

Water chemistry and ecotoxicity of an acid mine drainage-affected stream in subtropical China during a major flood event

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Abstract

Field and laboratory work was carried out to investigate the chemistry and ecotoxicity of stream water affected by acid mine drainage in a tributary catchment of the Pearl River in subtropical China during a major flood that corresponded to a return period of 100 years. The results indicate that stream water was affected by acid mine drainage from the Dabaoshan mine at least to a distance of 25 km downstream of the mine water discharge point. It appears that H⁺ generated from sulfide oxidation in the waste rock dumps was readily available for exporting. The amount of H⁺ being discharged into the receiving stream depended on the volume of out-flowing waters. However, there was a lag time for the discharges of the metals. This may be attributed to the slower release of metals, relative to H⁺, because it might take more time for the dissolution of heavy metal-bearing compounds, particularly the sparsely soluble jarosites. Fe, Zn and Al were the major metals of potential toxicity contained in the AMD-affected stream water, followed by Mn, Cu, Pb, As, Cd and Ni. The concentrations of these metals in the water decreased rapidly down the stream. This corresponds with an increase in the concentrations of reactive heavy metal fractions in benthic mud down the stream, reflecting the precipitation of heavy metal compounds with increasing pH and their subsequent deposition in the streambed. Toxicity tests show that the AMD-affected stream water at 3.5 km downstream of the discharge point was highly toxic to the test organism. At 25 km downstream of the discharge point where stream water pH was as high as 5.75, marked toxic responses of the test organism were still observed.

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1. Introduction

Metal sulfides commonly occur in ore-containing geological formations [1,2]. Mining frequently results in the exposure of sulfidic rocks to atmosphere and subsequently causes oxidation of metal sulfides to produce sulfuric acid and liberate heavy metals [3–6]. Runoffs from such mine sites are acidic and the term “acid mine drainage” (AMD) has been used to describe this process. AMD could have extremely adverse impacts on the downstream ecosystems [7–9].

Although the overriding chemical mechanism of AMD has now been reasonably understood, accurate assessment or prediction of its ecological impacts is still difficult due to complexity of the processes involved. Environmental factors such as climatic, hydrological, geomorphic, geological and biological conditions

could significantly affect the rate of sulfide-derived acid generation, and the mode of transport and transformation of sulfide oxidation products. These factors are geographically variable and therefore it is expected that the characteristics of AMD vary from place to place. While there have been numerous studies on AMD, most of the work was conducted in the developed world such as the United States, Canada, Australia and European countries [10–15], with little information in literature being available for Asia, Africa and South America. In some developing countries, illegal mining that operates without consideration of environmental protection is common. For example in China, it was reported that there were over 30,000 cases of illegal mining throughout the country in 2003. Clearly, the poor mine site management, as experienced in illegal mining operations is an important factor that needs to be taken into account in AMD research in these areas.

So far, most reports on temporal variation of AMD were based on regularly monthly measurements [16–18]. However, it is likely that massive acid discharges occur during flooding

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following heavy rainfall events [19]. There appears to be limited work on detailed examination of chemistry and ecotoxicity of AMD-affected streams during flood events. Such information is needed for predicting the likely ecological impacts from and developing cost-effective remediation strategies for AMD. In particular, tailings impoundments under poor management are subject to dam failures during excessive rainfall and the subsequent flooding [20–22]. The resulting environmental disaster from the release of substantial amounts of contaminants to the downstream ecosystems is not always recognized in the developing countries. It is therefore expected that such information could also assist in raising the awareness of severe environmental impacts from AMD among the government regulators and mining operators in these countries.

We have carried out a research project in an extremely degraded subtropical China mine site where illegal mining has been out of control for many years [23]. In June 2005, a flood that corresponded to a return period of 100 years occurred in the study area. This provided an opportunity to examine the environmental impacts of AMD on the receiving stream in a rarely encountered situation. This article reports the chemical dynamics and ecotoxicity of the AMD-affected stream water during this event.

The ecotoxicity of some AMD-affected waters has been assessed using various test organisms such as aquatic macroinvertebrates [8,9], Asian clams [24], microbes [10,16], daphnia [25,26] and fish [27], etc. Daphnia are a type of microinvertebrates that has an important role in aquatic food chain [28]. Because of this and other favorable traits such as reproduction by cyclical parthenogenesis, being easily cultured in the laboratory, and high sensitivity to common toxicants, this zooplankton has been widely used as a test organism for toxicity assessment of environmental samples [29,30]. Standard methods using *Daphnia magna* as a test organism have been documented by major international organizations [31]. However, the geographical distribution of *D. magna* is primarily limited to areas of high and mid-latitudes [32] and thus this daphnia species is ecologically not relevant to the study area. From the viewpoint of ecotoxicity testing, it is more desirable to use indigenous species than imported non-indigenous species [33]. In this study, an indigenous species *Daphnia carinata* is used for ecotoxicological assessment of the AMD-affected stream water.

