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TECHNICAL ARTICLE

# Spatial Distribution of As, Cr, Pb, Cd, Cu, and Zn in the Water and Sediment of a River Impacted by Gold Mining

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**Abstract** Historical and active mining has adversely affected the geochemistry of the Jiehe River in the Jiaodong Peninsula, which has the largest gold ore reserves in China. Water and sediment samples were collected along the 37.8 km long river during the critical low flow season. Samples were analyzed for their geochemical properties, total concentrations of As, Cr, Pb, Cd, Cu, and Zn in the sediment, and dissolved/particulate concentrations of trace elements in filtered/unfiltered water samples. Our results demonstrate that substantial amount of these elements have been released into the Jiehe River during the processes of extracting, selecting, processing, and smelting at the many historical and active gold mining sites in the watershed. High concentrations of potentially toxic elements (1.9–1,004 μg $L^{-1}$ As, 4.2–210 μg $L^{-1}$ Cr, 7.9–9,529 μg $L^{-1}$ Pb, 2.0–855 μg $L^{-1}$ Cd, 47.4–8,494 μg $L^{-1}$ Cu, and 105–11,336 μg $L^{-1}$ Zn) have seriously affected water quality in the region. In addition, these contaminants have accumulated in the bed sediment (7.7–181 mg $kg^{-1}$ As, 24.1–726 mg $kg^{-1}$ Cr, 9.9–1,100 mg $kg^{-1}$ Pb, 0.1–51.8 mg $kg^{-1}$ Cd, 22.1–1,524 mg $kg^{-1}$ Cu, and 53.5–5,484 mg $kg^{-1}$ Zn). Spatial distribution of these contaminants in water and sediment is controlled by the discharge from point and non-point sources as well as the reactive transport processes. Spatial analysis conducted on the sediment and stream concentration of As, Pb, Cd, and Zn suggests that two mining-related sources, at 4.3 and 17.6 km downstream of the headwaters, contributed most of the As, Pb, Cd, and Zn load as particulates. In contrast, high levels of Cr and Cu in the sediment are not related to the current loading pattern and may be due to historical sources. As the first comprehensive study on the pollution caused by intensive gold mining in this area, this research has provided much needed information to establish effective management and remediation strategies.

**Keywords** Trace element · Water quality · Sediment · Acid mine drainage

## Introduction

Mine drainage laden with high concentrations of contaminants is an important cause of environmental pollution throughout the world (Andrade et al. 2012; Cánovas et al. 2012; Carling et al. 2013; Caruso and Bishop 2009; Meunier et al. 2010; Runkel et al. 2012; Sarmiento et al. 2011). Extracting and processing of minerals from hard rock mines at an industrial scale can result in tremendous loading of trace elements into streams and rivers. Numerous studies have been conducted to characterize the geochemical speciation and reactive transport of trace element contaminants in mining-impacted streams (Cánovas et al. 2012; Caruso et al. 2008; Kimball and Runkel 2009). The spatial and temporal distribution of trace elements in surface water can be affected by various hydrological, geochemical, and microbiological processes. Understanding the physical and chemical processes controlling the distribution of trace elements is a prerequisite for developing remediation strategies in watersheds contaminated by mining (Cánovas et al. 2007; Kimball et al. 2010; Nordstrom 2011; Runkel et al. 2012).

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This study focused on the Zhao-Lai gold mineralization belt, the largest gold repository of China. The study site is located on the Jiaodong Peninsula, which is known as the “gold capital of China” (Liang et al. 2011; Yang and Zhou 2000). Its history of gold mining can be traced back to 595 A.D. in Chinese literature. Intensive gold mining started in the late eighteenth century and continues today. As of 2011, the area has a proven gold reserve of 750 Mg; 28.32 Mg of gold has been extracted and 40.96 Mg gold has been processed (Statistical Bureau of Zhaoyuan 2012). Mining and processing of gold in this area has substantially damaged the surrounding environment. Enormous amounts of mine wastes in the form of tailing ponds, barren piles, and heaps have accumulated in this area. Acid mine drainage (AMD) from mine sites can contain large amount of trace elements. In addition, a large fraction of the contaminants released from mining operations have been deposited in the bottom and bank sediment along stream channels. Seasonal changes in geochemical and hydrological conditions can cause the release of trace elements from stream sediment into the aqueous environment through processes such as mineral dissolution, surface desorption, and particle resuspension (Cánovas et al. 2007, 2012; Santos Bermejo et al. 2003).

Despite the detrimental effect of mining activities on human health and ecological quality, the environmental impact of large-scale intensive gold mining in the Jiehe River watershed has not been evaluated. An extensive literature review and personal interviews with local environmental regulators revealed that decision makers as well as general public do not know the severity of water and sediment contamination by gold mining in this area. Furthermore, the lack of scientific information on the speciation and distribution of contaminants has severely restricted the effective mitigation and remediation of water contamination in the region.

This is the first study is to report the extent and intensity of pollution in the Jiehe River watershed. Specifically, the objectives were to determine the spatial distribution of trace elements (As, Cr, Pb, Cd, Cu, and Zn) in water and sediment of the stream that receives discharge and runoff from historical and active gold mining, and to investigate the sources of the loading and the geochemical factors influencing the distribution of these elements in the river and its sediments.

