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RESEARCH ARTICLE

Health and ecological risk assessment of heavy metals pollution in an antimony mining region: a case study from South China

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Abstract In recent years, international research on the toxicity of the heavy metal, antimony, has gradually changed focus from early medical and pharmacological toxicology to environmental toxicology and ecotoxicology. However, little research has been conducted for sources identification and risk management of heavy metals pollution by long-term antimony mining activities. In this study, a large number of investigations were conducted on the temporal and spatial distribution of antimony and related heavy metal contaminants (lead, zinc, and arsenic), as well as on the exposure risks for the population for the Yuxi river basin in the Hunan province, China. The scope of the investigations included mine water, waste rock, tailings, agricultural soil, surface water, river sediments, and groundwater sources of drinking water. Health and ecological risks from exposure to heavy metal pollution were evaluated. The main pollution sources of heavy metals in the Yuxi River basin were analyzed. Remediation programs and risk management strategies for heavy metal pollution were consequently proposed. This article provides a scientific basis for the risk assessment and management of heavy metal pollution caused by antimony basin ore mining.

Keywords Heavy metal · Antimony · Arsenic · Health risk · Risk management · Pollution remediation

Introduction

Antimony (Sb) is a metalloid belonging to group 15 of the periodic table and often considered to behave similarly to arsenic (Casiot et al. 2007; Wilson et al. 2010). Antimony compounds were originally used for their high medicinal value in the treatment of cholera, schistosomiasis, and leishmaniasis (He et al. 2012) in the fourteenth century AD. In the nineteenth century, antimony was found to have multiple applications such as in bleaching, flame retardation, and catalysis. Thus, antimony is widely used in glass decolorants, flame retardants, catalysts, alloy hardeners, enamels, lead-acid batteries, and other industries (Wu et al. 2011).

Antimony and its compounds are considered to be hazardous to human health or even carcinogenic (Gebel. 1997; Hammel et al. 2000; Jiang et al. 2010). Antimony exposure pathways include inhalation, ingestion, and dermal contact, resulting in acute toxic effects on the skin, eyes, lungs, intestines, stomach, liver, kidney, and heart (Chai et al. 2016; Mubarak et al. 2015). Antimony also has chronic toxic effects on the respiratory system, the cardiovascular system, and the kidneys, as well as being a potential human carcinogen (Rawcliffe 2000). The average antimony content in the human body is 0.1 μg/g. Excessive use of antimony-containing drugs has significant toxic effects on the human body. For example, excessive use of sodium antimony gluconate can lead to acute liver poisoning and promotes the replication of HIV-1 (Barat et al. 2007; Tschan et al. 2009).

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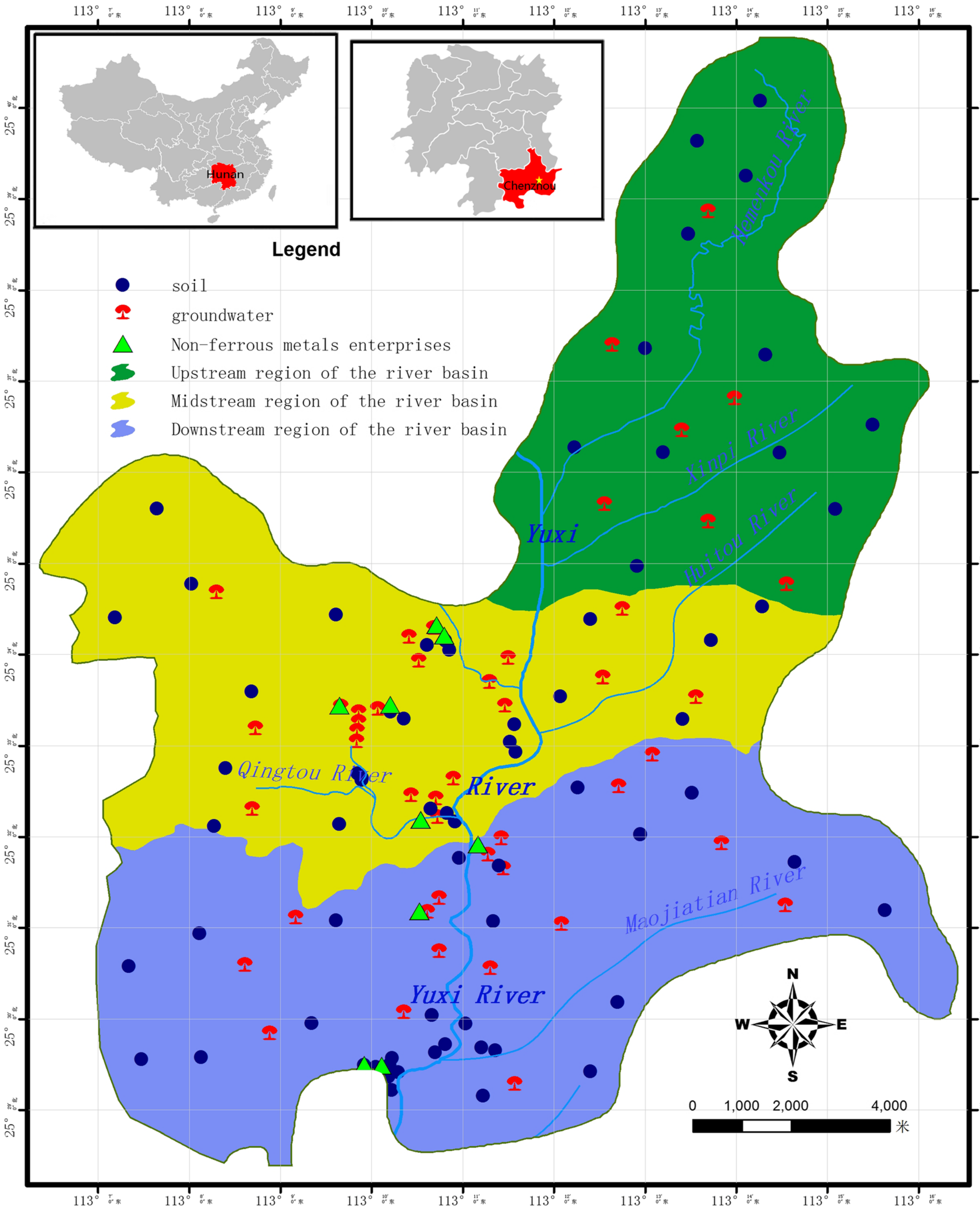

Fig. 1 Site location and distribution of sampling points

Apart from natural sources, antimony pollution is mainly due to mining, smelting, coal combustion, and antimony-containing products, of which mining and smelting are the most important sources (Filella et al. 2002; Wilson et al. 2004). Currently, there are approximately 114 antimony ore businesses in China, mainly distributed over 18 provinces and autonomous regions such as Guangxi, Hunan, Yunnan, and Guizhou (He et al. 2012). The annual consumption of antimony in major world countries averages between 120 and 150 thousand tons. Consumed antimony compounds are eventually abandoned in the environment, producing antimony pollution (Kentner et al. 1995).