2. Materials and methods

2.1. Study site

The investigated stream is a headwater tributary (Hengshishui Creek) of the Beijiang River, which interconnects with the Xijiang River and the Dongjiang River in the deltaic area to form the so-called Pearl River system. The study site is located in the northern Guangdong Province, South China (24°31'37"N; 113°42'49"E) (Fig. 1). The area experiences a humid subtropical climate. A range of metal ores (mainly iron and copper ores) has been extensively mined by the state-run Guangdong Dabaoshan Mining Limited since 1970s. Since 1990s, illegal mining has

extensively taken place in the area and this has greatly accelerated the environmental degradation in the area [34,35].

The results [35, our unpublished data] from waste rock characterization indicate that a diverse range of sulfide minerals existed in this mine site, including pyrite, sphalerite, chalcopyrite, galena and alabandite. Total reduced inorganic sulfur ranged from 0.3 to 15% with a mean content of about 3.5%. In general, Cd was mainly in exchangeable, carbonate-bound and sulfidic forms; Pb was mainly in iron and manganese oxide-bound and sulfidic forms; and Cu and Zn were predominantly in oxide-bound and sulfidic forms. Yellow efflorescent salts were common in the mined areas during dry periods and chemical analysis indicates that these yellow materials consisted of soluble and sparsely soluble sulfate minerals, mainly iron sulfates, zinc sulfates, aluminium sulfates, manganese sulfates, copper sulfates and jarosites.

In the southern part of the Mt. Dabaoshan, a dam wall was constructed across a major valley to intercept the floodwater and retain the mud being transported from the waste rock stockpiles on the top of the mountain. This mud-retaining impoundment (MRI) was not designed for disposal of mine tailings. However, the illegal miners who operated without constructing their own tailings dams used the MRI for disposing of the mine tailings. This, in combination with severe soil erosion in the hill slopes, markedly accelerated the siltation of the MRI. Currently, the MRI no longer has capacity to retain any floodwater from the catchment and the acidic mine water continuously overflows downstream all the year round.

The mine water discharging from the MRI flows along an unnamed first-order tributary creek (referred to as AMD-affected creek hereafter) and joins Hengshishui Creek at a distance about 15 km downstream of the discharge point. Before the AMD-affected creek joins Hengshishui Creek, there are a few joining small creeks, which are mostly non-AMD-affected. Hengshishui Creek originates from a limestone area and the pH of the stream water is above 8 upstream of the junction between the AMD-affected creek and Hengshishui Creek. Downstream of the confluence, Hengshishui Creek flows southwards and joins the Wengjiang River at a distance approximately 35 km from the mine water discharge point.

2.2. Water sampling

Three stations were selected for water sample collection. The first one was located about 3.5 km (Liangqiao) downstream of the mine water discharge point; the second one was at a distance about 16 km (Shangba) downstream of the discharge point in Hengshishui Creek, i.e. immediately downstream of the confluence between the AMD-affected creek and Hengshishui Creek; and the third one was approximately 25 km (Wengcheng) downstream of the discharge point.

The heavy rainfall event leading to the June–July 2005 flood started from 20 June 2005. Within 6 days (20–25 June 2005), over 200 mm of rainfall were recorded (according to the Xinjiang Meteorological station that is located within the investigated area). Rainfall variation during the period from 20 June to 13 August 2005 can be seen from Fig. 2.