## Materials and Methods

### Site Description

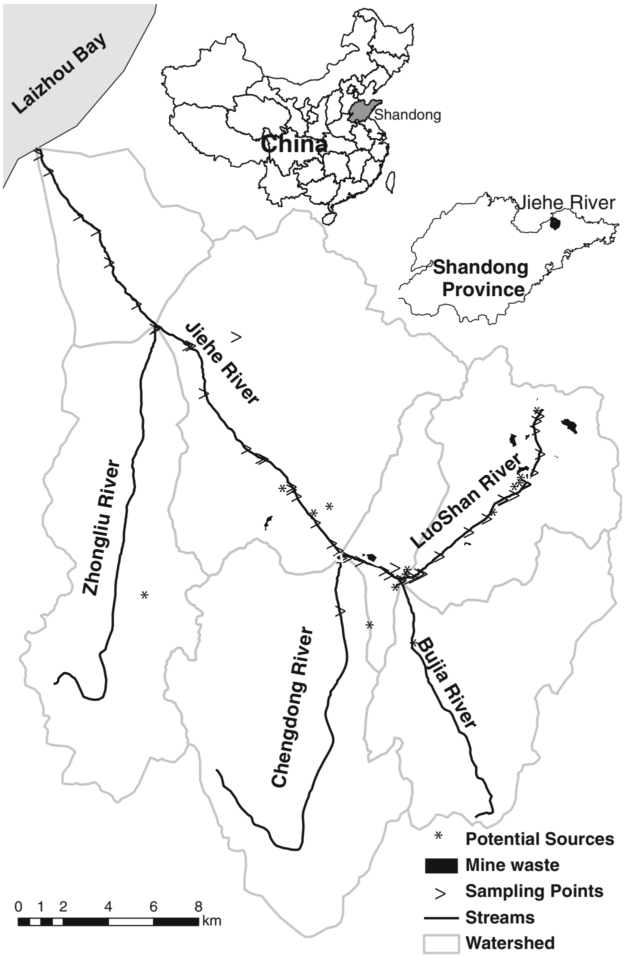

**Fig. 1** Location of the sampling points, potential pollutant sources, mine wastes, and stream reaches in the Jiehe River watershed

The Jiehe River is located in the northwest part of the Jiaodong peninsula at latitude 37°05′N–37°33′N and longitude 120°08′E–120°38′E (Fig. 1). The headwaters of the river originate from Luoshan Mountain, at an altitude of 759 m. Three major tributaries, the Bujia, Chengdong, and Zhongyou Rivers, contribute to the main stem of the Jiehe River as it flows northwest into the Laizhou Bay of the Bohai Sea. The entire watershed has an area of ≈585 km$^2$ and the reach length is ≈42 km. The width of the downstream river channel is 70–120 m. The Jiehe River is a seasonal river with average annual discharge of ≈1.4 × 10$^8$ m$^3$. During low flow season, the water depth is generally less than 0.65 m and the wetted perimeter is only about 13 m at the most downstream site. The flow velocity ranges between 0.1 and 1.3 m s$^{-1}$; the total discharge is ≈2.4 m$^3$ s$^{-1}$. The studied area has a temperate monsoon climate with a mean annual temperature of 11.5 °C and an annual precipitation of 679 mm, which is heavily concentrated in the summer season (June–August). Soils in the area were classified as Typic Eutrochrepts or Typic Hapludalfs. The gold ore deposits are associated with quartz mineralization with quartz veins and altered rocks in the Linglong granite along the Zhaoping fault zone. Gold is disseminated within the granite or within veins inside the sheared alteration zone (Liang et al. 2011; Yang and Zhou 2000).

### Water and Sediment Sampling

In April, 2012, a total of 44 water samples were collected in the Jiehe River Watershed; 32 samples were collected on the $\approx 37.8$ km reach of the main stem of the Jiehe River and 12 samples on tributaries and waste water discharges (Fig. 1). Temperature, pH, and electrical conductivity (EC) were measured in stream using an YSI 556 multi-parameter handheld water quality meter. The instruments were calibrated before field operation. Water samples were carefully collected from the shallow stream (depth $< 0.65$ m) using a plastic bucket without disturbing the bottom sediment. Water samples were stored in acid pre-cleaned Teflon bottles and a fraction of the water samples were filtered in the field through 0.45 µm Whatman syringe filters for dissolved metal analysis. Both non-filtered (for total metal analysis) and filtered (for dissolved metal analysis) water samples were acidified in the field to pH $< 2$ with suprapur $HNO_3$ (2 %) and then stored at 4 °C before analysis. Samples collected for anion determinations were filtered but not acidified. Composite samples of surface (0–5 cm) sediment were grabbed on the bottom of stream channel at the same locations as the water samples and stored in sealed plastic bags. Stream sediment samples were air dried and passed a 2-mm sieve before chemical analysis.

### Chemical Analysis

Chemical analyses were conducted in the Analysis and Testing Center of the Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences. Rigorous quality assurance and quality control measures including field blanks, field duplicates, and reference materials were employed. Metals in duplicate sediment samples were digested by aqua regia using a microwave digestion technique. Specifically, 0.2 g sediment samples were placed in a digestion vessel and concentrated acids ($HNO_3 + HCl + HF$) were added to digest the samples under high temperature and pressure conditions in a microwave until near-total dissolution. Particle size distribution (0.02 µm–2 mm) of the sediment samples was determined using a Malvern Mastersizer 2000 laser diffractometer. The percentages of clay (<2 µm), silt (2–50 µm), and sand (50 µm–2 mm) were calculated from particle size distribution curves. Total (unfiltered) and dissolved (filtered through 0.45 µm membrane filters) concentrations of As, Cr, Pb, Cd, Cu, Zn, Fe, Al, and Mn were determined by ICP-MS (ELAN DRC II, Perkin Elmer SCIEX, USA). The analytical errors (measured as standard deviation) were consistently less than 5 % and the differences between field duplicates were consistently within the range of certified values. The particulate fraction of trace element (mass associated with >0.45 µm suspended solids) was calculated as the difference between unfiltered and filtered concentrations. In addition, ferrous ($Fe^{2+}$) iron was determined using colorimetric method and ferric ($Fe^{3+}$) iron was calculated as the difference between dissolved iron and ferrous iron (Cánovas et al. 2007). Anions (F, Cl, Br, $NO_3$, $NO_2$, and $SO_4$) were determined by ion chromatography (Dionex ICS-3000, Thermo Fisher Scientific Inc, USA). Total organic carbon (TOC) and total inorganic carbon (TIC) were determined using a total organic carbon analyzer (TOC-VCPH, Shimadzu Scientific Instruments, Japan).