Antimony pollution has become the focus of attention of several countries and international organizations (Ettler et al.

Table 1 Reference doses (RfDs) for health risk assessment [*mg*/(*kg* · *d*)]

Element	Zn	As	Sb
RfD	0.3	3×10^{-4}	4×10^{-4}
Reference	(USEPA 2012b)	(USEPA 2012b)	(USEPA 2012b)

2007; Maher 2009). For example, antimony and antimony compounds have been listed as priority pollutants by the United States Environmental Protection Agency (Reisman 1991) and the European Union (Filella et al. 2002). The "Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and Their Disposal" (1989) classified antimony as a hazardous waste to limit antimony pollution resulting from transport across national boundaries. With the widespread use of antimony products and increased public perception of antimony toxicity, the environmental and health risks caused by antimony mining, smelting, and use has elicited greater concern. Consequently, toxicity studies on antimony have gradually changed focus from early medical pharmacy toxicology to recent environmental toxicology and ecotoxicology (Gebel et al. 1997). One of the important goals of environmental toxicology and ecotoxicology studies is the formulation of the exposure risks of natural pollutants. However, little research has been conducted for sources identification and risk management of heavy metals pollution by long-term antimony mining activities (Commission E 1998; De Wolff 1995; Mccallum 2005).

Hunan is the famous "hometown of non-ferrous metals" in China. Over the years, Hunan's wastewater discharges for antimony and heavy metals such as lead, zinc, and arsenic have been the highest in the country (Dai et al. 2015; Lei et al. 2017; Li et al. 2016; NBSC 2011). Non-ferrous mineral resources are particularly rich in the Yuxi River in Chenzhou City, Hunan province, which has a long mining history. In the 1990s, non-ferrous illegal mining burgeoned under the auspices of the "Making Water Run Faster" initiative for economic recovery. Random mining and excessive digging produced mine water, waste rock, and mine tailings from historical mining, river sediment, and abandoned smelters, which have all become important sources of pollution in the basin. The river basin was severely flooded in June 2011 due to continuous heavy rain. The ore slag (waste) from several coastal antimony ore enterprises was swept into the river, producing a sudden and abnormally high concentration of antimony in the surface water of the downstream basin.

This paper reviews a large number of investigations that were conducted on the temporal and spatial distribution of antimony and related heavy metal contaminants such as lead, zinc, and arsenic in the mine water, waste rock, tailings, agricultural soil, surface water and sediments of rivers, and groundwater, as well as on public exposure to pollution in the Yuxi River basin in Hunan province. These investigations were used to evaluate health exposure risks and ecological risks from the heavy metal pollution of the basin. The main sources of pollution were analyzed. Remediation programs and risk management strategies for heavy metal pollution were consequently proposed.

Materials and methods

Area studied and sample collection

The Yuxi River is located in Yizhang County, Hunan province, China. The river is the northern source for the Zhujiang River basin. The geographic coordinates of the county are longitude 112° 37′ 35″–113° 20′ 29′ and latitude 24° 53′ 38″–25° 41′ 53″. The county has a total area of 2142.72 km^2 and a population of 585,000. Yizhang is mainly mountainous with auxiliary hills, plains, and low-lying land. The climate is classified as subtropical monsoon. The Yuxi River that flows through Yizhang County is 18.2 km long, with a drop height of 120 m and an average slope of 9.3%. The drainage basin has an area of approximately 100 km^2. The annual mean runoff totals 121 million cubic meters. Flow and sediment transport are important in relation to several engineering topics, e.g., contaminants transport. The annual average flow is 3.85 m^3/s. The sediment concentration is 2.37 kg/m^3. The annual average sediment transport capacity is 287,750 tons.

Table 2 Default factors in health risk assessment for heavy metals in drinking water

Parameter	Symbol	Units	Adult value	Child value	Reference
Body weight	BW	kg	58.6	22.3	(Chai et al. 2010; Ministry of Health. 2007)
Exposure duration	ED	Years	58	10	(Ministry of Health. 2007)
Exposure frequency	EF	Day/year	365	365	(USEPA 2008)
Averaging time	AT	Day	365 × 58	365 × 10	(Ministry of Health. 2007; USEPA 2008)
Daily water intake	IR	L/(person/days)	2.2	1.8	(Chen et al. 2008)

Table 3 Default factors in health risk assessment for soil heavy metals

Parameter	Symbol	Units	Adult value	Child value	Reference
Body weight	BW	kg	58.6	22.3	(USEPA 2012a)
Exposure duration	ED	Year	42	10	(NBSC 2011)
Averaging time	AT	Day	365 × 42	365 × 10	(USEPA 2012a)
Exposure frequency	EF	Day/year	243	350	(Cheng and Nathanail 2009)
Conversion factor	CF	kg/mg	10^{-6}	10^{-6}	(USEPA 2012a)
Ingestion rate of soil particle	I_{sp}	mg/day	100	91	(Calabrese. 2001; USEPA 2012a)

In this study, mine water samples were collected from Yuxi basin, along with samples of waste rock, tailings, agricultural soil, surface water, river sediments, and groundwater sources of drinking water. The surface water and groundwater samples were collected quarterly (January, April, July, and October), and others were sampled only twice (January and July). The sampling points of mine water, waste rock, and tailings were set around the enterprises in Fig. 1. The surface water and river sediment samples were collected along the rivers, about one sampling point per kilometer.