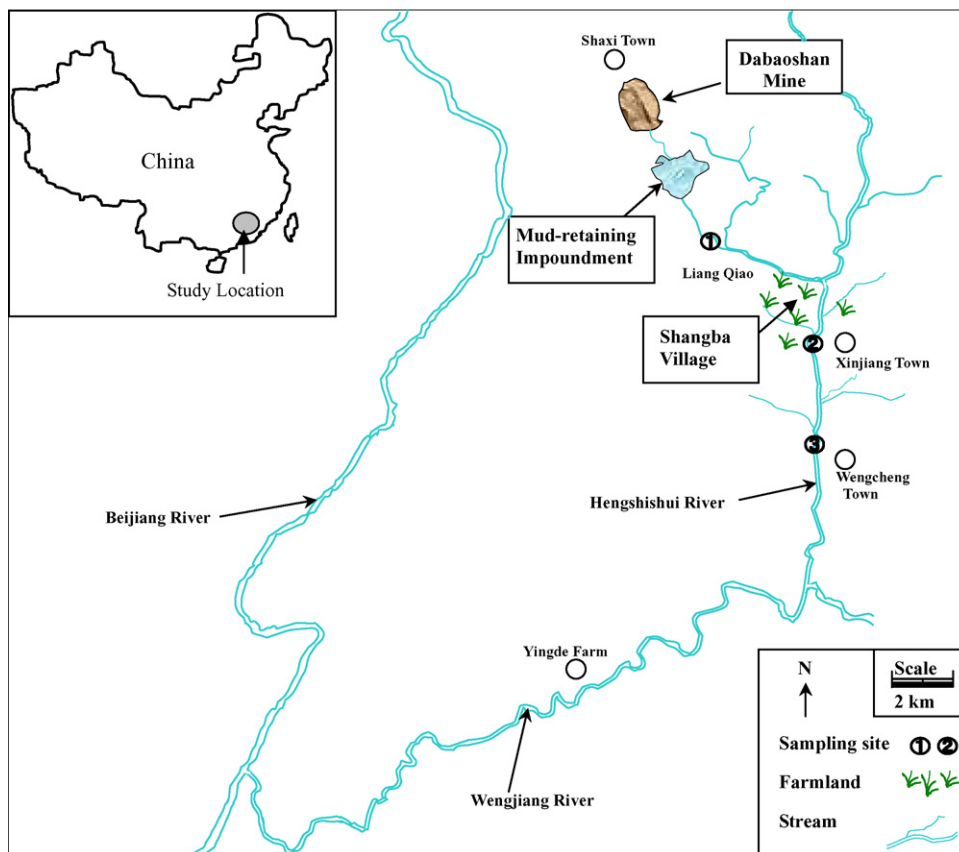


Fig. 1. Map showing the study area and sampling locations.

Water samples were collected from these three selected stations on three occasions: 26 June, 11 July and 5 August. Because hydrological stations were unavailable in the study area, relative elevations of river water level on each sampling occasion were determined by tapedown measurement from a fixed point at each of the water sample collection stations. The water samples were stored in a fridge within 6 h following collection.

2.3. Benthic mud sampling and pretreatment

Benthic mud samples were collected from the streambed at Liangqiao and Shangba stations following the flood event. At

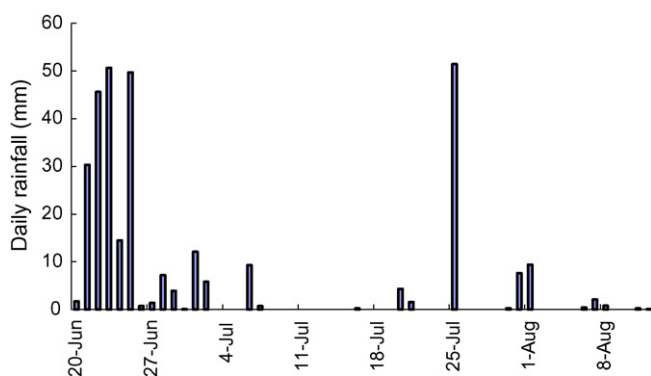


Fig. 2. Rainfall variation during the period from 20 June to 13 August 2005.

each location, approximately equal amounts of mud were collected from five spots to form a composite sample. The mud samples were stored in a fridge within 6 h following collection. The samples were oven-dried at 60 °C and then ground to pass a 2 mm sieve.

2.3.1. Chemical analysis

Prior to chemical analysis, the water samples were filtered using a 0.45 μm filter. pH was determined by a calibrated pH meter. Various heavy metals were measured by atomic absorption spectrometry (AAS). Al and As were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Total concentrations of selected heavy metals (Cu, Pb, Zn and Cd) in the benthic mud samples were determined by AAS, following digestion of a sample with HCl–HNO₃–HF–HClO₄. The improved BCR sequential extraction procedure [36] was used to separate the following three fractions of a heavy metal: (I) 0.11 M HCH₃COO-extractable metal, (II) 0.5 M NH₂OH·HCl-extractable metal and (III) 1 M NH₂CH₃COO-extractable metal after 30% H₂O₂ digestion. The concentrations of a heavy metal in all the extracts were determined by AAS. Fraction (I) is believed to include water-soluble, exchangeable and carbonate-bound heavy metal; Fraction (II) corresponds to heavy metal adsorbed to oxides of Fe and Mn, and Fraction (III) consists of organic-bound and sulfidic forms of a heavy metal.

2.4. Ecotoxicity test

2.4.1. The test organism

A stock of *D. carinata* was previously collected from the three-gorges reservoir in the middle reach of the Yangtze River (Changjiang River), China. Isolation of the starter clone for toxicity test purposes was done by repeatedly screening the population during a period of about 5 months in the laboratory. A healthy clone (Dc42) was eventually selected and cultured in a synthetic medium with green algae (*Scenedesmus obli.*) as the sole food source. *Scenedesmus obli.* was added to each culturing container at 8 a.m. every morning with an addition rate that made the density of the green algae in the container reaching approximately 2.0×10^5 cells/mL of water at the beginning of feeding.