### Data Analysis

Concentrations of the elements were log10-transformed to make the dataset approximate a normal distribution and the log-transformed concentrations were reassessed using the Kolmogorov–Smirnov test. Correlation analyses were performed on the log-transformed concentrations of elements in water and sediment using the bivariation method, with two-tailed significance and Pearson correlation coefficients. Statistical analyses were performed using SigmaPlot for Windows Version 11.0 (Systat Software, Inc., USA).

## Results

### Geochemical Characteristics of Stream Water

Summary statistics of the geochemical properties of stream water are given in Table 1 and spatial distributions of pH, EC, as well as concentrations of sulfate and TOC along the main stem of the Jiehe River are shown in Fig. 2. Total and dissolved concentrations of aluminum, manganese, and iron are displayed in Fig. 3. Field measured pH ranged between 4.0 and 7.9, with a median value of 7.3. The upper stream reach (4.3–11.0 km) was severely impacted by acid mine drainage as indicated by the low pH values. The rest of the stream had a circum–neutral pH. Field measured values of EC on the main stem varied between 0.2 and 7.2 mS $cm^{-1}$ with a median of 3.6 mS $cm^{-1}$. Major anions show values between 618.6 and 2,114.4 mg $L^{-1}$ of $SO_4$, 57.6 and 548.5 mg $L^{-1}$ of $Cl^-$, up to 14.0 mg $L^{-1}$ ${NO_2}^-$, 4.3 and 63.1 mg $L^{-1}$ of ${NO_3}^-$, and up to 19.3 mg $L^{-1}$ ${HCO_3}^-$. High dissolved concentrations of Fe (0.46–43.1 mg $L^{-1}$), Al (0.45–9.12 mg $L^{-1}$), and Mn (0.58–19.2 mg $L^{-1}$) were

**Table 1** Statistical description of sampling results obtained in the water and sediment of the Jiehe River

| | N | Mean | SD | Skewness | Median | Min | Max |
|---|---|---|---|---|---|---|---|
| Total content in stream sediment | | | | | | | |
| As (mg kg$^{-1}$) | 32 | 56.2 | 43.1 | 1.015 | 46.5 | 7.7 | 182 |
| Cr (mg kg$^{-1}$) | 32 | 339 | 227 | 0.299 | 301 | 24.1 | 726 |
| Pb (mg kg$^{-1}$) | 32 | 167 | 257 | 3.054 | 87.2 | 9.9 | 1,100 |
| Cd (mg kg$^{-1}$) | 32 | 4.1 | 9.3 | 4.755 | 2.0 | 0.1 | 51.8 |
| Cu (mg kg$^{-1}$) | 32 | 427 | 430 | 1.376 | 236 | 22.1 | 1,525 |
| Zn (mg kg$^{-1}$) | 32 | 639 | 1,045 | 3.678 | 250 | 53.5 | 5,484 |
| Clay (%) | 32 | 3.4 | 2.2 | 0.292 | 3.3 | 0.03 | 7.9 |
| Silt (%) | 32 | 42.2 | 21.7 | −0.0458 | 46.1 | 4.9 | 81.6 |
| Sand (%) | 32 | 54.5 | 23.7 | 0.0345 | 50.2 | 11.2 | 95.1 |
| Total concentration in stream water | | | | | | | |
| As (µg L$^{-1}$) | 44 | 124 | 206 | 3.562 | 46.2 | 1.9 | 1,004 |
| Cr (µg L$^{-1}$) | 44 | 29.1 | 45.6 | 3.24 | 14.7 | 4.2 | 210 |
| Pb (µg L$^{-1}$) | 44 | 401 | 1,671 | 5.55 | 64.7 | 7.9 | 9,529 |
| Cd (µg L$^{-1}$) | 44 | 41.9 | 149 | 6.34 | 11.0 | 2.0 | 855 |
| Cu (µg L$^{-1}$) | 44 | 1,358 | 2,100 | 2.359 | 419 | 47.4 | 8,494 |
| Zn (µg L$^{-1}$) | 44 | 2,518 | 2,955 | 2.094 | 1,179 | 105 | 11,336 |
| Fe (mg L$^{-1}$) | 17 | 8.62 | 11.2 | 2.597 | 4.23 | 0.74 | 49.4 |
| Al (mg L$^{-1}$) | 17 | 3.64 | 2.84 | 0.373 | 3.51 | 0.15 | 10.2 |
| Mn (mg L$^{-1}$) | 17 | 6.18 | 6.09 | 0.437 | 2.21 | 0.84 | 19.7 |
| Dissolved concentration in stream water | | | | | | | |
| As (µg L$^{-1}$) | 44 | 84.1 | 166 | 4.114 | 30.2 | 1.6 | 833 |
| Cr (µg L$^{-1}$) | 44 | 4.5 | 5.3 | 3.458 | 2.5 | 1.1 | 24.8 |
| Pb (µg L$^{-1}$) | 44 | 33.3 | 65.8 | 2.668 | 1.6 | 0.3 | 237 |
| Cd (µg L$^{-1}$) | 44 | 10.5 | 11.7 | 3.944 | 6.9 | 0.1 | 37.5 |
| Cu (µg L$^{-1}$) | 44 | 1,139 | 2,049 | 2.299 | 184 | 0.4 | 7,673 |
| Zn (µg L$^{-1}$) | 44 | 1,927 | 2,595 | 2.034 | 744 | 23.1 | 9,646 |
| Fe$^{2+}$ (mg L$^{-1}$) | 17 | 4.46 | 6.58 | 1.018 | 0.02 | 0.00 | 21.9 |
| Fe$^{3+}$ (mg L$^{-1}$) | 17 | 1.59 | 4.62 | 4.114 | 0.55 | 0.00 | 21.2 |
| Al (mg L$^{-1}$) | 17 | 1.87 | 2.14 | 2.142 | 0.78 | 0.45 | 9.12 |
| Mn (mg L$^{-1}$) | 17 | 5.83 | 6.09 | 0.429 | 2.23 | 0.58 | 19.2 |
| Geochemical properties of stream water | | | | | | | |
| pH | 42 | 6.7 | 1.1 | −0.891 | 7.3 | 4.0 | 7.9 |
| EC (mS cm$^{-1}$) | 42 | 3.7 | 1.4 | 1.322 | 3.6 | 0.2 | 7.2 |
| F$^{-}$ (mg L$^{-1}$) | 44 | 0.9 | 0.6 | 2.034 | 0.8 | 0.4 | 2.9 |
| Cl$^{-}$ (mg L$^{-1}$) | 44 | 281 | 134 | 5.903 | 244 | 57.6 | 549 |
| Br$^{-}$ (mg L$^{-1}$) | 44 | 0.4 | 0.2 | 1.082 | 0.4 | 0.0 | 0.7 |
| NO$_3^{-}$ (mg L$^{-1}$) | 44 | 28.2 | 13.8 | 0.549 | 23.8 | 4.3 | 63.1 |
| NO$_2^{-}$ (mg L$^{-1}$) | 44 | 2.2 | 3.5 | 2.065 | 0.7 | 0.0 | 14.0 |
| SO$_4^{2-}$ (mg L$^{-1}$) | 44 | 1,406 | 582 | 0.185 | 1,340 | 619 | 2,414 |
| HCO$_3^{-}$ (mg L$^{-1}$) | 44 | 7.6 | 6.1 | 2.799 | 6.9 | 0.1 | 19.3 |
| TOC (mg L$^{-1}$) | 44 | 15.3 | 12.3 | 4.134 | 11.0 | 3.0 | 51.3 |