Surface soil samples (0–20 cm) were collected using a global positioning system (GPS) to identify the locations. In mining- and industry-impacted areas, sampling density was one sample per 1 km^2, whereas in forest and agricultural land, sampling density was one sample per 2 to 3 km^2. The moisture soil samples were air-dried and sieved (< 0.15 mm) to determine the content of heavy metals. Some of the sampling sites are shown in Fig. 1.

Sample analysis

All the soil, sediment, and tailing samples were air-dried and sieved (< 0.15 mm), and then stored in a Kraft envelope (Zheng 2004). Three hundred milligrams of soil sample was weighed and placed in a Teflon crucible, to which 10 mL of 68% nitric acid, 5 mL of 1:1 sulfuric acid, and 5 mL of 47% hydrofluoric acid were added. The crucible was placed on an electro-thermal plate at a temperature of 230 °C and heated until the solution turned gray (Wang et al. 2010). The solution was cooled slightly, after which 3 mL 1:1 HCl was added to dissolve and digest the residue. The digestion solution was then transferred to a 50-mL volumetric flask, to which 5 mL of 10% ammonium chloride solution was added. Deionized water was then added to bring the total volume of the solution up to the required volume. The solution was filtered, and the total antimony concentration in the solution was measured using ICP-MS. The antimony concentrations in the surface water and groundwater were measured by graphite furnace atomic absorption spectrometry.

Geostatistical analysis

Geostatistics has a very wide range of applications. It can be used to study the structure and randomness of spatially dependent data, spatial correlations, and spatial variation patterns, as well as for data processing as in the optimizing unbiased interpolation for spatial data and simulating discretization and volatility in spatial data. Geostatistics consists of two main components: variogram analysis for spatial variability and structure and related parameters, and Kriging interpolation for local space estimation. Kriging has been widely applied

Table 4 Relationship between E_r^i and the level of ecological risk

Single metal threshold	Risk factor classification	Multiple metal threshold	RI classification
$E_r^i < 40$	Minor ecological risk	RI < 100	Slight risk
$40 \leq E_r^i < 80$	Moderate ecological risk	100 ≤ RI < 200	Medium risk
$80 \leq E_r^i < 160$	High ecological risk	200 ≤ RI < 400	High risk
$160 \leq E_r^i < 320$	Very high ecological risk	RI ≥ 400	Severe risk
$E_r^i \geq 320$	Extremely high ecological risk		

Table 5 Heavy metal concentrations in the midstream and downstream regions of the Yuxi River basin

Location	Item		Pb	Zn	As	Sb
Midstream region	Mine tailings (mg/kg)	Number	56	56	56	56
		Mean	728.92	130.53	97.73	3165.83
		Minimum	509.12	99.65	89.42	3812.52
		Maximum	910.25	150.68	106.33	2891.18
	Waste rock (mg/kg)	Number	60	60	60	60
		Mean	3074.02	971.11	107.74	803.56
		Minimum	2756.22	761.25	89.58	69.23
		Maximum	3589.67	112.36	132.26	97.12
	Farmland (mg/kg)	Number	50	50	50	50
		Mean	70.6	276.1	26.9	53.1
		Minimum	66.2	198.4	19.2	48.2
		Maximum	79.6	294.1	29.3	57.6
	River sediment (mg/kg)	Number	20	20	20	20
		Mean	1877.40	482.70	57.81	180.85
		Minimum	1652.25	395.12	62.36	210.37
		Maximum	1963.32	502.36	48.25	162.59
	Mine water (mg/L)	Number	20	20	20	20
		Mean	ND	ND	ND	266.33
		Minimum	ND	ND	ND	26.25
		Maximum	ND	ND	ND	717.49
	Surface water (mg/L)	Number	88	88	88	88
		Mean	ND	ND	0.00034	0.9646
		Minimum	ND	ND	0.00010	0.0020
		Maximum	ND	ND	0.00045	2.5040
	Ground water (mg/L)	Number	92	92	92	92
		Mean	ND	ND	ND	0.1991
		Minimum	ND	ND	ND	0.0020
		Maximum	ND	ND	ND	0.7800
Downstream region	Mine tailings (mg/kg)	Number	40	40	40	40
		Mean	84.73	63.78	35.41	9153.25
		Minimum	52.14	45.89	12.36	726.12
		Maximum	99.65	86.79	79.27	11,000
	Waste rock (mg/kg)	Number	50	50	50	50
		Mean	194.90	108.20	32.10	865.63
		Minimum	162.02	65.29	10.23	698.25
		Maximum	221.36	125.69	120	983.36
	Farmland (mg/kg)	Number	60	60	60	60
		Mean	50.7	293.9	24.3	34.4
		Minimum	25.37	125.01	10.26	12.26
		Maximum	65.36	326.53	29.52	41.03
	River sediment (mg/kg)	Number	20	20	20	20
		Mean	32.40	80.90	39.97	9.24
		Minimum	19.65	102.36	53.23	2.36
		Maximum	39.53	73.01	21.58	13.25
	Mine water (mg/L)	Number	20	20	20	20
		Mean	ND	ND	0.0168	0.426
		Minimum	ND	ND	0.0018	0.200
		Maximum	ND	ND	0.0317	0.661
	Surface water (mg/L)	Number	60	60	60	60
		Mean	ND	ND	0.0009	0.0907
		Minimum	ND	ND	0.0003	0.0020
		Maximum	ND	ND	0.0014	0.1655
	Ground water (mg/L)	Number	72	72	72	72
		Mean	ND	ND	ND	0.2156
		Minimum	ND	ND	ND	0.0020
		Maximum	ND	ND	ND	0.3906

ND not detected

because of its unbiased character and advantages in geostatistical techniques relative to other methods (e.g., the inverse distance weighted method, IDW) (Tavares et al. 2008). For this reason, the Kriging method was used in the spatial analysis of the environmental risks of heavy metals in soil and groundwater.

Detailed algorithms of geostatistical theory and kriging methods have been found in many textbooks and monographs (Saito and Goovaerts 2000; Webster and Oliver 2001).