The organisms used for toxicity testing were subject to individual culture. Individual neonates were placed in 1000 mL of culture medium in 1000 mL beakers. The culture medium was replenished with 50% of new medium every 3 days. On the water change days, 1 mL of food suspension was added to the new medium immediately after water change. The animals were allowed to grow up and produce offspring for being used in various experiments.

2.4.2. Culture conditions

Both mass and individual cultures were kept at 20 ± 0.5 °C and a day/night cycle of 14/10 h (light intensity: 1200 lx) [37,38]. Fully aerated tap water was used as a culture medium. The major water quality parameters were as follows: pH 7.20–7.35 (adjusted with HCl or NaOH solutions), DO: 7.2–8.4 mg/L; chloride: 30–32 mg/L; hardness (as CaCO₃): 82.0–91.2 mg/L and alkalinity: 56.1–58.0 mg/L; EC: 0.230 dS/m.

2.4.3. Determination of mortality percentage

Ten animals (2-day-old neonates) were placed in 100 mL test solution in each beaker (150 mL capacity). The animals were not fed during the experiment. Continuous observation was made during the first 8-h. The number of mobile animals was counted in each beaker. Those animals did not move within 15 s following gentle agitation of the beakers were considered as dead. The number of dead animals was used to calculate the mortality percentage (MP). All treatments were in six replicates.

2.4.4. Statistical analysis

The data are expressed as the mean \pm standard error of the mean. Significant differences were tested at 0.05 level by using Duncan's multiple range test.

3. Results

3.1. Water quality at Liangqiao (3.5 km)

Various chemical parameters obtained by analysis of water samples collected on three occasions at the Liangqiao station (3.5 km) are shown in Table 1. pH of the creek water was all below 3 with pH measured on 11 July 2005 being slightly lower than that measured on 26 June and 5 August. For Fe,

Table 1

pH and the concentrations of various metals in the floodwater samples collected from the Liangqiao station (3.5 km) on 26 June, 11 July and 5 August 2005

Chemical parameter	Unit	26 June 2005	11 July 2005	05 August 2005
pH		2.670	2.560	2.630
Al		–	63.900	–
Zn	mg/L	11.490	25.960	32.500
Mn	mg/L	9.410	–	25.550
Fe	mg/L	4.770	78.910	65.220
As	mg/L	0.009	0.041	–
Cd	mg/L	0.057	0.101	110.000
Ni	mg/L	0.077	0.164	216.000
Cu	mg/L	3.200	4.870	4.270
Pb	mg/L	1.170	7.150	0.710

Zn, As, Cd, Ni, Cu and Pb, there was a trend that each metal measured from the water sample collected on 26 June were lower than the same metal measured from the water sample collected on 11 July. Concentrations of metals measured from the water samples collected on 5 August were similar to those measured from the water samples collected on 11 July, except for Pb.

3.2. Water quality at Shangba (16 km)

Unlike the Liangqiao site where pH remained little change during the period of observation from 26 June to 5 August, pH of the stream water collected from the Shangba site increased over time. The pH of the stream water was 3.52, 4.39 and 5.96 on 26 June, 11 July and 5 August, respectively. Concentrations of various metals measured at different times were in the following decreasing order: 26 June > 11 July > 5 August, except for Fe, As and Pb which were higher in the water sample measured on 11 July than that measured on 26 June (Table 2).

3.3. Water quality at Wengcheng (25 km)

Water sample at Wengcheng site was not collected on 26 June due to technical problems. The available results show that pH of the stream water measured on 11 July and 5 August was 5.75 and 6.35, respectively. Concentrations of various metals were higher

Table 2

pH and the concentrations of various metals in the floodwater samples collected from the Shangba station (16 km) on 26 June, 11 July, and 5 August 2005

Chemical parameter	Unit	26/06/2005	11/07/2005	05/08/2005
pH		3.520	4.390	5.960
Al	mg/L	–	1.520	0.010
Zn	mg/L	2.120	1.670	0.090
Mn	mg/L	1.990	1.490	0.380
Fe	mg/L	0.030	8.960	0.010
As	mg/L	0.002	0.004	–
Cd	mg/L	0.012	0.007	0.001
Ni	mg/L	0.002	0.004	0.000
Cu	mg/L	0.800	0.360	0.000
Pb	mg/L	0.190	0.220	0.000

Table 3
pH and the concentrations of various metals in the floodwater samples collected from the Wengcheng station (25 km) on 26 June, 11 July, and 5 August 2005

Chemical parameter	Unit	26/06/2005	11/07/2005	05/08/2005
pH			5.760	6.350
Al	mg/L	–	0.930	0.010
Zn	mg/L	–	1.120	0.620
Mn	mg/L	–	1.080	0.010
Fe	mg/L	–	5.380	0.020
As	mg/L	–	0.008	–
Cd	mg/L	–	0.005	0.001
Ni	mg/L	–	0.000	0.000
Cu	mg/L	–	0.190	0.010
Pb	mg/L	–	0.090	0.000

in the water sample collected on 11 July than that collected on 5 August (Table 3).

