research conducted at several important Hg mining areas in the world, including the Wanshan area where the present study was conducted. Despite that most Hg mines have been shut down, the local environment around the Hg mines continues to be contaminated. Hg is usually extracted from cinnabar (HgS) by calcination. In this process the ore is crushed and pyrolyzed at more than 600 °C, reducing Hg(II) in the cinnabar to volatile Hg^0 which is captured by distillation. The main products of this roasting process are elemental Hg and calcine waste. Because this procedure was not 100% efficient, some Hg inevitably remained in the calcine. Parts of this residual Hg are readily mobilized through erosion (Biester et al., 1999) causing contamination of surface waters. The roasting process and Hg residues in calcines are also important sources of Hg emission to the atmosphere. Hg escaping the distillation process as well as evaporation of elemental Hg in the calcines caused and causes elevated Hg concentrations in the ambient air and subsequent deposition in surrounding areas, as well as long range atmospheric transport.

Globally, an accumulated production of close to one million tons of metallic Hg is reported throughout history (Hylander and Meili, 2003). Almaden in Spain, Idrija in Slovenia, coastal range of California, USA, and Monte Amiata in Italy are the top four Hg producing areas in the western countries. Together, these four mining areas accounted for over 70% of the global total production by the year 2000 (Hylander and Meili, 2003). However, the total production of Hg in these mines was significantly reduced from around 8 000 tons per year in 1970s to around 1 800 tons in 2000 (Hylander and Meili, 2003). The rest of the main Hg production has been made in Guizhou in China, Khaidarkan in Kyrgyzstan and Algeria (UNEP, 2006). Both Spain and Algeria terminated Hg mining operations in 2003 and 2004, respectively (UNEP, 2009), while China has increased their production of Hg considerably. In 2009 the global production was estimated to be 1 920 tons, of which China accounted for 1 400 tons, Kyrgyzstan 250 tons and Peru 140 tons (USGS, 2010). Considerable research has been conducted to document the Hg levels in local environment around the mines, investigating the pollution dispersion, bioaccumulation pathways and assessing impacts of Hg contamination. Almaden, Idrija, coastal range of California and Wanshan are the places where most research have been conducted and are therefore chosen as illustrative cases in this thesis to present an overview of the Hg related research in mining areas.

Almaden in Spain has been the world largest Hg producer in history, accounting for about one third of the total Hg world production. It has been active since the Roman times and up to the year 2000 (Hernandez et al., 1999; Saupe, 1990; Hylander and Meili, 2003). Idrija mining district in Slovenia was the second largest Hg mine after Almaden. The total production of Idrija Hg Mine during its 500-year production period summed up to about 110 000 tons of metallic Hg, this is about 12% of the global total production (Hylander and Meili, 2003). The Hg mineral belt in California extends for 400 km along the Coast Range and includes the New Idria and New Almaden mines, as well as many smaller deposits. Nriagu (1994) estimated that 61 400 tons of Hg was dispersed in North American environment between 1850 and 1900 due to the extraction of precious metals. Production ended in the early 1970s due to decreased demand for Hg. The total production of Hg in North America was around 140 000 tons, which accounts for 15% of the global total production (Hylander and Meili, 2003).

Hg use in China has a long history. Cinnabar was used as a drug and preservative, as well as pigment for the bright red color in temples and palaces for over 1000 years (Liu, 2000). Data on Hg production in China before the 20th century are scarce, but one report suggest that around 46 000 tons of Hg was produced until the year 2000 (Hylander and Meili, 2003). The

Hg mined in China after 2000 increased from 203 tons in 2000 (EBCNMI, 2009) to 1 400 tons in 2009 (USGS, 2010). The main historic Hg production in China was found in Guizhou Province since it is situated in the center of the circum-Pacific mercuriferous belt (Gustin et al., 1999). So far, at least 12 large Hg mines have been operated in the province, of which the major mines are located in Wanshan, Wuchuan, Lanmuchang and Danzhai. Wanshan Hg mine, which was the largest in China, was closed in 2001 due to depletion of ores. At that time the production started to decline also elsewhere in Guizhou Province. In 2008 more Hg was produced in Shaanxi (671 tons) than in Guizhou (662 tons) (EBCNMI, 2009). Between 1949 and early 1990s approximately 126 million tons of Hg contaminated calcines (waste material from the roasting process of Hg ore in limestone) had been dispersed in the environment in the Wanshan Hg mining areas (Liu, 1998).

Fig. 4. Map of Wanshan showing the main watercourses

Wanshan Hg mine, located in east Guizhou Province, was selected as the study site for the present study. Guizhou is a province located in the southwestern part of China. The main historic Hg production in China was found in Guizhou Province since it is situated in the center of the circum-Pacific mercuriferous belt (Gustin et al., 1999). So far, at least 12 large

Hg mines have been operated in the province, of which the major mines are located in Wanshan, Wuchuan, Lanmuchang and Danzhai. Wanshan Hg Mine is the largest. Total area of Wanshan county is 338 square kilometers and population is 62 000. Main rivers in Wanshan are Gaolouping, Xiaxi, Aozhai and Huangdao (Fig. 4). Wanshan has subtropical monsoon climate with yearly average temperature 13.4 °C. July is the hottest month with an average temperature at 23.9 °C, while January as the coldest month has an average temperature at 2.0 °C. Annual precipitation is about 1 400 mm. Most rainfall happens in summer and fall[2]. The Hg ore at Wanshan is mainly cinnabar and is found in sedimentary bedrock of predominantly dolomite, limestone and some sandstone (Zhang et al., 2004). Surface water in the area is generally alkaline due to this presence of carbonate-bearing bedrock and a large number of calcines tailings. The form of Hg in the calcine waste is dominantly elemental Hg, metacinnabar, and Hg sulfate and chlorides (Kim et al., 2000).

Wanshan Hg mine is the earliest Hg mine in China, it has also been the biggest Hg mine in China. The production in Wanshan can be traced back to Tang Dynasty (686 AD). Wanshan is therefore called the ‘Mercury Capital’ of China. The massive production started after the foundation of People’s Republic of China. Hg used to be the main export product of China, especially for the payback of debt to former Soviet Union[2]. The mine started to become exhausted in the 1980s and the area's long history of Hg mining finally ended in May 2002, when the mine entered government-enforced bankruptcy. Until large-scale Hg mining and retorting were shut down approximately 22 000 tons of Hg and 6 000 tons of cinnabar had been produced (Qiu et al., 2005). Between 1949 and early 1990s an estimated 126 million tons of Hg contaminated calcines (waste material from the roasting process of Hg ore in limestone) had been dispersed in the environment in the Wanshan Hg mining areas (Liu, 1998).

4.1 Hg in water in mining areas

Literature values for Hg levels in water close to Hg mining sites are listed in Table 1. Total Hg (THg) concentration in stream water exceeds 10 μg L^{-1} in the most severely impacted mining areas. However, concentrations are found to drop quickly downstream so that a large part of the leached Hg remains locally. This is due to that Hg has a strong tendency to be sorbed onto surfaces and is therefore to a large extent bound to suspended particulate matter

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[2] http://www.hudong.com/wiki/万山特区

suspended in water. In addition a significant fraction of the leached Hg is in the form of eroded particulate cinnabar.

Data from Wanshan show that there are clear seasonal fluctuations in THg concentration in the rivers draining the mining area. The mean concentration of THg during high-flow season was almost twice as high compared to that measured during base-flow season (Li et al., 2009). In both seasons, particulate Hg constituted a large portion of the THg. Suchanek et al. (2009), studying the more acid Sulphur Bank mining site in the US, found a linear regression between flow rate and THg concentration.