Health risk assessment methods

Humans and animals can come into contact with heavy metals in the environment in a variety of ways, such as through ingesting drinking water and food (Wang et al. 2011a), dermal contact (Wang et al. 2011b), and inhalation (Wang et al. 2010). Children and mining workers are the critical receptors in this area. The main characteristics of the exposure scenarios are the local people generally drink high concentrations of antimony-containing surface water and groundwater, and the content of antimony in farmland soil is high, and the risk cannot be neglected. A human non-carcinogenic health risk assessment from ingestion of drinking water and soil exposure vectors (i.e., dermal contact with soil and dust, inhalation, and oral intake) is given below.

Water environmental health risk assessment

Surface waters are often used for drinking water purpose in this region. To assess the overall potential health risk for non-carcinogenic effects posed by more than one heavy metal, a hazard quotient (HQ) calculated for each heavy metal is summed and expressed as a hazard index (HI) (USEPA 2012a). The following equation was used to determine the chronic daily intake of HM in drinking water:

$$HI = HQ_{\mathrm{Pb}} + HQ_{\mathrm{Zn}} + HQ_{\mathrm{As}} + HQ_{\mathrm{Sb}} \tag{1}$$

$$HQ = \frac{CDI}{RfD} = \frac{C \times IR \times EF \times ED}{BW \times AT \times RfD} \tag{2}$$

Table 6 Health risk assessment result of surface water for children

Location	HQ (As)	HQ (Sb)	
Spring water in the upper reaches of Changchengling mine	≈ 0	≈ 0	≈ 0
Changchengling mine	≈ 0	> 20	> 20
downstream of Changchengling mine	0.11	>20	>20
Yuxi River 1	0.34	> 20	> 20
Qingtoujiang River	0.09	> 10	> 10
Hydropower station on the Qingtoujiang River	0.09	> 10	> 10
Paddy field water in Qingtoujiang village	0.09	> 10	> 10
Yuxi River 2	≈ 0	> 10	> 10
Downstream of Xialian	≈ 0	0.61	0.61
Paddy field water in Xialian	0.36	> 10	> 10
Downstream of Xialian (paddy field water)	0.12	0.20	0.32

where HQ is the ratio of the chronic daily intake (CDI, mg kg^{-1} d^{-1}) of a chemical to a reference dose (RfD, mg kg^{-1} d^{-1}) defined as the maximum tolerable daily intake of a specific element that does not result in any deleterious health effects (USEPA 2012a). C is heavy metal concentration in drinking water (mg L^{-1}), IR is the daily ingestion rate of groundwater (L $person^{-1}$ d^{-1}), EF is the exposure frequency (d y^{-1}), ED is the average duration of exposure (year), BW is the average body weight (kg), and AT is the average exposure time (365 × ED d y^{-1}). Detailed information of the parameters in Eq. (2) is provided in Tables 1 and 2.

Lead is a special substance when undertaking risk assessment, for which the health criterion is based on uptake rather than intake, so the risk assessment approach is not used for lead in this research (Environment Agency 2002).

Health risk assessment for soil heavy metals

There are three soil exposure pathways: (1) oral, (2) respiratory, and (3) dermal. The reference dose *RfD* is only provided for oral uptake in China's "Soil Environmental Quality Risk Evaluation Criteria for Industrial Enterprises" (HJ/T25-1999) and the U.S. Environmental Protection Agency's methods (USEPA 2012b), so the direct soil exposure risk was calculated using the following formula:

$$HQ = \frac{CDI_{ingestion}}{RfD} = \left(C_S \times I_{sp} \times CF\right) \times \frac{EF \times ED}{BW \times AT \times RfD} \tag{3}$$

Detailed information of the parameters in Eq. (3) is provided in Table 3.

Ecological risk assessment

Several methods were considered in assessing the ecological risk from the deposition of heavy metals in the soil, including the potential ecological risk index method, the soil cumulative index method, the pollution load index method, and regression analysis (Min et al. 2013; Xie et al. 2013). The potential ecological risk index method was used in this paper to assess the soil ecological risk:

$$C_f^i = \frac{C_D^i}{C_R^i}, \quad E_r^i = T_r^{i*} C_f^i, \quad RI = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i * \frac{C_D^i}{C_R^i} \tag{4}$$

where C_f^i is the pollution parameter of a certain metal; C_D^i is the measured concentration of the heavy metal in the deposits; C_R^i is the reference value required in the calculation; E_r^i is the potential ecological risk; T_r^i is the toxic response