3.4. Acute toxicity of the stream water at Liangqiao (3.5 km) on 11 July

Acute toxicity test using *D. carinata* as a test organism shows that when the creek water was diluted with aerated tap water with a dilution factor <17.85, all the tested animals died within 24 h. When the dilution factor increased to 100, the MP of the tested animals was 62, 94 and 100 at 24, 48 and 72 h, respectively. When the dilution factor was 1000, the MP recorded at various time intervals was still significantly higher, compared to that for the control, except that when the dilution factor increased to >178.57, there was no statistically significant difference in MP of *D. carinata* between the control and the test samples (Table 4).

Table 4
Acute toxicity of the creek water collected from the Liangqiao station (3.5 km)

Dilution factor	Mortality percentage (MP)			
	24 h	48 h	72 h	96 h
Control	3.82 ± 2.34 c	8.00 ± 4.90d	10.00 ± 6.32 c	19.09 ± 8.79 b
10.00	100.00 ± 0.00 a	100.00 ± 0.00 a	100.00 ± 0.00 a	100.00 ± 0.00 a
17.85	100.00 ± 0.00 a	100.00 ± 0.00 a	100.00 ± 0.00 a	100.00 ± 0.00 a
100.00	62.00 ± 9.17 b	94.00 ± 2.45 a	100.00 ± 0.00 a	100.00 ± 0.00 a
178.57	20.00 ± 9.49 c	62.00 ± 5.83 b	84.00 ± 5.10 b	100.00 ± 0.00 a
312.50	3.82 ± 2.34 c	39.09 ± 8.73 c	80.18 ± 3.31 b	100.00 ± 0.00 a
1000.00	9.09 ± 5.75 c	39.45 ± 10.99 c	84.00 ± 8.12 b	94.00 ± 2.45 a

Means with the same letter within the same column were not significantly different ($P > 0.05$) using Duncan's multiple range test.

Table 5
Acute toxicity of the creek water collected from the Shangba station (16 km)

Dilution factor	Mortality percentage (MP)			
	24 h	48 h	72 h	96 h
Control	3.82 ± 2.34 c	8.00 ± 4.90d	10.00 ± 6.32e	19.09 ± 8.79 b
1.00	100.00 ± 0.00 a	100.00 ± 0.00 a	100.00 ± 0.00 a	100.00 ± 0.00 a
1.33	16.00 ± 7.48 bc	65.00 ± 6.32 b	87.50 ± 5.81 ab	100.00 ± 0.00 a
1.78	13.64 ± 5.92 bc	44.12 ± 11.67 bc	64.20 ± 9.86 bc	95.96 ± 2.49 a
2.50	8.00 ± 5.83 bc	20.00 ± 7.07d	38.00 ± 11.14d	96.00 ± 2.45 a
3.12	23.27 ± 4.55 b	46.55 ± 8.53 bc	76.00 ± 12.49 abc	98.00 ± 2.00 a
5.55	12.00 ± 5.83 bc	29.45 ± 6.35 cd	60.73 ± 5.53 cd	96.00 ± 2.45 a

Means with the same letter within the same column were not significantly different ($P > 0.05$) using Duncan's multiple range test.

Table 6
Acute toxicity of the creek water collected from the Wengcheng station (25 km)

Dilution factor	Mortality percentage (MP)			
	24 h	48 h	72 h	96 h
Control	3.82 ± 2.34d	8.00 ± 4.90d	10.00 ± 6.32 c	19.09 ± 8.78 a
1.00	96.00 ± 2.45 a	98.00 ± 2.00 a	100.00 ± 0.00 a	100.00 ± 0.00 b
1.33	78.00 ± 8.60 ab	84.00 ± 5.10 ab	96.00 ± 2.45 ab	100.00 ± 0.00 b
1.79	62.00 ± 4.90 b	84.00 ± 5.10 ab	96.00 ± 4 ab	100.00 ± 0.00 b
2.38	62.00 ± 8.00 b	74.00 ± 8.90 bc	88.00 ± 4.90 ab	100.00 ± 0.00 b
3.13	35.82 ± 7.64 c	66.91 ± 5.44 bc	84.36 ± 3.92 b	100.00 ± 0.00 b
5.56	32.00 ± 9.17 c	58.00 ± 11.58 c	90.00 ± 4.47 ab	98.00 ± 2.00 b

Means with the same letter within the same column were not significantly different ($P > 0.05$) using Duncan's multiple range test.