*SD* standard deviation, *EC* electrical conductivity, *TOC* total organic carbon

observed in the stream water, especially in stream reaches impacted by AMD. In addition, Fe$^{2+}$ varied between 0 and 21.93 mg L$^{-1}$, which constituted a large fraction of the dissolved iron. Particle size distribution analysis showed that all of the sediment samples were mostly silt and sand, with a very small amount of clay (<8 %).

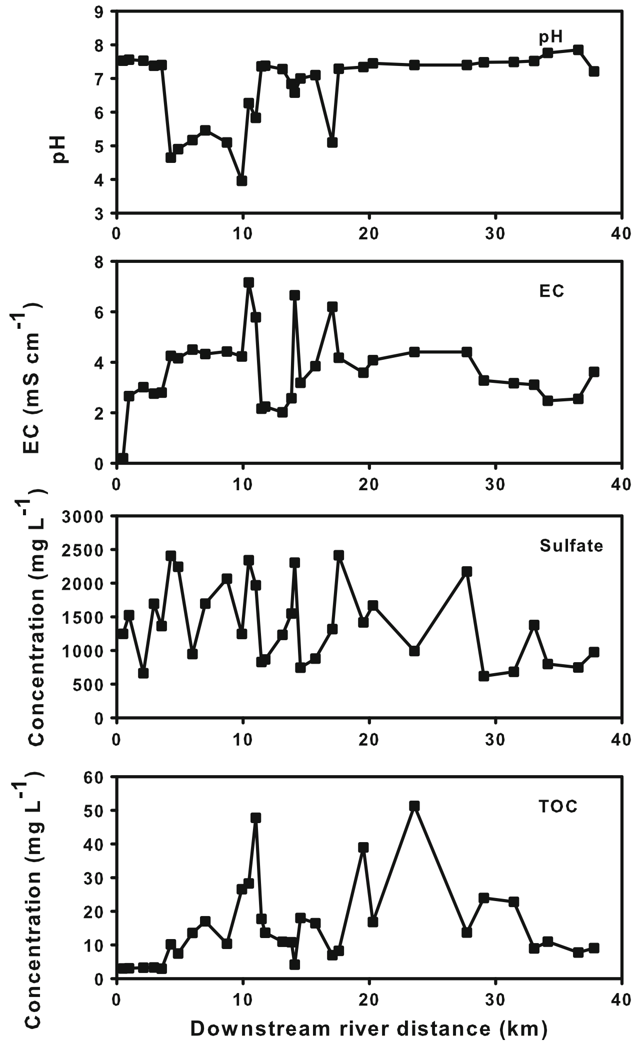

**Fig. 2** Geochemical characteristics (pH, specific conductivity, sulfate, and total organic carbon concentrations) along the sampled stream reach

## Trace Elements in Water

Total and dissolved concentrations of As, Cr, Pb, Cd, Cu, and Zn in the water samples are summarized in Table 1; their spatial distribution along the main stem of Jiehe River is shown in Fig. 4. The concentrations were compared to the criteria listed in Chinese environmental quality standards for surface water (SEPA 2002). High concentrations of all six elements were observed in both dissolved and particulate forms in most of the water samples. The observed trace element concentrations showed large variations, which reflect changes in water geochemistry along the stream reach. For example, the total concentration of As (1.9–1,004 μg L$^{-1}$) ranged over three orders of magnitude with a median concentration of 30.2 μg L$^{-1}$. Arsenic was mostly dissolved (1.6–833 μg L$^{-1}$); two peak concentrations, clearly illustrated on Fig. 4, were at 4.3 km (total and dissolved concentrations of 1,004 and 833 μg L$^{-1}$, respectively) and 17.6 km (total and dissolved concentrations of 460 and 10.2 μg L$^{-1}$) along the main stem. The total and dissolved concentrations of Cr ranged between 4.2–210 μg L$^{-1}$, and 1.1–24.8 μg L$^{-1}$, respectively. At the two concentration peaks, observed at 8.7 km (total and dissolved concentrations of 182 and 9.09 μg L$^{-1}$, respectively) and 17.6 km (total and dissolved concentrations of 210 and 1.44 μg L$^{-1}$, respectively), chromium was mainly in the particulate form. The spatial patterns of Pb and Cd were quite similar, showing a single concentration peak at 17.6 km along the stream reach. The maximum total and dissolved concentrations of Pb were 9,529 and 237 μg L$^{-1}$, respectively, while the total and dissolved for the peak concentration of Cr were 210 and 24.8 μg L$^{-1}$, respectively. The spatial distribution of Cu and Zn were rather complex, showing multiple concentration peaks. In addition, their concentrations span five orders of magnitude, reflecting the exceptionally high variability of the two metals in the river water.