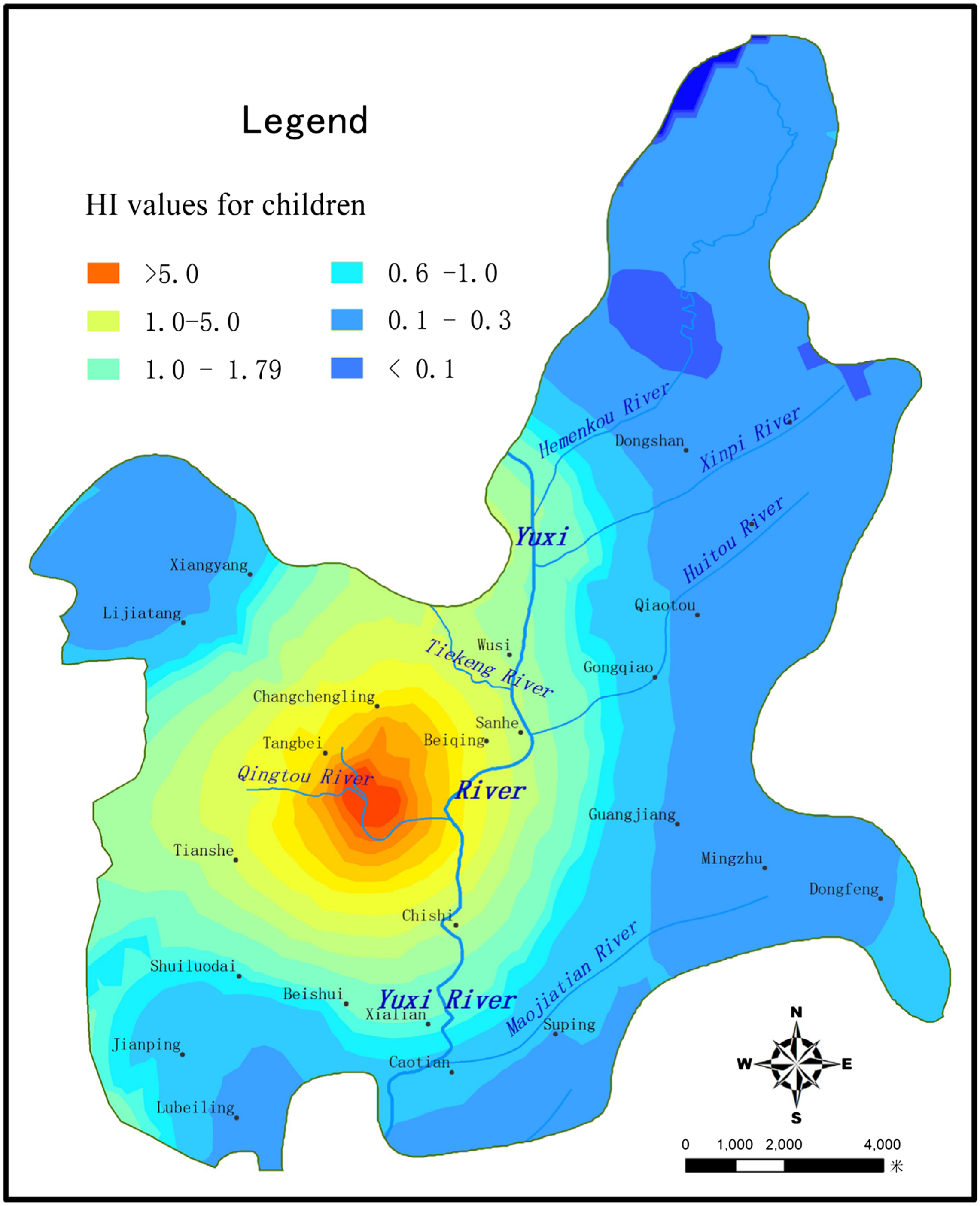

Fig. 2 Child health risk from groundwater polluted by heavy metals

parameter for a single pollutant (20, 10, 30, 1, 5); and *RI* is the potential ecological risk index for a variety of metals. When RI < 100, risk is considered to be slight, and when RI ≥ 400, risk is considered to be severe. The degree of pollution corresponding to the range of *RI* values and the potential ecological risk indexes are shown in Table 4 (Hakanson 1980).

Results and discussion

Current heavy metal pollution in the Yuxi River basin

According to historical data and monitoring values for undeveloped areas, the environmental background of lead, zinc, arsenic, and antimony for the region is 0–

Table 7 Health risk assessment result of groundwater for children

Location	Sb concentration (mg/L)	HQ
Tiger spring in Qingtou village	0.78	> 10
The old bridge on the Qingtou River	1.679	> 10
Near the intersection of Qingtou River and Yuxi River	0.5413	> 10
Yuxi village	0.0787	> 10
Changchengling mine	0.1144	> 10
Changchengling village(a)	0.0032	0.65
Changchengling village(b)	0.0031	0.63
Changchengling village(c)	0.0093	1.88
Changchengling village(d)	0.0445	8.98
Chishi mine	0.0416	8.39
Chishi village	0.0029	0.59
Tiekeng mine	0.054	> 10
Pingguang village	0.0077	1.55

a, b, c, d represent the east, south, west, and north, respectively

0.003 mg/L, which is relatively low. The basin was divided into upstream, midstream, and downstream regions, based on the distribution of the mining enterprises in the Yuxi River basin (Fig. 1). The upstream region of the basin is approximately 30 km^2 in area and uncontaminated. Due to the absence of non-ferrous metal mining, ore-dressing, or smelting enterprises, this region has not been impacted by heavy metal pollution. The environmental quality of the basin is relatively good. Thus, the analysis presented below focused on heavy metal pollution in the midstream and downstream regions.

Midstream region of the basin

Mining, ore-dressing, and smelting enterprises are concentrated in the midstream region. Five mining enterprises are located over an area of approximately 28 km^2 (Fig. 1). This region is the main antimony reservoir in Yizhang County, and its geological environment has been seriously compromised by mining, including the utilization of land resources, and heavy metal pollution of the water and soil.

Monitoring data showed that the content of heavy metals in surface water and sediment in wet season

Table 8 Health risk assessment result of heavy metals for farmland soils

Location	HQ (adult)				HI (adult)	HQ (children)				HI (children)
	Pb	Zn	As	Sb		Pb	Zn	As	Sb	
Xialian village	-	-	-	0.20	0.20	-	-	0.02	0.68	0.70
Xialian village	-	-	-	0.02	0.02	-	-	-	0.07	0.07
Xialian village	-	-	-	0.02	0.02	-	-	-	0.05	0.05
Xialian village	-	-	-	0.04	0.04	-	-	-	0.13	0.13
Xialian village	-	-	-	0.04	0.04	-	-	-	0.14	0.14
Chishi village	-	-	0.09	0.02	0.11	0.01	-	0.30	0.06	0.38
Chishi village	-	-	0.09	0.06	0.16	0.01	-	0.32	0.21	0.55
Tiekeng village	-	-	0.10	0.09	0.18	0.03	-	0.34	0.29	0.67
Tiekeng village	-	-	0.06	0.02	0.08	0.01	-	0.22	0.07	0.30
Baiqing village	-	-	0.08	0.02	0.10	0.01	-	0.27	0.07	0.36
Baiqing village	-	-	0.05	0.04	0.09	0.01	-	0.16	0.14	0.32
Pingguang village	-	-	0.04	0.04	0.07	0.01	-	0.13	0.13	0.27
Near the Xialian	-	-	0.07	0.39	0.46	0.01	-	0.23	1.35	1.59
Near the Xialian	-	-	0.05	0.03	0.08	0.01	-	0.17	0.09	0.28
Zhifu bridge	-	-	0.10	0.38	0.48	0.01	-	0.34	1.31	1.67
Zhifu bridge	-	-	0.09	0.33	0.43	0.01	-	0.33	1.14	1.48
Zhifu bridge	-	-	0.04	0.21	0.25	0.02	-	0.15	0.71	0.88
Qingtoujiang village	-	-	0.09	0.16	0.25	0.01	-	0.32	0.56	0.89
Chishi village	-	-	0.19	0.15	0.34	0.02	-	0.65	0.50	1.19
Xingwang	0.02	-	0.30	0.11	0.41	0.06	-	1.02	0.38	1.47
Beside the river in	-	-	0.07	0.10	0.17	0.02	-	0.25	0.35	0.62
Beside the Chishi	-	-	0.08	0.09	0.17	0.01	-	0.28	0.30	0.60
Beside the Chishi	-	-	0.12	0.05	0.18	0.01	-	0.42	0.18	0.62
Beside the Chishi	-	-	0.12	0.05	0.17	0.01	-	0.41	0.19	0.62