Research conducted at less impacted lakes showed much lower impact from mines and a higher contribution from atmospheric deposition (Quemerais et al., 1999). Randall et al. (2004) found that redox conditions (Eh) and pH have important influences on the mobility of Hg. In general, inorganic Hg is very insoluble in sediments over a wide pH range. Being a soft or type B heavy metal it exhibits a very high affinity for sulfide in mildly reducing environments, such as stream and lake sediments, forming insoluble HgS (Wang and Driscoll, 1995). Dissolved Hg also sorbs strongly to sediment and suspended solids, including Fe oxyhydroxides (Balogh et al., 1997).

4.2 Hg in calcine/sediment/soil in mining areas

THg levels in calcine/sediment/soil samples from mining areas are listed in Table 2. THg levels in calcine and mine gangue tailings depend very much on the original Hg content in the ore and retorting efficiency. Biester's (1999) sequential extraction technique revealed that Hg forms differ with the age of the tailings due to the processing of different ores with different roasting techniques. High THg content in ore and low efficiency can result in high Hg in calcines. In older tailings the predominant Hg species is cinnabar (HgS), due to incomplete roasting, whereas in tailings of the 20th century the amount of cinnabar in the material decreased due to a higher efficiency of the roasting process. In younger tailings, metallic Hg (Hg^0) sorbed to mineral matrix components, such as dolomite and Fe oxyhydroxides, became the predominant Hg form in addition to unbound Hg^0 and traces of HgO. Leaching tests show that in younger tailings high amounts of soluble Hg exist in reactive form. Literature values for Hg content in calcines ranges from 1.8 to 34 000 mg kg^{-1} (Table 2). THg level in Almaden is higher than that of Idrija and of that found in Hg mine gangue in California. THg levels in calcines found in Wanshan mining area are the lowest among the studied sites. This can be explained by that the ores in Almaden and Idrija are richer in Hg.

Table 1, Hg concentrations in water in different mining areas (ng L^{-1})

Name of mine	Location	Sampling Period	THg	MeHg	Reference
Almaden, Spain	Downstream	1995-1997	<110 - 20300		Berzas Nevado et al., 2003
Almaden, Spain	Downstream	Jun. 2003	7.6 - 13000	0.41 - 30	Gray et al., 2004
Almaden, Spain	Downstream	2005-2006	2.5 - 136 (DHg)	0.04 - 4.9	Berzas Nevado et al., 2009
Asturias, Spain	Downstream	Unknown	<100 - 800		Loredo et al., 2003
Asturias, Spain	Downstream	Unknown	< 500		Loredo et al., 2010
Idrija, Slovenia	Downstream	Unknown	2.8 - 322	0.01 - 0.6	Hines et al., 2000
Idrija, Slovenia	Downstream	2003	11 - 81	0.049 - 0.154	Zizek et al., 2007
New Idria, USA	Downstream	May, Oct. 1997, Jan. 1999	2900 - 12400		Ganguli et al., 2000
CA Coast Range, USA	Calcine drainage	Unknown	2100 - 450000	0.07 - 47	Rytuba et al., 2000
CA Coast Range, USA	Downstream	Unknown	1400 - 19600	0.96 - 4.50	Rytuba et al., 2000
Sulphur Bank, USA	Downstream	1998-2001	1.2 – 108		Suchanek et al., 2009
Wanshan, China	Calcine drainage	Sep. 2000	10 580	0.410	Horvat et al., 2003
Wanshan, China	Downstream	Sep. 2000	20.0 - 550	0.012 - 0.210	Horvat et al., 2003
Wanshan, China	Downstream	Baseflow	15 - 6200		Qiu et al., 2009
Wanshan, China	Downstream	Highflow	35 - 9300	0.31 - 25	Qiu et al., 2009
Wanshan, China	Downstream	Jun. 2008	4.5 - 3200		Paper 1
Wanshan, China	Downstream	Aug. 2007	2.9 - 1200	<0.035 - 3.4	Zhang et al., 2010a,b
Wanshan, China	Downstream	Jun. 2008	2.6 - 3200	<0.035 - 11	Zhang et al., 2010a,b
Wanshan, China	Downstream	Sep. 2008	1.9 - 12000		Zhang et al., 2010a,b
Wanshan, China	Downstream	Unknown	92 - 2300	2.6 - 7.9	Li et al., 2008b

Table 4, Hg concentrations in various biota in different mining areas (µg kg^{-1} w.w.)

Name of mine	Sample description	Sampling Period	THg	MeHg	Reference
Almaden, Spain	Bivavle	1995-1997	1310 - 4100	980 - 3090	Berzas Nevado et al., 2003
Almaden, Spain	Roots of Local Plants	Unknown	30 - 1278000		Molina et al., 2006
Almaden, Spain	Fish of Valdeazogues River	2005-2006	0.8 - 8.6	0.8 - 8.2	Berzas Nevado et al., 2009
Almaden, Spain	Bivavle	2005-2006	10 - 110	3 - 19	Berzas Nevado et al., 2009
Almaden, Spain	Aerial part of lavender	2003-2006	30 - 550		Sierra et al., 2009
Idrija, Slovenia	Filamentous algae	Spring 2003	1380 - 6800	7.3 - 159	Zizek et al., 2007
Idrija, Slovenia	Periphyton	Summer, Autumn 2003	137 - 86100	2.48 - 458	Zizek et al., 2007
Sulphur Bank, USA	Carp from Clear Lake	1992-2004	50 - 660 (210)	95% THg	Suchanek et al., 2008b
Sulphur Bank, USA	Catfish from Clear Lake	1992-2004	70 - 1500 (470)	93% THg	Suchanek et al., 2008b
Sulphur Bank, USA	Largemouth bass from Clear Lake	1992-2004	30 - 1940 (290)	97% THg	Suchanek et al., 2008b
Wanshan, China	Rice irrigated by calcine downstream	Sep. 2000	10 - 710	8.4 - 120	Horvat et al., 2003
Wanshan, China	Rice irrigated by calcine downstream	Dec. 2006	3.2 - 220	0.8 - 28	Feng et al., 2008
Wanshan, China	Rice irrigated by calcine downstream	Unknown	10 - 1120	1.6 - 174	Qiu et al., 2008
Wanshan, China	Grass carp	Unknown	61 - 680	24 - 98	Qiu et al., 2009
Wanshan, China	Rice irrigated by calcine downstream	Mar. 2005	18 - 390	2.5 - 21	Li et al., 2009
Wanshan, China	Commercial rice on market	Mar. 2005	13 - 20	3.9 - 8.7	Li et al., 2009
Wanshan, China	Rice irrigated by calcine downstream	Aug. 2007	7.4 - 508	1.2 - 44	Zhang et al., 2010c

Table 2, Hg levels in calcine/sediment/soil in different mining areas (mg kg^{-1} d.w.)