3.5. Acute toxicity of the stream water at Shangba (16 km) on 11 July

The undiluted creek water caused 100% death of the tested animals within 24 h of exposure time. When the dilution factor was increased to 1.33, the MP at 24, 48, 72 and 96 h was 16.67%, 64.58%, 87.50% and 100%, respectively. When the dilution factor was between 1.78 and 5.55, there was no trend to show the decrease in MP with increasing dilution factor (Table 5).

3.6. Acute toxicity of the stream water at Wengcheng (25 km) on 11 July

The undiluted creek water caused 96%, 98% and 100% death of the tested animals within 24, 48 and 72 h of exposure time, respectively. When the dilution factor was increased to 1.33, the MP at 24, 48 and 72 h was 78%, 84% and 96%, respectively. When the dilution factor was between 1.78 and 5.55, MP decreased with increasing dilution factor for 24 and 48 h observation intervals. However, there was no trend to show the decrease in MP with increasing dilution factor for the 72 h observation interval (Table 6).

3.7. Heavy metals in benthic mud at Liangqiao and Shangba

Fig. 3 compares various heavy metals between the benthic mud samples collected from the Liangqiao station (3.5 km) and the Shangba station (16 km). Total Cu or each of the Cu(I), Cu(II) and Cu(III) in the benthic mud had lower concentration at the Liangqiao station than at the Shangba station. Total Pb in the benthic mud was much higher at the Liangqiao station than at the Shangba station; concentration of either Pb(I), Pb(II) or Pb(III) at both stations was similar and only accounted for a small proportion of the total Pb, particularly at the Liangqiao station. For both Zn and Cd, the total amount in the benthic mud was higher at the Liangqiao station than at the Shangba station, but each of the various fractions was lower at the Liangqiao station than at the Shangba station.

4. Discussion

The water level of the AMD-affected creek at the Liangqiao station (3.5 km) was 0.35 or 1.03 m higher on 26 June than on 11 July or 5 August, respectively (data not shown). The maintenance of low pH during the entire period of field investigation suggest that H^+ generated from sulfide oxidation in the contamination source (i.e. the waste rock dumps upstream of the Liangqiao station) was readily available for discharging and the amount of H^+ being transported outwards depends on the volume of out-flowing waters (both surface and underground runoffs). In contrast to H^+ , the concentration of heavy metals in the stream water at this station tended to increase with decreasing flow from 26 June to 5 August. The likely sources of metals in the floodwater were metal sulfates, which form efflorescent salts during dry periods. Possibly, the dissolution of metal sulfates requires an extended period of time and this may explain the observed lag time for the discharges of the heavy metals. This is particularly the case for the dissolution of sparsely soluble basic sulfate minerals such as jarosites [39]. Heavy metals, particularly Pb, are known to be associated with jarosites [40–42]. Previous research results suggested that jarosite became unstable after flooding in the presence of organic matter and a sufficiently long period of time was required for initiation of jarosite dissolution [39,43].

Melanterite is a ferrous iron sulfate mineral that frequently occurs as a major efflorescent salt in sulfidic mine waste dumps [44]. The iron in melanterite can be substituted by zinc, copper and other metals. It has been demonstrated that melanterite prefers copper over zinc and this results in a higher ratio of Zn/Cu during dry seasons and a lower ratio of Zn/Cu during wet seasons [45]. At the Liangqiao station which is immediately downstream of the mine water discharge point, the Zn/Cu ratio of the creek water on 26 June (during high flow immediately following heavy rainfall) was about 3.6. In contrast, on 5 August (during low flow after a period dominated by no rain days), the Zn/Cu ratio was about 7.6. These results are in good agreement with the above-mentioned research findings [45].

The Shangba station is about 1 km downstream of the confluence between the AMD-affected tributary and the main channel