- means < 0.01

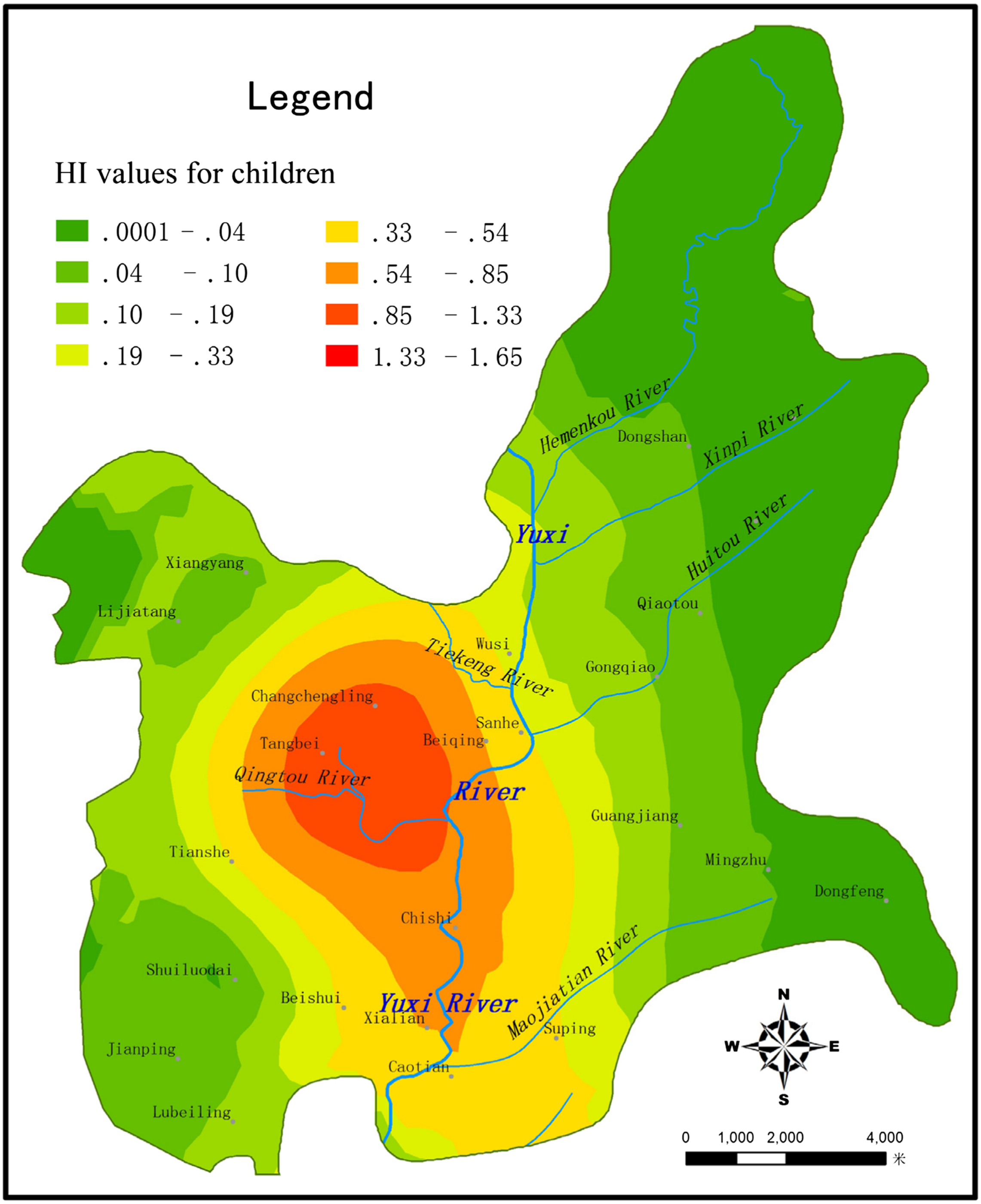

Fig. 3 Child health risk from soil polluted by heavy metals

(April, July) was higher than that in dry season (January, October), indicating that much of the pollution came from rain leaching from the earth's surface. Metals analysis showed that lead, zinc, and arsenic levels were not excessive in the mine water for the pertinent mining enterprises of the region, but the antimony concentration (26.25–717.49 mg/L) was found to be relatively high (Table 5). The lead and zinc mine in the Changchengling exhibited the highest antimony level, at more than one thousand times the Chinese surface water limit of 0.005 mg/L ((SEPA 2002); Pb $\leq$ 0.05 mg/L, Zn $\leq$ 1.0 mg/L, As $\leq$ 0.05 mg/L, Sb $\leq$ 0.005 mg/L). In addition to the high antimony content of the mine water, another important source of heavy metal pollution was rainwater

Table 9 Ecological risk assessment result of heavy metals for farmland soils

Location		Potential ecological risk				RI
Village	Site no.	Pb	Zn	As	Sb	
Changchengling	1	6.	0.9	32	96	136
	2	6	1	9	1380	1396
	3	6	0.9	19	1042	1070
	4	6	1	10	740	759
	5	6	1	17	655	679
	6	7	1	30	467	506
	7	8	1	3	802	815
	8	6	1	11	468	487
Yuxi	1	14	1	3	1138	1156
	2	5	1	11	232	249
Xialian	1	13	1	18	1522	1556
	2	8	0	13	2051	2073
	3	32	0.8	308	18,980	19,323
	4	13	0.9	6	227	247
	5	10	1	20	103	136
	6	27	1	22	2825	2876

leaching of open-air stores of mine tailings and waste rock. The lead, arsenic, and antimony levels in the mine tailings and waste rock for four of the five mining enterprises in this region clearly exceeded the standards for soil remediation of heavy metal contaminated sites ((SRHMC 2016); Pb ≤ 600 mg/kg, Zn ≤ 700 mg/kg, As ≤ 70 mg/kg, Sb ≤ 60 mg/kg). The antimony levels in the mine tailings surrounding the Changchengling mine were higher than for the other metals, at more than 40 times the remediation standards for soil of 60 mg/kg (SRHMC 2016). The slag in the Zeng Wangang antimony smelter, which is only 10 m away from the Yuxi River, exhibited an antimony content of approximately 3%; the antimony concentration in the nearby surface water could easily be increased by rainwater leaching.