Name of mine	Location	Sampling Period	THg	MeHg (μg kg^{-1})	Reference
Almaden, Spain	Calcine/Tailing	Jun. 2003	160 - 34000	<0.2-3100	Gray et al., 2004
Asturias, Spain	Calcine/Tailing	Unknown	14 - 2224		Loredo et al., 1999
Asturias, Spain	Calcine/Tailing	Unknown	2 - 1045		Loredo et al., 2003
New Idria, USA	Calcine/Tailing	Unknown	29.6 - 865		Gustin et al., 2003
Sulphur Bank, USA	Calcine/Tailing	Unknown	58 - 3310		Gustin et al., 2003
Sulphur Bank, USA	Calcine/Tailing	Unknown	18 - 1400		Nacht et al., 2004
Wanshan, China	Calcine/Tailing	Sep. 2000	78.9	22	Horvat et al., 2003
Wanshan, China	Calcine/Tailing	Nov. 2002	5.7 - 4400	0.17 - 1.1	Qiu et al., 2005
Wanshan, China	Calcine/Tailing	Unknown	1.8 - 650		Li et al., 2008b
Almaden, Spain	Sediment	1995-1997	5.5 - 1005		Berzas Nevado et al., 2003
Almaden, Spain	Sediment	Jun. 2003	935	3.0	Gray et al., 2004
Almaden, Spain	Sediment	2005-2006	0.44 - 74	2.4 - 881	Berzas Nevado et al., 2009
Asturias, Spain	Sediment	Unknown	58 - 70		Loredo et al., 2003
Idrija, Slovenia	Sediment	1991 and 1995	100 - 1000		Gosar et al., 1997
Idrija, Slovenia	Sediment	Unknown	0.13 - 1229		Biester et al., 2000
Idrija, Slovenia	Sediment	1991, 1995-1996	0.10 - 23.30		Covelli et al., 2001
Idrija, Slovenia	Sediment	2003	5 - 727	3 - 10	Zizek et al., 2007
Idrija, Slovenia	Sediment	1991, 1995, 2001, 2005	3.2 - 4121		Gosar 2008
New Almaden, USA	Sediment	Dec. 2000	0.1 - 1.2		Conaway et al., 2004
Sulphur Bank, USA	Sediment	2000	0 - 1200	0.1 - 3.5	Suchanek et al., 2008a
Sulphur Bank, USA	Sediment	1992 and 2003	<1.0 - 438		Suchanek et al., 2009
Wanshan, China	Sediment	Nov. 2002	90 - 930	3.0 - 20	Qiu et al., 2005
Wanshan, China	Sediment	Jun. 2008	1.1 - 480		Paper 1
Khaidarkan, Kyrgyzstan	Sediment	May 2008	3.5 - 217		Solberg, 2009
Almaden, Spain	Soil	Unknown	6 - 8889		Higueras et al., 2003
Almaden, Spain	Soil	Unknown	5 - 1710		Millan et al., 2006
Almaden, Spain	Soil	Unknown	0.13 - 2695		Molina et al., 2006
Almaden, Spain	Soil	Unknown	3.4 - 7315		Conde Bueno et al., 2009
Almaden, Spain	Soil	2003-2006	3.8 - 10.1		Sierra et al., 2009
Asturias, Spain	Soil	Unknown	1.7 - 472		Loredo et al., 1999
Asturias, Spain	Soil	Unknown	5 - 895		Loredo et al., 2003
New Idria, USA	Soil	Unknown	8.4 - 82		Gustin et al., 2003
Wanshan, China	Soil	Sep. 2000	8.10 - 156	1.3 - 23	Horvat et al., 2003
Wanshan, China	Soil	Nov. 2002	5.1 - 790	0.13 - 15	Qiu et al., 2005
Wanshan, China	Soil	Jun. 2008	8.0 - 130		Paper 1
Wanshan, China	Soil	Aug. 2008	0.29 - 311	0.14 - 12.1	Zhang et al., 2010c
Wanshan, China	Soil	Unknown	1.1 - 48		Li et al., 2008b
Khaidarkan, Kyrgyzstan	Soil	May 2008	0.4 - 52.3		Solberg, 2009

Heavily contaminated stream and lake sediments have been reported from several Hg mines worldwide (Table 2). For instance, THg concentrations in stream-sediment samples were as high as 1.0 g kg^{-1} at Almaden, Spain (Berzas Nevado et al., 2003) and 4.1 g kg^{-1} at Idrija Hg mine in Slovenia (Gosar 2008). THg in soil and sediment have a large range of concentration values which is mainly determined by their geographic locations relative to the point source. Soil and sediment collected immediately downstream of mines and their gangue tailings and retort calcine waste dumps inevitably contain more Hg.

MeHg content found in paddy soil is generally lower than that measured in calcine waste and stream sediments (Table 2). This may be due to that the sulfate in seepage from calcine retort tailings enhances methylation of Hg by sulfate reducing bacteria. MeHg concentrations in stream sediments were usually higher at shallow depth. This is likely due to that the redox gradient in the sediment/water interface is especially favorable environment for anaerobic bacteria methylating inorganic Hg to MeHg (Roulet et al., 2001; Ullrich et al., 2001).

4.3 Hg in air in mining areas

Literature values for Hg levels in air in mining areas are listed in Table 3. Generally, the longer time since the mine/calcination was closed, the lower is the ambient air Hg concentration. Typical air Hg concentrations range from less than 10 ng m^{-3} to around 10 000 ng m^{-3}. Hg in air over the Idrija region, where the world’s second largest Hg mine was located, decreased significantly over the last decades since the mine was closed in 1970s, from more than 20 000 ng m^{-3} in the early 1970s to values below 100 ng m^{-3} in the 1980s, and finally reached a level of 10 ng m^{-3} or even lower during the summer of 2004 (Kotnik et al., 2005). The values for Hg in air in Hg mining areas in China are much higher than those observed in northern Europe (1.8–2 ng m^{-3}) or Canada (1.3–1.8 ng m^{-3}) (Higueras et al., 2006; Wangberg et al., 2001).

Table 3, Hg concentrations in air in different mining areas (ng m^{-3})

Name of mine	Form of Hg	Hg	Flux (ng m^{-2} h^{-1})	Reference
Almaden	TGM	2 - 9485		Higueras et al., 2006
Almaden	TGM	0 - 3180		Gomez et al., 2007
Asturias, Spain	TGM	100 - 203700		Loredo et al., 2007
Idrija, Slovenia	TGM	2.5 - 2000	20.7 - 80.9	Kotnik et al., 2005
New Idria, USA	TGM	7.6 - 384	6 - 9600	Gustin et al., 2003
Sulphur Bank, USA	TGM	24.5 - 717	188 - 9499	Gustin et al., 2003
Sulphur Bank, USA	GEM	3.6 - 670	40 - 11000	Nacht et al., 2004
Wanshan, China	TGM	17.8 - 1102	162 - 27827	Wang et al., 2007

Ambient air concentrations of Hg and the dominating form of Hg are greatly affected by the distance to large point sources. Gosar et al. (2006) studied the percentage of cinnabar bound and non-cinnabar bound Hg in attic dust and soil and found that they decreased and increased, respectively, with the distance from the pollution source. Non-cinnabar fractions were found to be enriched in distant areas where fine grained material was deposited. Coarse grained particles which consist mainly of cinnabar-bound Hg, settled in the immediate vicinity of the smokestack of the smelter, whereas the fine grained fraction were dispersed further away. Gaseous Hg^0 is probably bound to fine and ultra fine aerosols with longer residence time in the atmosphere (Gosar et al., 2006).

The soil/air Hg flux show large spatial variation ranging from 20 to 80 ng m^{-2} h^{-1} in Idrija, Slovenia (Kotnik et al., 2005), up to 27 800 ng m^{-2} h^{-1} in Wanshan, China (Wang et al., 2007) (Table 3) . These fluxes are significantly greater than those reported for background sites: The range of Hg emission fluxes observed over the background soils in the Tahquamenon River watershed, in Michigan, USA, is 1.4-7.6 ng m^{-2} h^{-1} (Zhang et al., 2001). The mean flux in a deciduous forest of Sweden is 0.8-2 ng m^{-2} h^{-1} (Shroeder et al., 1989; Xiao et al., 1991).