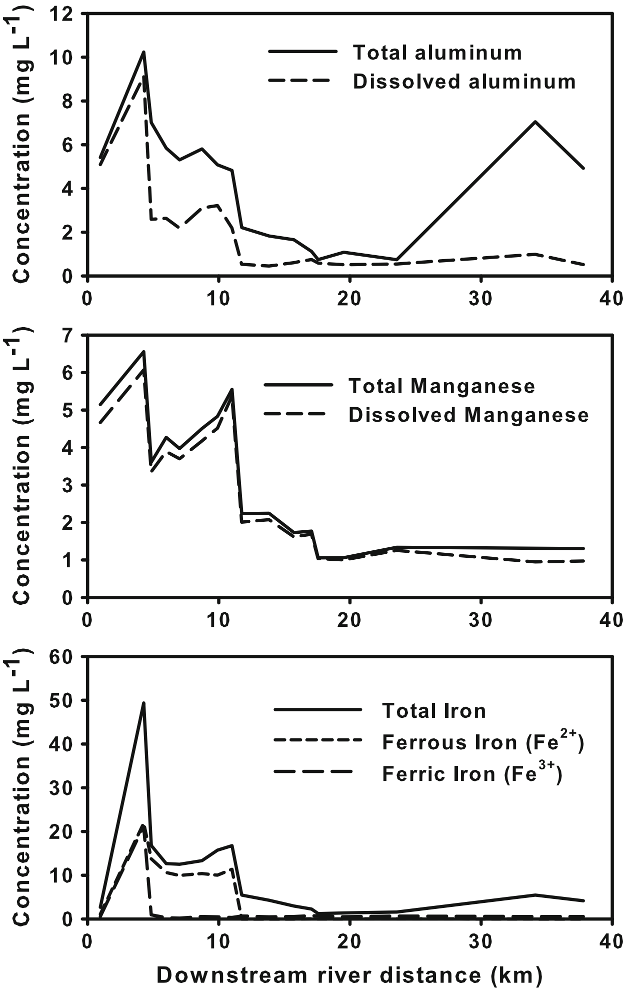

**Fig. 3** Concentrations of aluminum, manganese, and iron in stream water along the sampled reach

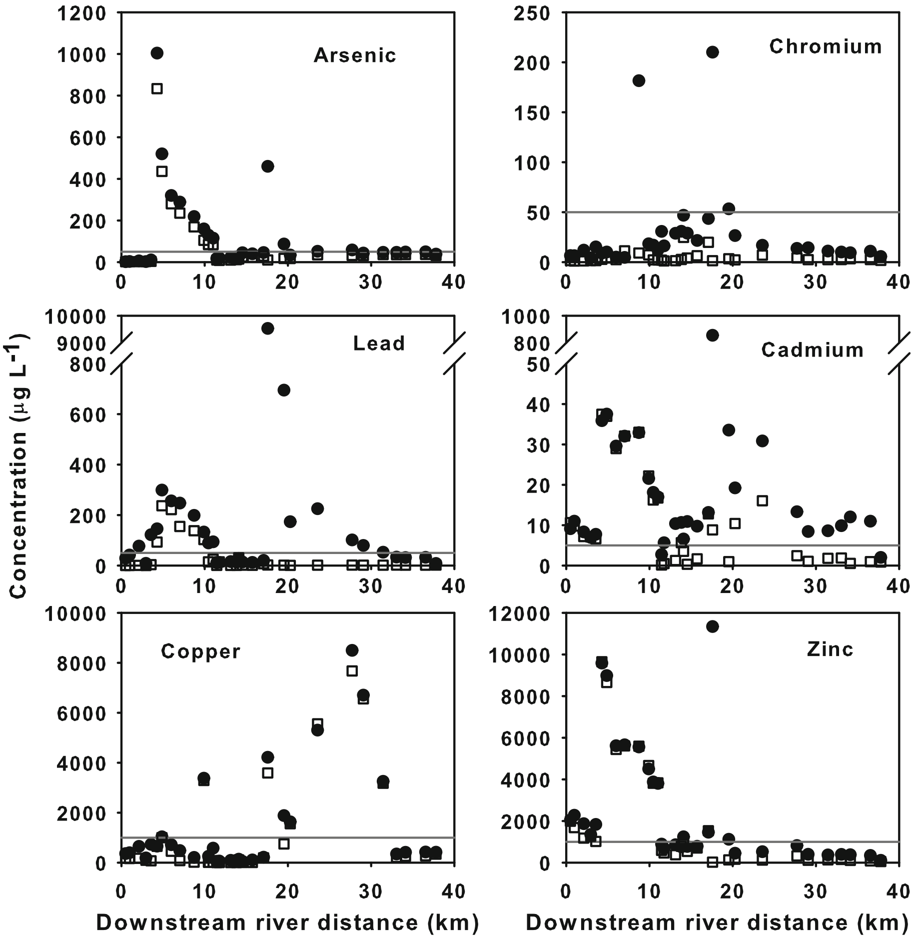

**Fig. 4** Total and dissolved concentrations of chromium, lead, cadmium, copper, and zinc in water samples along the sampled stream reach in comparison with the Chinese environmental quality standards for surface water

### Trace Elements in Bed Sediment

Sediment contents of As, Cr, Pb, Cd, Cu, and Zn as well as the particle size distribution data are summarized in Table 1; their distributions are plotted in Fig. 5. Severe contamination of stream sediment by the contaminants was clearly observed, as indicated by the elevated levels measured after acid digestion. As was the case for the water samples, the level of contaminants in the bed sediment showed very large variations; detailed examination of the distributions demonstrated various spatial patterns. High levels of As (7.7–182 mg kg$^{-1}$) and Cr (24.2–726 mg kg$^{-1}$) were observed in stream sediment at multiple locations on both upper and lower reach of the main stem. In contrast, Pb and Cr contamination of sediment were confined to short stretches of the river. The peak contents of sediment Pb (1,100 mg kg$^{-1}$) and Cd (52 mg kg$^{-1}$) overlapped with the peak concentrations in stream water at 17.6 km downstream. For Cu (22.1–1,525 mg kg$^{-1}$) and Zn (53.5–5,484 mg kg$^{-1}$), extremely high sediment contents were observed at multiple hot spots.