Relative to the Chinese surface water limit (SEPA 2002), the Yuxi River surface water was not significantly polluted by heavy metals such as lead, zinc, and arsenic. These elements were below the Chinese surface water limit at all monitoring sites. However, antimony levels clearly exceeded the limit and the environmental background for the region (0–0.003 mg/L) in most areas. Over the entire river basin, the areas with antimony levels over 200 times the regulatory limit ((SEPA 2002); Sb ≤ 0.005 mg/L) was mainly located in the midstream region, with the highest antimony level at nearly 500 times the regulatory limit ((SEPA 2002); Sb ≤ 0.005 mg/L). Lead, zinc, and arsenic were undetectable in the groundwater which was used for drinking water purpose, but the antimony concentrations exceeded the standards for drinking water quality in China ((SDWQ 2006); Pb ≤ 0.01 mg/L, Zn ≤ 1.0 mg/L, As ≤ 0.01 mg/L, Sb ≤ 0.005 mg/L) in approximately 63% of the samples, which was significantly higher than the environmental background (0–0.003 mg/L) in the region, with the highest antimony level at 155 times the regulatory limit ((SDWQ 2006); Sb ≤ 0.005 mg/L).

Downstream region of the river basin

Ore-dressing enterprises are centralized in the downstream region of the river basin, which has an area of approximately 40 km^2. There are two polymetallic ore-dressing plants in the northern part of the region, approximately 50–100 m from the Yuxi River. The plant ores were stored in the open air without any protective measures, and the mine tailings were relatively high in heavy metals, such as arsenic and antimony. In the southern part of the region, the arsenic and antimony concentrations in the tailings and waste rock from the Xialian polymetallic ore-dressing plants were relatively high, with the highest concentrations at 120 and 11,000 mg/kg, respectively. Lead, zinc, and arsenic levels were below the regulatory limits (SEPA 2002) in the lixivium from the tailings. Only antimony levels were significant in the lixivium, at 40–100 times the regulatory limit ((SEPA 2002); Sb ≤ 0.005 mg/L), corresponding to an average concentration of 0.43 mg/L.

The antimony concentrations in the surface water and groundwater in the downstream region also clearly exceeded the regulatory limit of 0.005 mg/L (SDWQ 2006; SEPA 2002), but less severely than the midstream region. Furthermore, our analysis showed that the farmland water in the midstream and downstream regions of the river basin was severely polluted. The rice paddy water from the Qingtou River and the water downstream of the Xialian ore-dressing plant, adjacent to the rice paddy fields, exhibited antimony concentrations over 50 times the regulatory limit ((SEPA 2002); Sb ≤ 0.005 mg/L), indicating sewage irrigation was used for agricultural production.

Assessment of health risks

Water environmental health risk

Adult health risk assessments showed that antimony presented the main health risk from surface water in the river basin (Table 6). Approximately 75% of the samples produced risks greater than unity, and a few risks were even greater than 10: in particular, the risks were higher for the surface water bodies near the Changchengling mining area. The potential heavy metal risk for children was significantly higher than for adults; the child health risk near the Changchengling mining area was greater than 20. These results revealed