4.4 Hg in biota in mining areas

Literature values for Hg levels in biota in mining areas are listed in Table 4. The Hg concentrations in fish in all mining areas showed elevated Hg concentration, many of which had MeHg concentration higher than FAO/WHO’s Codex Alimentarius Value of 0.5 mg MeHg kg^{-1} (FAO/WHO, 1995). It is noteworthy that the MeHg percentage found in Chinese fish are significantly lower than fish sampled from other areas, despite higher THg values in the fish; MeHg account for 90% of the THg in fish in Almaden, Idrija and USA, while the value for fish in Wanshan, China, is lower than 35%. There are several reasons for this difference. Fish used for human consumption in China is generally from fish farms and have therefore usually lower trophic level, less complicated food webs and are of younger age, resulting in a lower extend of bioaccumulation of MeHg. Zizek’s et al. (2007) documented the biomagnification through food chain by finding that the percentage of Hg as MeHg increased with trophic level from algae (0.5–1.3%), periphyton (1.6–8.8%) to macroinvertebrates (0.1–100%), which indicates active transformation, accumulation and magnification of MeHg.

Bioaccumulation factor (BAF) is the ratio between the concentrations in biota relative to the concentration in ambient medium (water or soil). The BAF values for MeHg in fish from Almaden area ranged from 3.6 to 4.6 (log units), suggesting a considerable bioaccumulation of MeHg in fish (Berzas Nevado et al., 2009). These values are similar to what is reported from other studies in a variety of aquatic habitats, including small and large lakes (Wayne et al., 1996; Gustin et al., 1994; Hines et al., 2000). No significant trends of change through time were found, although THg concentrations in water have decreased significantly at the studied sites. This suggests that MeHg levels in fish and bioaccumulation is governed more by other environmental factors than of the THg concentrations in the environment (Suchanek et al., 2008b).

Hg concentrations in rice were investigated in Wanshan, China. Generally there is not found any significant correlation between THg concentrations in rice and THg in the paddy soil in which it is growing (Zhang et al., 2010b), nor between THg and MeHg in soil and in rice. This clearly indicates that the uptake and retention of Hg in rice is influenced by a number of factors, of which the concentration of MeHg in soil may only be one, and not the most important, of the governing factors. THg concentrations in rice growing in polluted areas, such as Wanshan, are higher than the Chinese national standard for crop (20 μg kg^{-1} d.w.) (MOH, 2005).

BAF for MeHg in rice was 5.6 (range: 0.71-50) in the most seriously contaminated area, 6.9 (1.6-31) in the less-impacted area and 4.4 (0.9-11) at the control sites. Multiple regression analyses showed that the MeHg level and the organic matter content (OM) of the paddy soil in which the plant is growing were statistically significant factors ($P < 0.001$ for both) explaining the MeHg in the rice ($MeHg_{grain} = 1.35MeHg_{soil} + 2.0OM_{soil} - 2.5$) (Zhang et al., 2010c). MeHg in rice grain is present almost exclusively as CH_3Hg-L-cysteinate (CH_3HgCys), which is a complex that permits the transport of MeHg across the blood–brain and placental barriers. It should be noted, however, that cooking of rice effectively converts most, if not all, of the CH_3HgCys to other forms of MeHg, although the identity and toxicity of the degradation products remain unknown (Li et al., 2010b).

4.5 Hg exposure to human and its health implications

The toxicity effects of high doses of Hg on the central nervous and urinary systems have been known for decades. Literature values for Hg exposure levels in various mining areas are listed in Table 5. The joint FAO/WHO Expert Committee on Food Additives (FAO/WHO, 2003) lowered the Provisional Tolerable Weekly Intake (PTWI) of MeHg from 3.3 μg kg^{-1} b.w. per week to the current level 1.6 μg kg^{-1} b.w. per week. In 1997, the US Environmental Protection Agency (US EPA) set a new guideline for MeHg in the diet of 0.1 mg kg^{-1} b.w. day^{-1}) (US

EPA, 1997). In the absence of occupational exposure, human intake of Hg is dominated by two sources; dietary and amalgam dental fillings. The average concentration of Hg in fresh and marine fish is approximately 0.2 mg kg^{-1}. In practical terms this means that an average person weighing 60 kg can only consume approximately 30 g of fish per day (Mahaffey et al., 1997). Fish consumption is therefore generally believed to be the most important human exposure pathway, but rice consumption was found by Feng et al. (2008) to be another important source for MeHg exposure in China. Relatively recent studies substantiate this and document that rice is an import exposure pathway of Hg for populations which have rice as staple food (Feng et al., 2008; Li et al., 2009; Zhang et al., 2010d). Studies in Wanshan showed that intake of MeHg though eating rice was partly over the US EPA (0.1 μg kg^{-1} b.w. day^{-1}) standard and FAO/WHO standard (0.23 μg kg^{-1} b.w. day^{-1}). This means the consumption of rice in Wanshan poses certain health concern.

Table 5, Hg exposure in different mining areas (μg kg^{-1} b.w. d^{-1} of 60 kg person)

Name of mine	Exposure pathway	Sampling Period	THg	MeHg	Reference
Wanshan, China	400 g rice per day	Sep. 2000	0.053 - 1.2	0.05 - 0.96	Horvat et al., 2003
Wanshan, China	Common daily diet	Dec. 2006		0.013 - 0.214	Feng et al., 2008
Wanshan, China	600 g rice per day	Mar. 2005		0.025 - 0.209	Li et al., 2009
Wanshan, China	Rice	Aug. 2007		0.012 - 0.44	Zhang et al., 2010c

In mining areas occupational exposure through respiratory uptake may be more serious than intake through diet. Gomez et al. (2007) conducted a survey of mining workers and found that highest human exposure to Hg occurred during drilling, with values up to 2 260 ng Hg m^{-3} in air resulting in 2 194 μg Hg L^{-1} in urine and 374 μg Hg L^{-1} in blood. Furnace operation and cleaning were the tasks with the highest air concentration values during the processing of Hg, peaking up to 3 370 ng m^{-3}. Tratnik et al. (2009) found that THg in blood and urine in people living in the area of the former Hg mine in Idrija was significantly higher (median values 0.81 and 0.92 μg L^{-1}, respectively) than in the rural area (median values 0.63 and 0.38 μg L^{-1}, respectively), but did not differ significantly between the area of the former Hg mine and the urban area (median values 0.99 and 0.75 μg L^{-1}, respectively).

5. Design and implementation of this study

Hg contamination in the environment has been documented in different regions, though the processes governing mobilization, transportation and fate of Hg and Hg fractions in the environment are not well understood. Hg in water was fractionated into THg, DHg, RHg and

MeHg. Hg is bound to soil and sediment in various forms and to different constituents, representing different pools of Hg. The potential mobilization and transport of Hg in the environment is determined by governing factors acting upon these Hg pools. Information on major Hg fractions in soil and sediment is, therefore, required in order to assess efficient and sustainable abatement strategies and to predict the effect of future changes in the environment.