## Discussion

The effects of AMD on water geochemistry in the Jiehe River are clearly illustrated (Figs. 2, 3) as decreased pH, increased sulfate levels, and high concentrations of dissolved iron. In addition, substantial acidification could be due to anaerobic weathering, with Fe(III) as the oxidizing agent, acidic weathering of aluminum silicates, and subsequent aluminum hydrolysis, all of which can release contaminants into the environment (Andrade et al. 2012).

In addition to AMD, the Jiehe River receives numerous point source discharges from industrial and municipal sources as it flows downstream to Laizhou Bay. The location of potential pollutant sources and major sites of mine wastes are revealed in Fig. 1. The effect of point sources loadings on water chemistry was partly reflected by variations in EC, sulfate concentration, and TOC (Fig. 2). As a result, the river is characterized having a high ionic strength, as indicated by the EC.

Concentrations of trace elements (As, Cr, Pb, Cd, Cu, and Zn) in water and sediment exhibited extremely high

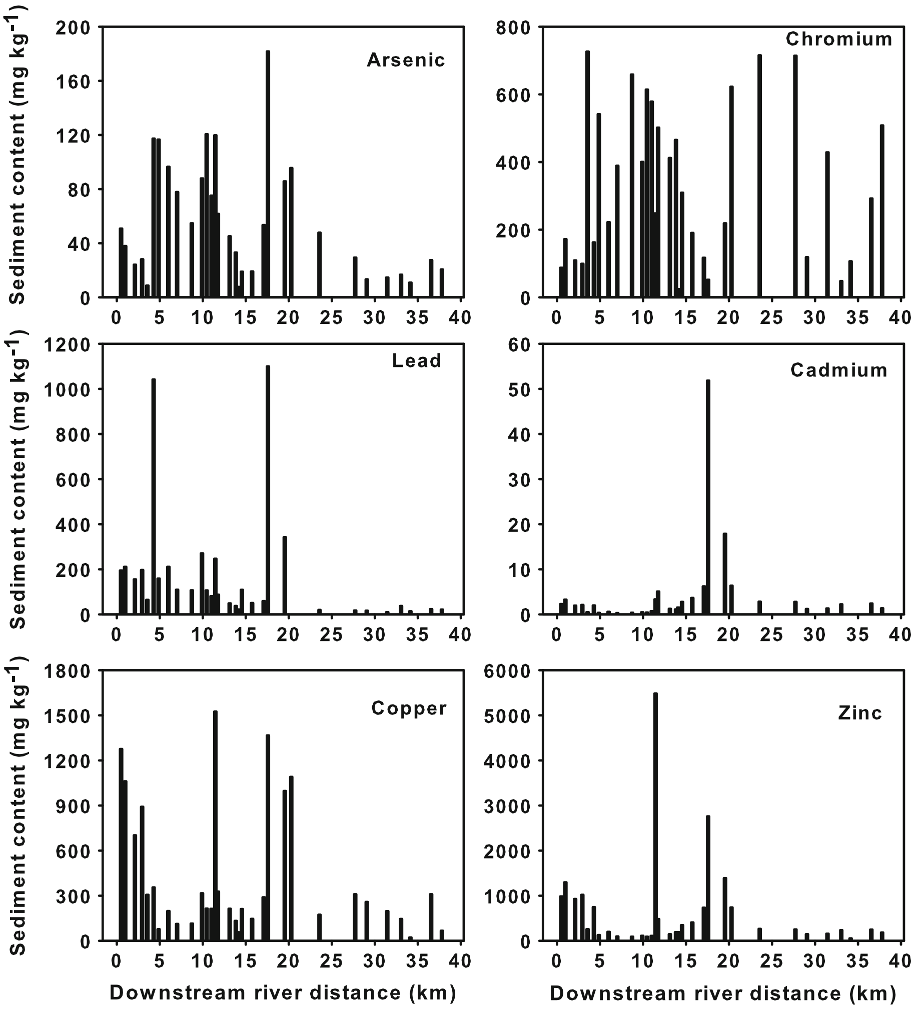

**Fig. 5** Total content of chromium, lead, cadmium, copper, and zinc in sediment samples along the sampled stream reach

variation. For all six elements, the measured total concentrations spanned three to four orders of magnitudes. This high spatial variation and localized peak concentrations (Fig. 4) clearly demonstrated the dominant impact of various sources on the spatial distribution of contaminants. Detailed examination of the concentration changes revealed that trace elements loadings might come from: the gold processing facilities, AMD from mine waste dumps, and other industrial activities. In addition, polluted ground water (Caruso and Dawson 2009) and release or resuspension of elements from contaminated sediment (Beltran et al. 2010) as a response to early diagenesis can also influence trace element concentrations.

As shown on Fig. 4, high total concentrations of all six elements were observed at the sampling site 17.6 km downstream of the headwaters, which was located 100 m downstream of the discharge of the Jinchiling mine, a major gold and silver processing facility. However, dissolved concentrations (As = 10.2 μg $L^{-1}$; Cr = 1.4 μg $L^{-1}$; Pb = 2.4 μg $L^{-1}$; Cd = 8.8 μg $L^{-1}$; Zn = 23.1 μg $L^{-1}$) were comparably low, except for Cu (3,589 μg $L^{-1}$). The observed element distribution captured the loading from this mining facility well. Even though wastewater treatment facilities had been installed, our monitoring data showed that a large loading of particulate elements were still discharged from this mine processing site. Another identifiable source was located approximately 4.3 km downstream of the headwaters. Our spatial analysis and field observations showed that discharges from a tailings pond and a metal processing factory mixed here and flowed into the river. The acidic discharge is characterized by its high loadings of dissolved arsenic and zinc, which was captured by a sampling point 50 m downstream of the discharge. In addition to the two major sources, several other sources might also contribute to the documented contaminant loading. For instances, a source of particulate Cr might exist at 8.7 km downstream of the headwaters and a source of dissolved Cu might exist on the lower reach of the Jiehe River. Our sampling results provide a basic dataset to explain the response of stream water quality to trace element loading from various sources.