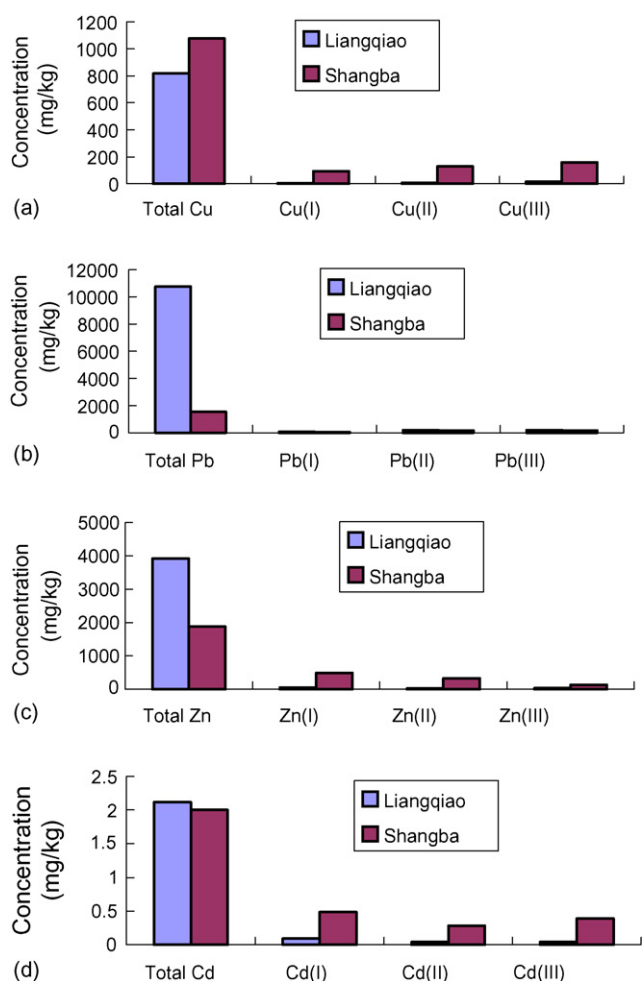


Fig. 3. Comparison of various heavy metals in the benthic mud between the Liangqiao station and the Shangba station.

of Hengshishui Creek. Hengshishui Creek originates from a limestone area and has a water pH > 8 upstream of the confluence with the AMD-affected tributary [23]. During periods of low flow, the stream water pH is around 6 at this station (our unpublished monthly monitoring data), which suggests that the slightly alkaline water from main channel of Hengshishui Creek has sufficient capacity to neutralize the acidic mine water from the AMD tributary in non-flooding period. Clearly, on 26 June immediately following the 6-day heavy rainfall, the water quality at the Shangba station was markedly degraded due to an acid input from mine site in excess of the acid neutralizing capacity of the alkaline water from Hengshishui Creek; until 11 July after another 15 days, the water pH was still below 4.5; on 5 August, the water pH was 5.96, which was still slightly lower than that in the usual situations. These results appear to suggest that the AMD from the Dabaoshan mine could cause over 1 month's depression of stream water pH at a location of 16 km downstream of the discharge point following an extremely large flood event even though the upstream water of the main channel was alkaline.

At Wengcheng station (25 km), the usual pH of stream water is around 6.3 (our unpublished monthly monitoring data). On 11 July, the recorded water pH at this station was 5.78, indicating the influence of the stream water by acidic mine water. Stream water pH at this station was not available for dates prior to 11 July. However, based on the pH results obtained at the Shangba station, it is reasonable to assume that stream water pH at the Wengcheng station should have been less than 5.78 prior to 11 July. The stream water pH recorded on 5 August indicates that water pH was back to usual at least before 5 August. In terms of pH, the influence of AMD on the stream water at a location of 25 km downstream of the discharge point is relatively minor.

The results obtained on 11 July are used to demonstrate the downstream variation of various chemical parameters from stations 1–3 (Fig. 4). Fe, Zn and Al were the major metals of potential toxicity contained in the AMD-affected stream water. The concentrations of these three metals decreased rapidly from Liangqiao to Shangba, and then decreased gradually to Wengcheng. Mn, Cu and Pb were in the second highest concentration group of soluble metals contained in the AMD-affected stream water. For Cu and Pb, the downstream variation in concentration was similar to that of Fe, Zn and Al. However, there was no marked change in Mn concentration among the different sampling locations. As, Cd and Ni were the lowest concentration group of metals contained in the AMD-affected stream water. The downstream variation in concentrations of the metals was similar to that of the first group.

Comparison of various heavy metals in the benthic mud between the Liangqiao station and Shangba station suggest that the more reactive forms (i.e. metal (I): soluble, exchangeable and carbonate-bound; metal (II): iron and manganese oxide-bound; metal (III): organic and sulfide-bound) of each examined heavy metal only accounted for very small proportions of the total concentration of that metal at the Liangqiao station. This indicates that heavy metals in the benthic mud immediately downstream of the mine site are predominantly in tightly bound forms that occur as structural parts of lattices of mineral crystals. Their