Fig. 5, Calcine tailing at Xiaxi headwater (left); *in situ* measurement at Xiaxi River

Three sampling campaigns were conducted to collect water, rice paddy soil and sediment samples along Xiaxi River in Wanshan Hg mining area. The sampling took place in September 2007, June 2008 and August 2008, which represented different flow regimes. Samples were analyzed in the laboratory and used as input parameters for modeling. Measurements *in situ* were also conducted during sampling, including the flow, rive geometry and site observation. Fig. 5 shows the view of the study area.

5.1 Sampling and data collection

Water samples were collected in acid pre-cleaned Teflon bottles. An unfiltered sample was stored in a 200 mL borosilicate glass bottle (for measurements of total Hg), and another sample was filtered *in-situ* with a 0.45 µm polyvinylidene fluoride filter (Millipore) (for measurements of DHg, and major cations and anions). The borosilicate glass bottles were rigorously pre-cleaned including baking for at least 45 min in a muffle furnace at 500 ˚C. During sampling the filtration equipment and sample bottles were rinsed three times with sample water prior to filling. All water samples, except aliquots for anion analysis, were preserved by adding 0.4% (v/v) of distilled ultrapure HCl within 24 h. Sediment samples were collected from streambed where possible. Soil samples were collected from rice paddy fields receiving irrigation water from the adjacent contaminated streams. Sample sites for soil, sediment and water do not necessarily coincide because of the erratic distribution of rice paddy fields and lack of fine sediment at some sites. All water, soil, sediment samples were collected twice at the same site during different hydrological regimes on Sep. 4, 2007 and Aug. 8, 2008.

Data of runoff intensity is needed in order to model the transport of Hg. This was modelled using GIS modeling tools with Digital Elevation Model (DEM, Fig. 6) data. Precipitation data were obtained from the nearest meteorological monitoring station (Tongren)[3]. The geometry of the stream is needed data for modeling hydrology. The bottom width, side slope and elevation of sampling sites were therefore measured *in-situ* by belt ruler and GPS.

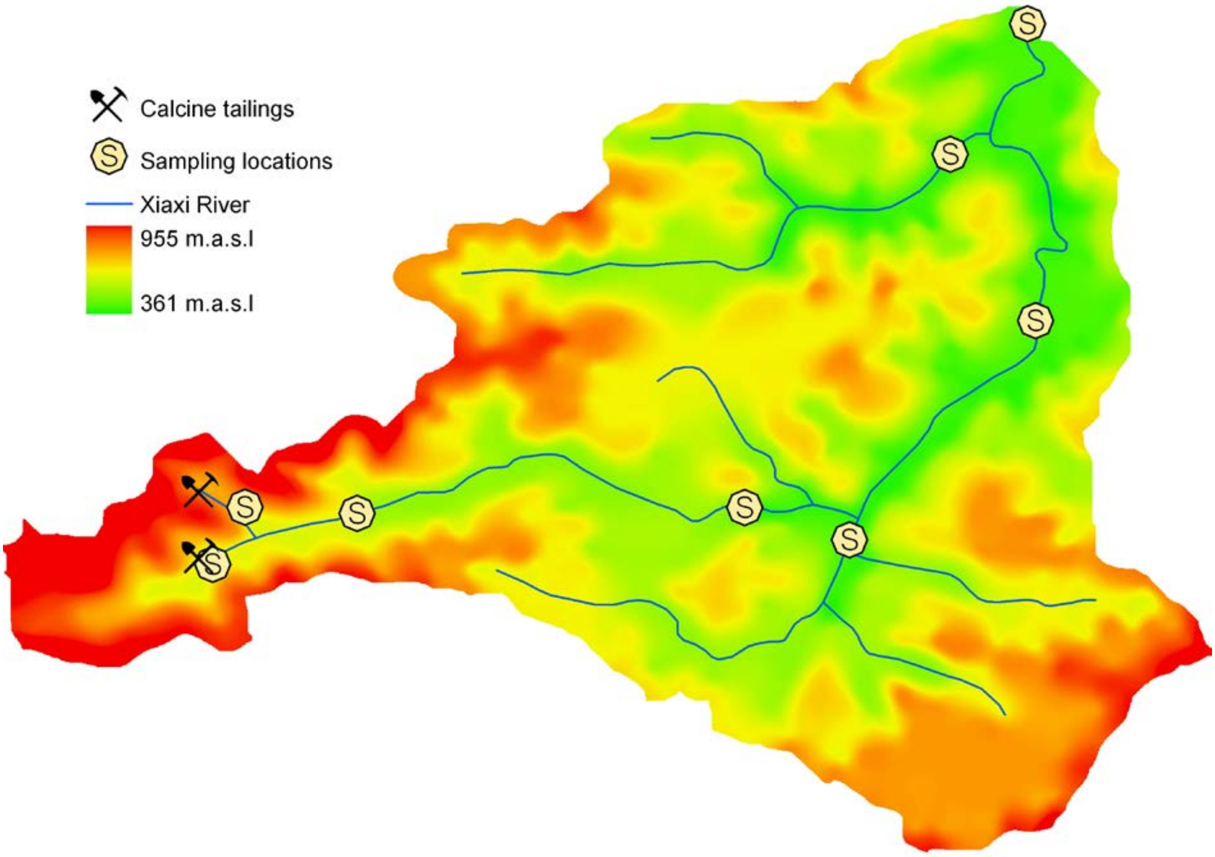

Fig. 6, Digital Elevation Model (DEM) of Xiaxi watershed, showing the tailings and sampling locations.

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[3] http://cdc.cma.gov.cn/

5.2 Analysis and instrumentation

Hg in water was fractionated into THg, DHg, RHg and MeHg. Hg in these fractions was determined using a dual stage Au amalgamation method and Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS) detection (USEPA, 1999). Reactive Hg was measured after $SnCl_2$ reduction. DHg and THg were determined following BrCl oxidation and $SnCl_2$ reduction. The particulate fraction (PHg) was obtained by subtracting DHg from the THg. Table 6 summarize the instruments and methods that have been used for analysis.

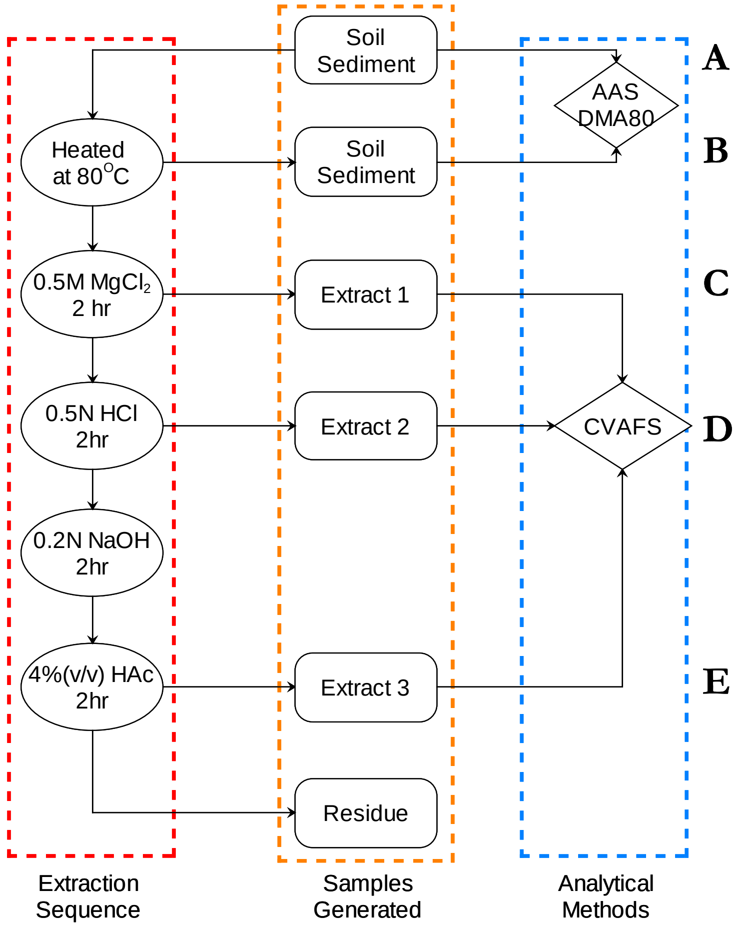
Table 6, Analytical instruments and methods for each parameter