Further studies will be conducted to account for the trace elements loadings from background, point, and non-point sources in the watershed.

Stream sediment can act as contaminant sink through chemical reactions such as precipitation and adsorption and physical processes including deposition and burial (Beltran et al. 2010; Caruso 2004). However, under favorable environmental conditions, trace elements accumulated in the sediment can be released back into the water through desorption, particle resuspension, and mineral dissolution. Under high flow conditions, particle resuspension contributes to the transport of metals in water and sediment. For the current study, the sampling was conducted during low-flow conditions with a relatively low-flow velocity. Our analysis shows that the particulate forms of these elements were mainly released from pollutant sources rather than particle resuspension.

The examination of trace elements in bed sediment can provide insight into the historical record of pollutant loading to the stream as well as predict future scenarios of trace element dynamics. Our results showed that large amounts of trace elements released into environment from various mining sources had accumulated in the bed sediment. The spatial pattern of sediment contamination varied between elements, which might due to: different history of source loadings, different chemical forms of elements, different reactions of elements on suspended particles and in bed sediments. Overall, reactive transport of these elements in water and sediment might be controlled by the hydrological conditions of stream flow and reactivity on water/solid interfaces. Detailed investigation of sediment contents suggested that mobility varied between different elements. For example, the mobility of Pb and Cd in sediment was rather limited, as indicated by the highly localized sediment concentration peaks (Fig. 5). Our observations showed that Pb and Cd contamination of sediment were essentially restricted to 3 km downstream of their sources. In contrast, Cr showed very high mobility along the stream reach, as reflected by high sediment contents along the entire stream reach. To explain the different behavior and fate of the contaminants, farther studies are being carried out to build numerical models to simulate reactive transport in water and sediment.

**Table 2** Correlation between log-transformed concentrations of trace elements in water and sediment

| | As | Cr | Pb | Cd | Cu |
|---|---|---|---|---|---|
| Sediment content | | | | | |
| Cr | 0.251 | | | | |
| Pb | 0.726** | −0.162 | | | |
| Cd | 0.227 | −0.292 | 0.315 | | |
| Cu | 0.432* | −0.104 | 0.614** | 0.672** | |
| Zn | 0.307 | −0.347 | 0.569** | 0.796** | 0.836** |
| Particulate Concentration in Water | | | | | |
| Cr | 0.416* | | | | |
| Pb | 0.493** | 0.487** | | | |
| Cd | 0.437* | 0.620** | 0.583** | | |
| Cu | −0.024 | 0.148 | 0.541** | 0.242 | |
| Zn | 0.370 | 0.675** | 0.728** | 0.591** | 0.367 |
| Dissolved Concentration in Water | | | | | |
| Cr | 0.456** | | | | |
| Pb | 0.799** | 0.477** | | | |
| Cd | 0.379* | 0.233 | 0.570** | | |
| Cu | 0.201 | 0.125 | 0.099 | 0.318 | |
| Zn | 0.370* | 0.235 | 0.628** | 0.644** | −0.263 |

* Significant at level of $p < 0.05$

** Significant at level of $p < 0.01$

Correlations between various elements in sediment, particulate, and dissolved forms were also analyzed (Table 2). Significant positive correlations between element pairs indicate that they have similar spatial pattern. For dissolved concentrations of the elements, the correlation analysis indicated that the discharge pattern of Cu was distinct from other elements, which can be explained by the high Cu loading in the lower Jiehe River. The correlation coefficients for elements in the sediment revealed that Cr had a different contamination pattern than the other five elements (As, Pb, Cd, Cu, and Zn), which suggest that Cr accumulated in sediment might come from sources other than mining. This is supported by anecdotal evidence that multiple textile and electroplating factories had existed in this area and closed during the last decade. In addition, although the particulate Cr concentration correlated with As, Pb, Cd, and Zn, no significant correlation was found between dissolved Cr with the other elements. We postulate that substantial amounts of the dissolved Cr might be due to release from sediment rather than pollutant discharges. Overall, four elements (As, Pb, Cd, Zn) had similar spatial distribution patterns in sediment, particulate, and dissolved forms, as indicated by significant positive correlations. Based on our spatial analysis and field observations, we conclude that the elevated concentrations of As, Pb, Cd, and Zn in the water and sediment of the Jiehe River was caused by gold mining.

To explore the relationship between elements in stream water and bottom sediment, correlation analysis was conducted on the six elements (Table 3). Significant positive correlation ($p < 0.05$) were found between particulate As, Cd, and Zn in the bottom sediment and particulate forms of the elements in the overlying water, which indicate that large fractions of particulate contaminants were deposited on the stream bed in the vicinity of the mine discharges. In contrast, no significant correlation was observed between concentrations of Cr and Cu in sediment and water, which

**Table 3** Correlation between log-transformed concentrations of different forms of trace elements

| | As | Cr | Pb | Cd | Cu | Zn |
|---|---|---|---|---|---|---|
| Sediment versus particulate | 0.500** | 0.018 | 0.324 | 0.553** | 0.223 | 0.401* |
| Sediment versus dissolved | 0.350* | −0.095 | 0.247 | −0.247 | 0.040 | −0.189 |
| Particulate versus dissolved | 0.711** | 0.243 | 0.126 | −0.336 | 0.156 | −0.425* |