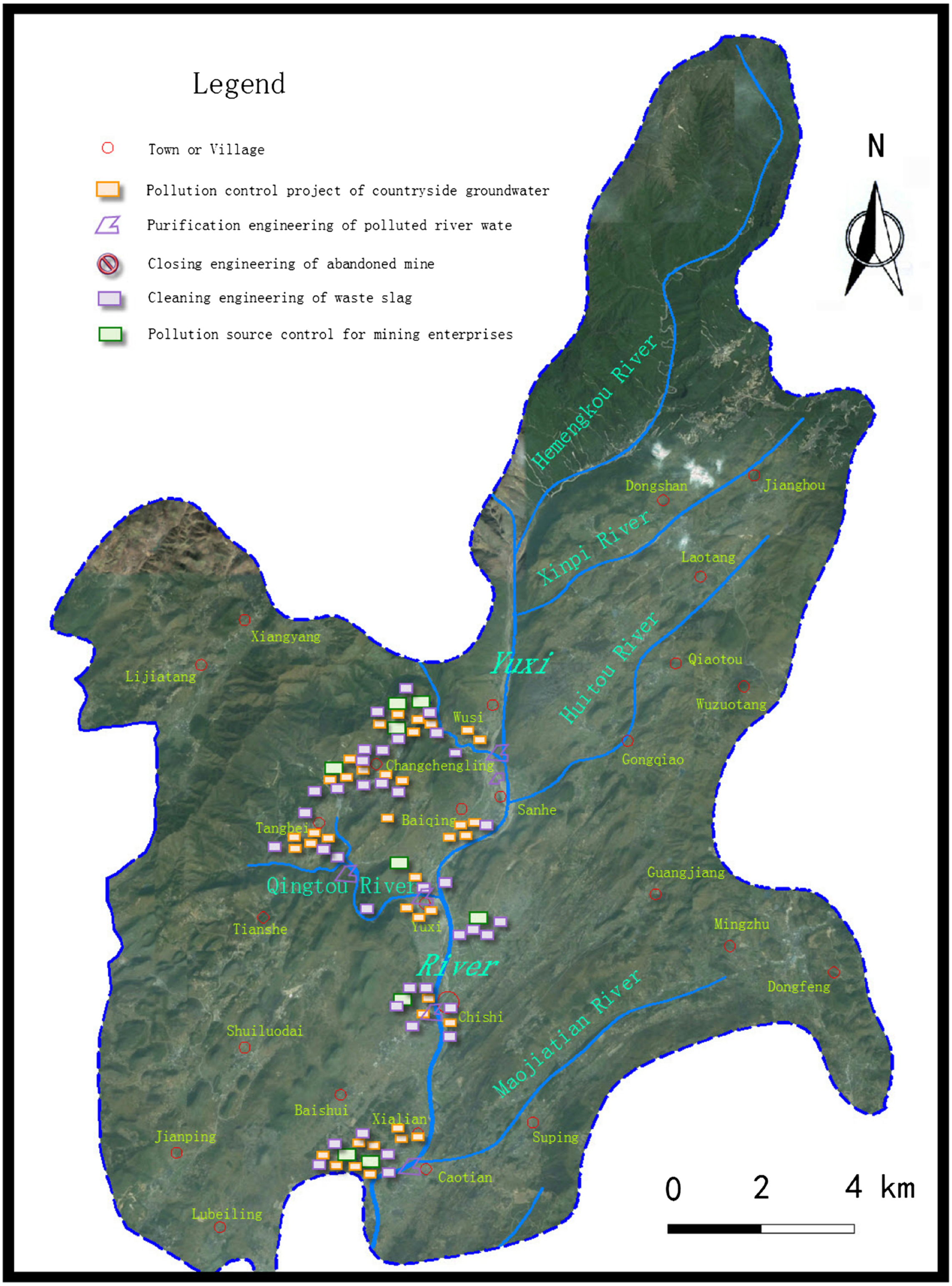

Fig. 4 Map of proposed comprehensive treatment of heavy metal pollution sources

that antimony-contaminated surface water poses a higher health risk for the vulnerable group of local children, which should be caused for concern for the local people and the relevant governmental departments.

The groundwater health risk assessment in the Yuxi River basin and geostatistical analysis (Fig. 2) showed that the risk exceeded the threshold value of unity at approximately 75% of the monitoring sites. The contaminated groundwater areas were mainly located in the midstream region. The groundwater health risk was especially high in the Qingtou River basin, exceeding 10 at multiple sites (Table 7).

Health risk assessment of soil heavy metals

Levels of zinc, arsenic, and antimony in the soil did not pose significant health risks to adults, with all the composite risks being less than unity. However, the adult health risk in some areas exceeded the threshold, as with the child health risk (Table 8).

Geostatistical analysis (Fig. 3) showed that the high-risk areas were mainly located in the midstream and downstream regions of the basin, especially in the Qingtou River area. The risk gradually went down from the Qingtou River area to the downstream region along the Yuxi River. The place mainly uses river water to irrigate crops. The nearer the area is to the river or a mining area, the higher the risk, implying that rainwater leaching of the mine slag and tailings, mine waste dust dispersal by wind or hydric erosion of waste piles, and farmland irrigation with heavy-metal-contaminated river water have greater contributions to the soil health risk. Exposure from other metals was not considered in this study, and the human health risk was not assessed for ingestion of crops in which heavy metals have accumulated. Thus, accurate risk assessment requires further sampling, investigation, and in-depth analysis.

Ecological risk assessment

Ecological risk assessment, based on soil concentrations of heavy metals such as lead, zinc, arsenic, and antimony in the midstream and downstream regions of river basin (Table 9), showed that antimony posed the highest potential ecological risk, with a 0% minor ecological risk and a 56% strong ecological risk. In contrast, arsenic posed only a weak potential ecological risk in these areas. Arsenic posed a minor ecological risk in most samples and a strong ecological risk of 308 in only one case, a downstream eggplant field in the village of Xialian. Lead and zinc posed only minor ecological risks for all samples. Therefore, antimony was the dominant contribution to the ecological risk for the region.

The hillside soil in the Changchengling, Tongbei village, and the uncontaminated farmland in the village of Xialian posed a moderate potential ecological risk for metals. The potential ecological risk indexes for a variety of metals in all samples were higher than 240, which was in the high-risk category. Significantly high ecological risks were exhibited at 75% of all the sampling locations, with the highest risk index at 19,323 presented by the soil in the eggplant field downstream of the village of Xialian.

Risk management analysis and pollution remediation

Heavy metal pollution in the region is caused by the accumulation of metals from long-term mining, processing, and industrial processes. Based on the risk assessment analysis, we find the priority site for remediation, such as the Changchengling mine area, the Qingtou River area, and the eggplant field downstream of the village of Xialian. Then, we propose a heavy metal pollution remediation project in the basin area, including mining administration and beneficiation enterprises for pollution source control, clean-up of historical heavy metal pollution, river water purification in key river reaches, pollution control of groundwater sources of drinking water, quality control of drinking water in rural areas, and ecological protection and restoration of farmlands, rivers, and abandoned mines (Fig. 4).

Conclusion

In this study, a large number of investigations were conducted on the pollution levels and population exposure risks to contaminants such as antimony, lead, zinc, and arsenic in the Yuxi River basin in the Hunan province, China. The scope of the investigations included mine water, waste rock, tailings, agricultural soil, surface water, river sediments, and groundwater sources of drinking water. The results of the investigations showed that the antimony concentrations in the river sediments, surface water, and groundwater in the midstream and downstream regions significantly exceeded the regulatory limit. Farmland water bodies have also been seriously polluted; the average arsenic and antimony concentrations in the farmland soil surrounding mining enterprises exceeded the regulatory limit. Antimony concentrations in approximately 63% of the groundwater samples in the midstream and downstream regions exceeded the regulatory limit. The polymetallic composite health risks for approximately 75% of the groundwater monitoring sites exceeded the threshold value of unity. The potential risk of heavy metals for children was significantly higher than for adults. Rainwater leaching of mine slag and tailings and farmland irrigation with heavy-metal-contaminated river water presented a significant soil health risk. Resolution of historical pollution, mainly from antimony pollution in the Changchengling mine area in the midstream region, was found to be essential for improving environmental quality. Remediation and control of heavy metal pollution requires the establishment of a complete regulatory system and long-term risk management.

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