Parameter	Type of sample	Instrument	Method
Hg	Water	PSA Merlin, England	USEPA Method 1631
Hg	Soil/Sediment	DMA 80	Atomic absorption spectrophotometer
MeHg	Water	Tekran	USEPA Method 1630
Particle size distribution	Water/Slurry	Coulter Counter	-
Major anions	Water	Ion Chromatography	ISO 10304-1:2007
TSS	Water	0.45 µm filter	Constant weight at 105˚C
TOC	Water	Tekmar Dohrmann Apollo 9000 HS	NS-ISO 8245

A sequential extraction technique for Hg in soil and sediment samples (Lechler et al., 1997) was modified and employed in this study (Paper 1). This modified procedure produced data on the following pools of Hg in soil and sediment: THg, elemental Hg, exchangeable Hg, strongly-bound Hg and organically-bound Hg. Fig. 7 shows the sequential extraction scheme. Hg in soil and sediment samples was extracted by five steps, including heating, and extraction with $MgCl_2$ solution, HCl, acetic acid and finally residue.

The different fractions of Hg are operationally defined and each fraction may be derived from several specific Hg compounds in the soils. The Hg in the extracted solution was analyzed by PSA Merlin CVAFS method. Analytical method used to determine other chemical and physical parameters are listed in Table 6.

The relative percent difference (RPD) on analyses of Hg on the CVAFS was assessed by analyzing blind duplicates. Furthermore, each sample was analyzed three times on each run to achieve an estimate of standard deviation (RSD). Both RPD and RSD of THg analysis were below 8%. Matrix spikes were used to calculate the percent recovery, which ranged from 92% to 110% for THg analysis. The limit of detection was 0.1 ng/L for THg in water samples. For DMA-80 analysis the RSD and RPD were below 15%. Samples with high Hg concentration were diluted using graphite; the upper limit for this method was 600 ng Hg. The lower limit of determination on the DMA-80 was 0.05 ng Hg.



A=Total Hg

A-B=Element Hg

C=Exchangeable Hg

D=Strongly-bound Hg

E=Organic Hg

B-C-D-E=Residue Hg

Fig. 7, Sequential extraction scheme for soil and sediment samples

5.3 Hydrological and Hg modeling tools

Visual MINTEQ[4] is a chemical equilibrium model designed by KTH (Royal Institutte of Technilogy, Sweden) for the calculation of metal speciation, solubility equilibrium, sorption etc. for natural waters. In this study, Visual MINTEQ was used to model Hg fractionation in the water environment.

The Geospatial Hydrologic Modeling Extension (HEC-GeoHMS) is a tool that uses ArcGIS Desktop and the Spatial Analyst extension to develop a number of hydrologic modeling inputs for the Hydrologic Engineering Center's Hydrologic Modeling System (HEC-HMS)[5]. By analyzing the watershed's digital elevation model (DEM), the HEC-GeoHMS model transforms the drainage paths and watershed boundaries into a hydrologic data structure that

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[4] Visual MINTEQ Homepage: http://www2.lwr.kth.se/English/OurSoftware/vminteq/index.html

[5] Homepage: http://www.hec.usace.army.mil/software/hec-hms/index.html

represents the drainage network. Once the drainage network and watersheds had been determined, the Hydrologic Modeling System (HEC-HMS) was applied to simulate the watershed's precipitation-runoff processes. Hydrographs produced by the HEC-HMS model were subsequently used as hydrological input data for the Hg transport modeling.

Water Quality Analysis Program (WASP)[6] was developed to simulate the transport and transformation of various water body constituents. Mass balance equations account for all material entering and leaving model segments through direct and diffuse loading, advective and dispersive transport, and any physical or chemical transformation. WASP Hg module (MERC7) is a subroutine within WASP for Hg simulation. It was developed to specifically compute Hg speciation and kinetic transformation. For this study, two species of Hg are modelled, inorganic Hg (Hg(II)) and MeHg. MERC7 is also capable of modeling three distinct solid types: silts and fines, sands and organic solids. Therefore, this study simulated dissolved fractions as well.

6. Main results and findings

6.1 Hg species and fractions in water

THg concentrations in the studied river during relatively high flow ranged between 3.8 ng L^{-1} and 2 100 ng L^{-1}, with a geometric average of 67 ng L^{-1} ($n = 24$). During low flow regime the maximum THg concentrations reached 1 200 ng L^{-1}, with a geometric average of 30 ng L^{-1} ($n = 24$). THg concentrations showed significantly higher concentration at relatively high flow ($p < 0.01$), while DHg concentrations did not show a similar pattern ($p = 0.960$). MeHg concentrations constituted less than 5% of THg concentrations in most water samples. The highest concentration of MeHg (11 ng L^{-1}) was found immediately downstream of the calcines deposits. Concentrations of MeHg reached higher levels during high flow, with values ranging between 0.09 to 11 ng L^{-1}, with a geometric average of 0.34 ng L^{-1} ($n = 22$). During low flow the maximum MeHg concentration reached 3.4 ng L^{-1}, with a geometric average of 0.36 ng L^{-1} ($n = 7$), which was similar to that of low flow. No significant difference was therefore found in MeHg concentration between the different flow regimes.

The main Hg fraction in all water samples is PHg due to that Hg is highly affiliated to particles. Speciation using Visual MINTEQ showed that the most important inorganic ligands interacting with Hg(II) in these surface waters are OH^-, Cl^- and CO_3^{2-}, though over 98% of

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[6] Homepage: http://www.epa.gov/athens/wwqtsc/html/wasp.html

dissolved Hg is complexed with dissolved natural organic matter (DOM) for all samples. The measured DOC and DHg concentrations also showed linear correlation (R^2=0.57, $p < 0.01$, n=12). $Hg(OH)_2$ is the dominant form of inorganic species when pH is above 7, while HgClOH and $HgCl_2$ dominate when pH is below 7.

6.2 Hg pools in rice paddy soil

THg content in the rice paddy soil samples ranged from 8.0 to 130 mg kg^{-1}. Levels of THg in soil collected in rice paddy fields did not show a consistent spatial trend downstream from the main Hg mine tailings as could be expected based on the Hg levels in stream water and sediments. Irrigation practices may explain this inconsistency as many local farmers do not use water from the main Hg contaminated rivers during periods of high flow because they then have access to uncontaminated water from tributaries. The farmers are aware of the high Hg loadings in the main stream and therefore avoid using the contaminated water when possible. During dry periods, however, they are dependent on the water from the Hg contaminated streams. Hg loading in the stream is then usually lower due to less particle transport.