* Significant at level of $p < 0.05$

** Significant at level of $p < 0.01$

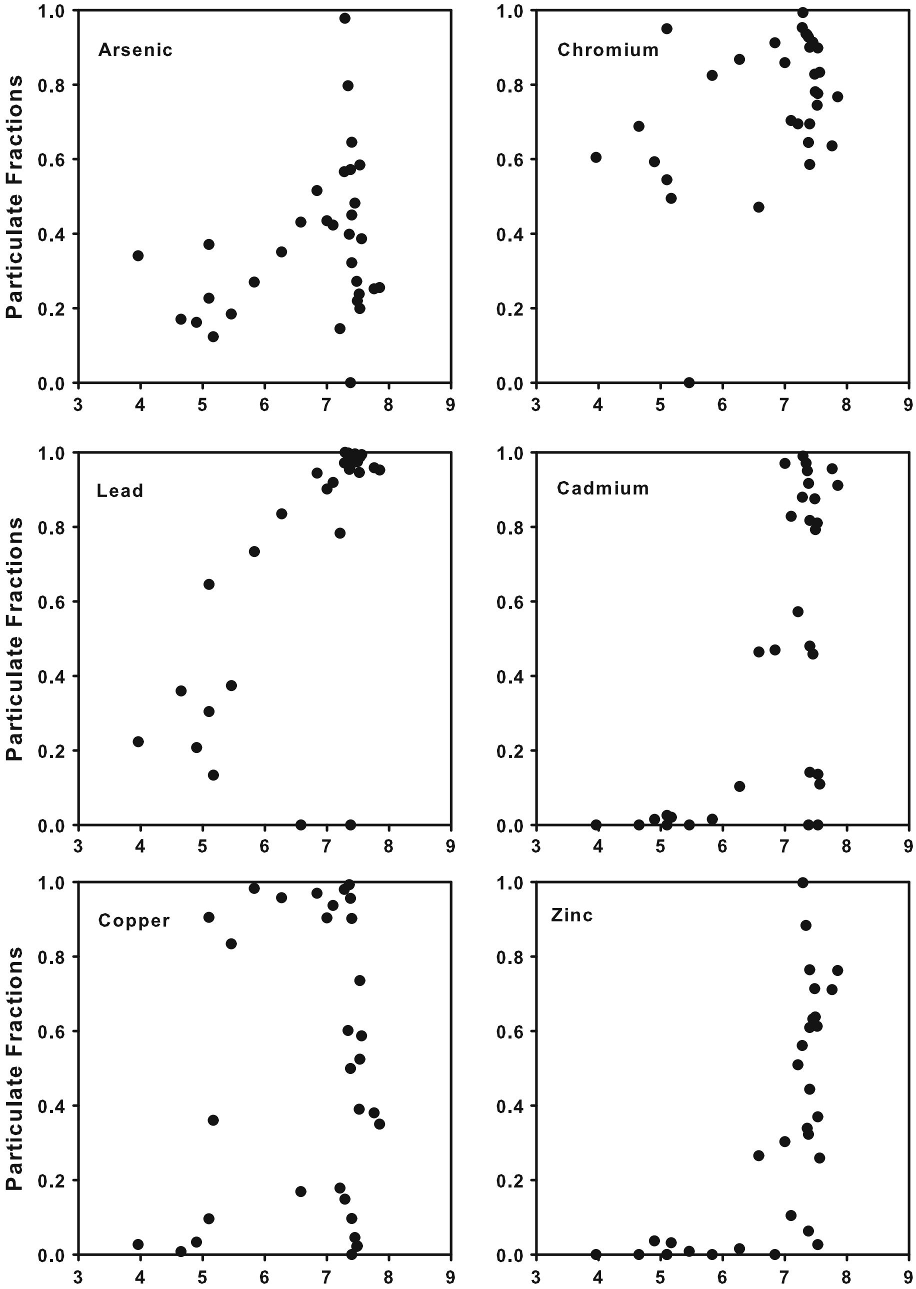

**Fig. 6** Particulate fractions of arsenic, chromium, lead, cadmium, copper, and zinc in stream water samples as a function of pH

supports the hypothesis that high Cr and Cu levels in the sediment might be due to historical pollutant sources, and not to the current loading pattern.

The dissolved concentrations of trace elements showed essentially no correlation with their sediment or particulate contents (Table 3), which suggests that release/retention on bed sediment surfaces or suspended particles might not be the controlling factor of dissolved forms of these elements. Geochemical properties of the water can also affect speciation and distribution of trace elements on water–solid interfaces (Broshears et al. 1996; Nordstrom 2011). We examined the distributions of elements in particulate and dissolved forms [represented by values of particulate fractions (particulate/total)] as a function of pH (Fig. 6). In general, dissolved As, Pb, Cd, and Zn increased under acidic conditions (low pH). The results indicate that kinetic dissolution from minerals containing As, Pb, Cd, and Zn might be the dominant in-stream process affecting the release of these elements in their dissolved form. Further characterization of sediment and suspended particles is needed, in combination with geochemical modeling, to reveal the interface reactions of the contaminants.

## Conclusions

Elevated concentrations of As, Cr, Pb, Cd, Cu, and Zn were observed in both water and sediment along the approximately 37.8 km of the Jiehe River that were sampled. Extremely high variations of the total concentrations, which spanned three to four orders of magnitudes, were observed for the six trace elements. The upper reach (4.3–11.0 km) was severely impacted by AMD, characterized by low pH and high levels of dissolved sulfate and metals (Fe/Al/Mn). Detailed examination demonstrated that two mining-related sources at 4.3 and 17.6 km downstream of the headwaters contributed most of the As, Pb, Cd, and Zn loading in the particulate forms. A large fraction of the contaminants released into the environment have accumulated in the sediment in the vicinity of the pollutant sources. In comparison, high levels of Cr and Cu in sediment might be due to historical pollutant sources rather than the current loading pattern. The results of this study provide information that will be essential to establish management and remediation plans for restoration of the Jiehe Watershed.

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