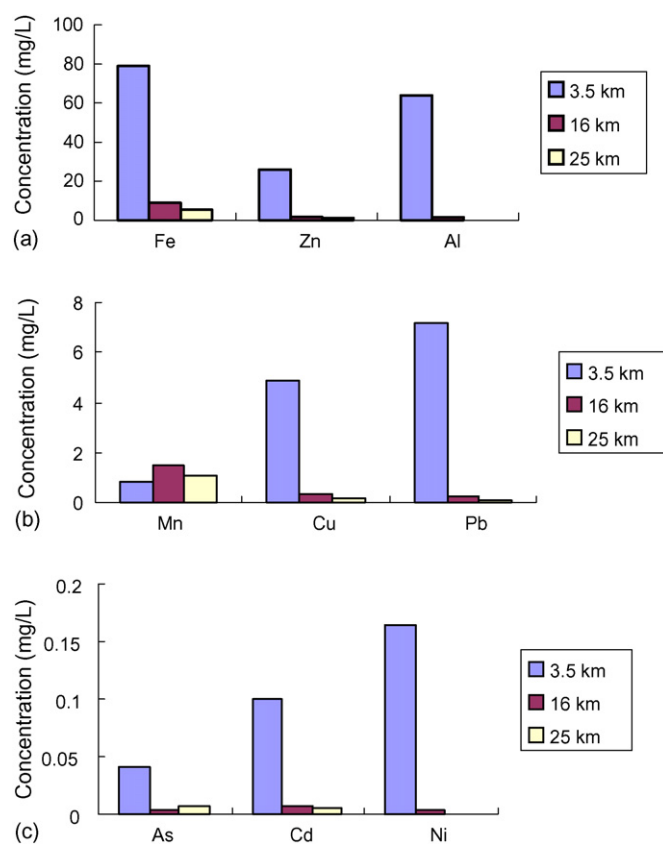


Fig. 4. Downstream variation of various chemical parameters from station 1–3 on July, 2005.

translocation from the mined areas to the creek was probably mainly through a physical rather than a chemical mechanism. Further downstream, the proportion of reactive forms in the total concentration of a heavy metal markedly increased. It is likely that the reactive heavy metal fractions mainly formed as a result of adsorption or precipitation of metals originally dissolved in the mine water. The pH of mine water at the Liangqiao station is constantly very low (our unpublished monthly monitoring data) and therefore may not favour the precipitation of heavy metal compounds. This explains why the benthic mud at this location contains very little reactive heavy metals. However, at the Shangba station, the stream water pH is much higher, particularly during the non-flooding period, which enhances the formation of heavy metal-containing precipitates. It must be realized that the above results reflect the long-term effects of AMD on differential accumulation of various heavy metals at different locations of a stream rather than the short-term effect of a single flood event.

At the Liangqiao station where the mine water was already diluted by surface runoffs from non-mining areas, toxic effects of the stream water were still observable even after 1000 times dilution with aerated tap water in the laboratory. The significant reduction in ecotoxicity of stream water at the Shangba station may be attributed to marked increase in pH at this location due to mixing of the AMD-affected tributary water with abundant stream water originating from limestone areas. At the Wengcheng station, the stream water pH was

much higher (5.75), compared to that at the Shangba station (4.39) on 11 July. It is interesting to note that the ecotoxicity of stream water, as indicated by the response of *D. carinata*, was even weaker at the Shangba station than at the Wengcheng station. Soucek et al. [46] reported that aquatic macroinvertebrates could be significantly impacted by acid mine drainage even in the river reach beyond the pH depression zone. He suggested that the major cause of acute toxicity to macroinvertebrates was the precipitation of aluminium in neutral conditions. This process is expected to take place when the stream water was diluted for ecotoxicity testing in the laboratory. The observed stronger toxicity to *D. carinata* at the Wengcheng station than at the Shangba station appears to suggest that the aluminium precipitation also have adverse effects on microinvertebrates.

5. Conclusion

During the June–July 2005 flood event that corresponded to a return period of 100 years, stream water was affected by acidic mine water from the Dabaoshan mine at least 25 km downstream of the mine water discharge point. Water acidity increased (as indicated by decrease in pH) with increasing flow while the concentration of heavy metals in the stream water at the Liangqiao station (3.5 km downstream of the discharge point) tended to increase with decreasing flow during the period of study. This suggests that H^+ generated from oxidation of metal sulfides contained in the waste rock dumps was readily available for discharging and the amount of H^+ being transported outwards depended on the volume of out-flowing waters. This may be attributed to the relatively slower release of heavy metals through dissolution of metal sulfates, especially the sparsely soluble jarosites that were present in efflorescent forms. Fe, Zn and Al were the major metals of potential toxicity contained in the AMD-affected stream water, followed by Mn, Cu, Pb, As, Cd and Ni. The concentrations of these metals in the water decreased rapidly down the stream. This corresponds with an increase in the concentrations of reactive heavy metal fractions in benthic mud down the stream, reflecting the precipitation of heavy metal compounds with increasing pH and their subsequent deposition with benthic mud in the streambed.

Acute toxicity tests show that the AMD-affected stream water at 3.5 km downstream of the discharge point was highly toxic to the test organism. At 25 km downstream of the discharge point where stream water pH was as high as 5.75, marked toxic responses of the test organism were still observed. The results here were in agreement with Soucek et al.'s finding that aquatic life could be significantly impacted by acid mine drainage even in the river reach beyond the pH depression zone.

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