Sequential extraction results showed that exchangeable (11–35%), strongly-bound (18–38%) and residual Hg (25–46%) were the main Hg pools in the rice paddy soils. In most paddy soil samples elemental Hg accounted for less than 10% of the THg, but was significant at sites with significant point sources; e.g. calcines tailings and artisanal smelters still in operation. The fraction of organically bound Hg was 1–9% of the THg in rice paddy soil. The exchangeable Hg fraction in soil increased downstream from the large tailings and streams receiving seepage from tailings with sedimentation ponds had higher fraction of exchangeable Hg. The reason for this might be that coarser Hg-bearing particulates (such as cinnabar) are deposited in the pond, while smaller particles are suspended in the water and may escape the ponds and be transported further downstream. These finer particles preferentially absorb Hg as a result of inherent larger surface area and higher exchange capacity. The organic content of the soil samples was relatively low and results showed that the fraction of soil organically-bound Hg was of less importance compared to the exchangeable and strongly bound Hg fractions. No significant correlation between the fraction of organically-bound Hg and the organic content of the soil was found. Most of the residual Hg in the soil samples is cinnabar that has entered the stream as particulates due to erosion from the calcines and mine tailings.

6.3 Hg pools in stream sediment

Concentrations of THg in stream sediment samples ranged from 1.1 to 480 mg kg^{-1}, with a strong spatial relationship to the upstream location of large Hg tailings piles. Sequential extraction results showed that exchangeable (9–43%), strongly-bound (11–67%) and residual Hg (4–82%) were the main Hg fractions in most sediment samples. The THg levels in sediments were generally higher than that in rice paddy soil samples. The elemental Hg fraction in the stream sediment samples generally accounted for less than 6% of the THg, except for stream sediment collected close to retorts and tailings. Relative amounts of the elemental Hg fraction found in stream sediment was usually lower than that in soil, which may be due to stream flow transporting cinnabar particles, especially during high flow, increasing the residual Hg fraction. The fraction of organically-bound Hg was generally less than 5% of the THg in the sediments. Similar to soil samples, the exchangeable and strongly-bound Hg fractions in stream sediment were the dominant Hg fractions. Exchangeable Hg is more easily mobilized and transported downstream. The organically-bound Hg in sediment samples was lower than that found in soil samples. The reason for this is likely the slightly higher organic matter content in rice paddy soil samples, though there was no significant correlation between organically-bound Hg and the amount of organic matter in soil.

6.4 Modeling of Hg transport

Daily precipitation was used to model Xiaxi river flow from September 2007 to August 2008. Most precipitation occurred in a limited number of storm events, especially during the rainy season (Jun-Aug) when the sum of precipitation account for 48% of total annual amount. This is typical for the region, where rainfall is controlled by monsoon climate. During the dry winter season (Oct-Dec) flow dropped below 1 m^3 s^{-1} before increasing in the beginning in February. There were three distinct high flood events during the summer months (Jun. 8, Jul. 7 and Aug. 11), with the highest flow occurring on Jun. 8, 2008, reaching 35 m^3 s^{-1}.

According to the WASP model the concentration of TSS decreases within short distance downstream of the tailings and was significantly higher during high flow period compared to low flow period. The majority of particles were released during high flow events. TSS concentration increase with increasing water flow due to both soil erosion (from the river banks and the flood plain) and sediment re-suspension. The total amount of solids released annually was estimated to be 59 tons. The three sampled high flow events in summer were used to calculate the contribution of high flow events to particle transport. The total amount of solids released during these events was 23%, 5% and 6% of the annual total. Comparing modelled TSS concentrations with the observed values showed that the average modeling error for the TSS was 11% and 2.5% respectively for Sep. 4, 2007 and Aug. 8, 2008 sampling campaigns.

Concentrations of Hg fractions in the water (THg, DHg and MeHg) were also modeled by WASP. The modeled results coincided well with the measured values. The model gave relatively reasonable results for THg, DHg and MeHg, with relative error <10%.

The annual total input of Hg to the stream was estimated by the model to be 8.8 kg Hg, while total release of Hg at the end of the modelled river stretch was 2.6 kg Hg. About 70% of Hg was therefore estimated to be retained in the stream, mainly through sedimentation. The contribution of the three high-flow events described above was significant. The discharge of THg during these events accounts for 37%, 6% and 8% of total annual release of Hg, respectively. The sum of the three high flow events was therefore responsible for about 50% of the annual THg release.

7. Discussions

Heavily Hg contaminated water is produced during Hg mining activities as well as after closure of the mines. Leachate from Hg mine tailings and smelting residues (calcine) flows into nearby water bodies and may cause serious Hg pollution to the local environment.

Results from Wanshan mining area showed large temporal and spatial variation in THg concentrations in water. The THg concentrations in river water were 19 – 12 000 ng L^{-1} at high flow season while at low flow season the concentrations were 25 – 1200 ng L^{-1} (all five rivers in Wanshan, Fig. 4, Zhang et al., 2010a). The maximum THg concentration (2 100 ng L^{-1}) in Xiaxi stream water (this study) was lower than that recorded at Gouxi (12 000 ng L^{-1}) and Huangdao (3 200 ng L^{-1}) (Zhang et al., 2010a). The reason is likely that there were still running artisanal smelters along Gouxi during the sampling, and those smelters dumped their calcines wastes along the Gouxi River. The high concentrations in the Huangdao River are postulated to be due to a flood event in the year before the sampling that flushed out considerable amount of sediments into the downstream of Huangdao River. The results for Xiaxi river, reported in this study, is also lower than a previous study at Xiaxi River which documented highest THg to be 10 580 ng L^{-1} (Horvat et al., 2003). This can be explained by the shutdown of mines and implementation of strict regulation on artisanal smelting.

Although the THg concentrations are very high immediately downstream of tailings, the concentrations decrease very fast. This indicates that the leaching of tailings is a major source of Hg. The THg concentrations decreased to below 50 ng L^{-1} (Class I in Chinese surface water standard, SEPA 2002) within 10 km away from the tailing (Paper 1, Zhang et al., 2010a). The results are similar to other studies conducted at Sulphur Bank Mine, USA (Suchanek et al., 2009) and Carson River, Nevada, USA (Carroll et al., 2000). The concentration of THg in waters sampled upstream of the tailings ranged between 12 – 53 ng L^{-1} (Zhang et al., 2010a). This is close to the background values measured in tributaries draining side-valleys with no mining activities. The natural background concentration of water in the Wanshan area is 14 (1.0–69) ng L^{-1} (Paper 2). This is higher than the global background concentration for natural fluvial systems (0.10–20 ng L^{-1}) (Louis and Chamberland, 1995).

Concentrations of MeHg in surface waters ranged between 0.09 to 11 ng L^{-1}, with a geometric average of 0.34 ng L^{-1} in this study. This is comparable to studies conducted at Almaden (Gray et al., 2004), Idrija (Hines et al., 2000) and previous study at Wanshan (Li et al., 2008b). The highest MeHg concentrations were found in drainage from tailings, which is also found in other studies at mining areas. This suggests that calcine tailings are important sources of MeHg to the downstream environment (Zhang et al., 2010b).

It should be noted that water samples only represent snap-shot information under the particular hydrological conditions during the time of sampling. High concentration of Hg is likely due to leaching of calcines from retorted ore as well as high flow conditions during which increased PHg was flushed into the stream. The comparison of different studies cannot reflect the hydrological conditions, there is therefore certain inaccuracy of the comparison.

Studied sites for modeling Hg transport in mining areas usually have a well defined point source of Hg (from Hg mining or smelting in historic times). Leachate from these mine sources contains both particulate and dissolved Hg. But the leachate from different mines has different chemical characteristics. Mine tailing leachate in Wanshan, China and Nevada, USA have an alkaline environment (pH bigger than 7.5), but the pH of leachate from Sulphur Bank Mine in USA is lower than 7. The acid environment usually contains higher DHg fraction (Ullrich et al., 2001). The proportion of DHg in Clear Lake, which receives water from

Sulphur Bank Mine, is higher than that in Wanshan and Carson River. Due to higher suspended particles at high flow, the proportion of PHg is usually higher in the rainy season (Paper 3). This has been confirmed by other research as well (Suchanek et al., 2009).

The modeling of Hg transport in this study shows that that 70% of Hg is retained in the river through sedimentation. Mass balance budget studies of lakes usually also show that a high proportions of Hg that is retained. For example, the fraction that is retained in the Clear Lake is 98% (Suchanek et al., 2009). This is mainly due to the fact that lakes have low flow velocity and weak turbulence favoring sedimentation of particles. Although our modeling gives fairly good simulation results, the process can still be improved through including the air/water Hg exchange. In our current modeling process, atmospheric deposition and evasion from water are not accounted for. The air/water flux usually represents a minor fraction compared with particulate and dissolved phase (Feng et al., 2004; Suchanek et al., 2009), but where the concentrations have decrease downstream due to sedimentation of particulate Hg, the air/water Hg exchange may become relatively more important.

Soils in mining areas are usually heavily polluted due to mining activities. Topsoil usually contains relative high Hg concentrations due to high deposition of airborne Hg from the Hg smelter, especially artisanal smelters which have almost no emission control facilities. Studies at Wanshan found elevated THg concentrations in topsoil, but the concentrations decrease with depth. This indicates that the atmospheric deposition is the main reason for the high THg in topsoil (Li et al., 2008b). MeHg and THg in soil usually do not have significant correlation (Feng et al., 2008). The maximum THg concentration (130 mg kg^{-1}) in paddy soils in Wanshan, investigated in this study, was lower than the highest concentrations found in soil at both Almaden, Spain (8 889 mg kg^{-1}) and Idrija, Slovenia (420 mg kg^{-1}) (Higueras et al., 2003; Kocman et al., 2004). The highest concentration of Hg in Wanshan soil was found 4 km downstream from a major tailings pile at Xiaxi. The level of Hg contamination in paddy soils found in this study was generally lower than that documented in a previous study (Qiu et al., 2005).

The concentration of THg found in stream sediment in Wanshan was higher than in the soils and higher than the probable effect concentration (1.06 mg kg^{-1}), the Hg concentration above which harmful effects are likely to be observed in sediment dwelling organisms (MacDonald et al., 2000). The reason for the higher concentrations of THg in stream sediment samples than in soils is probably because sediment runoff is derived directly from upstream calcines and tailings. However, the maximum THg concentration (480 mg kg^{-1}) in these sediment samples was lower than that reported for Hg mine studies at both Almaden, Spain (1 000 mg kg^{-1}) and Idrija, Slovenia (1 000 mg kg^{-1}) (Berzas Nevado et al., 2003; Gosar et al., 1997).

Hg fractionation in soil and sediment has previously been carried out at Idrija, Slovenia, and Almaden, Spain (Biester et al., 2000; Bernaus et al., 2006). These studies revealed that Hg in the local environment is mainly found as cinnabar (HgS), accounting up to 89% of the THg in soil samples (Biester et al., 2000; Bernaus et al., 2006). Acid-soluble Hg is the second most abundant pool, indicating that Hg may be mobilized under more acidic conditions (Bernaus et al., 2006). A large part of this acid-soluble Hg fraction may be bound to organic matter (Higueras et al., 2003) in soil with high contents of organic matter. This study showed that the strongly-bound Hg (acid soluble in Bernaus' et al (2006) study) accounts for 20% – 40% of the total Hg, which is also the second largest fraction after residual Hg (mainly HgS). The HgS fraction (up to 82% of total) in this study is slightly less than what is found in studies in Almaden and Idrija. The organic fraction is usually low as there is almost no organic Hg found in sediment. Organic Hg in rice paddy soil is a bit higher compared with that in sediment, but is still less than 5% of total (Paper 1).

In order to reduce the release of Hg to the environment, large scale remediation work has been implemented at many mining area, including Wanshan Hg mining area. The remediation efforts include covering the tailings, adding drainage ditches and building sedimentation pond. Artisanal retorting has also been strictly regulated. This may explain the lower concentrations of THg in water in the Xiaxi river collected in this study compared to previous studies at the same site in 2002 (Horvat et al., 2003). At Sulphur Bank mine the THg in sediment did not show significant decrease after remediation (Suchanek et al., 2009). This difference is most likely related to the more acid environment at the Sulphur Bank mine which allows for more dissolved Hg species to exist in runoff. The THg concentration is thus less related to PHg from erosion of tailings. Remediation options must therefore consider both solid phase Hg bound to sediments and particles as well as dissolved Hg which may dominant in acid mine drainage. The covering of tailing may generate anaerobic conditions which may be favorable for methylation. It is therefore necessary to access the potential impact on MeHg changes as well since MeHg is more of a concern due to its toxicity and bioaccumulation through food web.

8. Conclusions

The levels of Hg in soil, sediment and water in Wanshan were generally high due to long-term and continued release from mining-related Hg contaminant sources. Concentrations of THg in stream sediment were much higher than that of rice paddy soil due to direct runoff from mine gangue and tailings of calcines from the retorting of Hg ore. The main form of Hg found in the slightly alkaline rivers was bound to particles. Concentrations of THg in the streams are therefore higher during high runoff periods due to that more suspended solids are eroded and re-suspended. Hg concentrations decreased within short distance downstream of the contamination point source. Sedimentation of suspended solids is the main mechanism for this initial fast decline. Sediment transport is more important during higher flow regime due to that the river then can carry a larger loading of suspended particles.

Hg(II) associated with DOM is the main form of DHg (over 98%), despite very low DOC concentrations. Hg adsorbed to Fe oxyhydroxide generally dominate the forms of Hg on suspended particulate matter, while co-precipitation of Hg on calcite is the main reason for decline of THg concentration at places where precipitation of calcite was observed.

Pools of Hg in soil and sediment, determined by a sequential extraction method, indicated that the Hg in contaminated soil were mainly exchangeable-, strongly-bound- and residual Hg. The exchangeable Hg pools are related to the presence of more soluble Hg compounds, and therefore, pose a greater potential for Hg mobilization. The amount of elemental Hg was only significant at sites with recent or active artisanal retorts. The organically-bound pool of Hg in the soil and sediments was generally low for most samples. Rice paddy soil samples contained a higher organically-bound Hg fraction than that of sediment samples.

A modeling method was successfully developed to simulate the Hg transport at places where there exists no routine hydrological monitoring. The GIS based hydrological model HEC-HMS was applied to simulate fluctuations in stream flow based on precipitation data. This method addresses the problem of a lack of flow data as an input to transport models. The hydrological model was coupled with the Hg fractionation model WASP in order to predict Hg transport and concentrations at different parts of the river at different flow regimes. Compared to measured values the model produces reasonable simulation results for TSS, THg, DHg and MeHg, with relative errors generally around 10%. The modeling results show that high flow events are the main contributors for release of both suspended particles and Hg. Three high flow events during the modelled summer accounted for about 50% of annual release of THg. The annual total input of Hg was 8.8 kg Hg high up in the stream and 2.6 kg was released out of the stream where the stream meets a large river 20 km downstream of the pollution source. Hence, about 70% of Hg is retained in the stream through sedimentation.

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