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# Well water contaminated by acidic mine water from the Dabaoshan Mine, South China: Chemistry and toxicity

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**Abstract**

An investigation into well water quality was carried out in a rural area subject to irrigation with acidic mine water from the Guangdong Dabaoshan Mine, southern China. The results of water pH measurements from 112 wells in two different seasons suggest that the well water has been contaminated to varying degrees in the investigated Shangba floodplain (approximately 11 km south of the Guangdong Dabaoshan Mine). There is a trend that well water pH increased southwards, suggesting that the impacts of acidic irrigation water on groundwater decreased with increasing distance to the entry point of acidic irrigation water. Water quality monitoring results of the selected wells show that Cu and Cd in the water exceeded the limits set in the Chinese National Standards for Drinking Water (GB 5749-85) for the wells close to the irrigation water source. If the World Health Organization (WHO) standard was considered, Cd in some wells was almost 10 times as high as the WHO guideline value (0.003 mg $l^{-1}$). Water collected from the location closest to the acidic irrigation water source was acutely toxic to the test organism (*Daphnia carinata*) even after 51 time dilution. It is likely that the extremely high mortality rate of the local population reported for the study area is at least partly related to the high levels of heavy metals, particularly Cd in the drinking well water.


*Keywords:* Well water; Acid mine drainage; Groundwater; Heavy metal; Toxicity

## 1. Introduction

Acid mine drainage (AMD) is frequently observed in mine sites that contain sulfidic rocks (Alpers and Blowes, 1994; Morin and Hutt, 1997). AMD is caused by oxidation of metal sulfides (mainly pyrite) to produce sulfuric acid and liberate metals of potential toxicity. Much attention has been paid to the degradation of downstream aquatic ecosystems affected by AMD (*e.g.* Cherry et al., 2001; David, 2003; Lin et al., 2003; Gerhardt et al., 2004; Olias et al., 2004). However, AMD may also have marked impacts on agricultural land systems that are irrigated with the acidic mine water or AMD-affected stream water. The long-term use of the acidic, heavy metal-laden mine water could cause contamination of groundwater and agricultural soils, which in turn threatens the health of people who consume drinking water and foods derived from such contaminated land systems.

We have carried out an integrated research project in a hotspot area of mine-related contaminated site in the southern China. The objectives of this project were to investigate the impacts of mining activities on the ecosystems and human health, and to develop cost-effective techniques for remediation of mining-affected ecological environments. The results on the impacts of mine water on aquatic ecosystems and agricultural soils have been previously published (Lin et al., 2005,2007). Here, we

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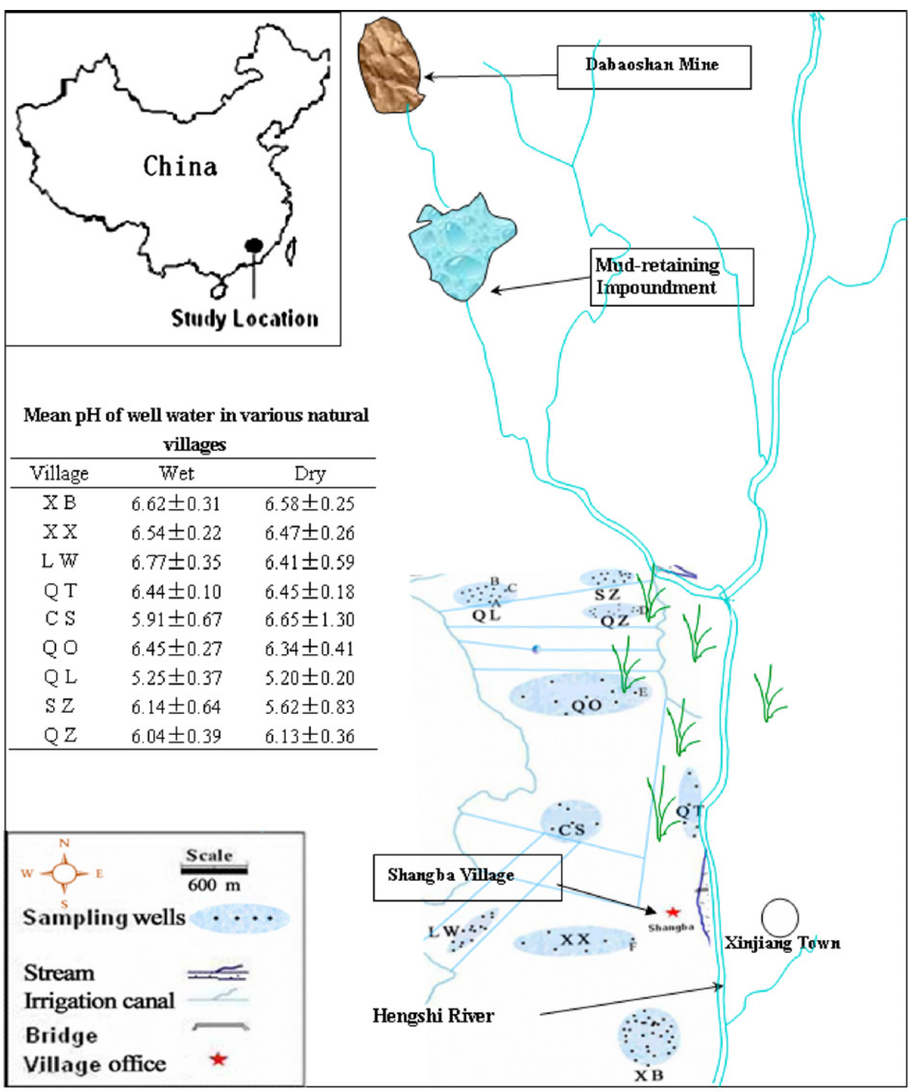
further present the results on the impacts of AMD on the groundwater, as indicated by the quality of well water in the same area.

## 2. Study site

The study site, the Dabaoshan Mine region, is located in the northern Guangdong Province (24°31′37″N; 113°42′49″E) (Fig. 1). This area has a long history of mining activities. Historical records show that the area was one of the largest copper mining and refining bases during the Song Dynasty (960–1279 AD). Since 1970s, large scale mining for iron and copper ores has been operated by the state-run Guangdong Dabaoshan Mining Corporation. Illegal mining for zinc/lead ores has also taken place intermittently since 1980s. 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 the 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, which has been used as a source of irrigation water for agricultural lands in the area.

Shangba floodplain (about 11 km south of the Guangdong Dabaoshan Mine) is selected for detailed examination of groundwater contamination. There are over 3000 people in the Shangba Administrative Village. This




Mean pH of well water in various natural villages

| Village | Wet | Dry |
|---|---|---|
| XB | 6.62±0.31 | 6.58±0.25 |
| XX | 6.54±0.22 | 6.47±0.26 |
| LW | 6.77±0.35 | 6.41±0.59 |
| QT | 6.44±0.10 | 6.45±0.18 |
| CS | 5.91±0.67 | 6.65±1.30 |
| QO | 6.45±0.27 | 6.34±0.41 |
| QL | 5.25±0.37 | 5.20±0.20 |
| SZ | 6.14±0.64 | 5.62±0.83 |
| QZ | 6.04±0.39 | 6.13±0.36 |

Fig. 1. Map of the Dabaoshan Mine region showing the location of sampling wells within the Shangba floodplain; mean well water pH measured on July 15, 2005 (representing wet season) and on January 11, 2006 (representing dry season) for the nine natural villages scattered in the study area is given as a table in the figure.

administrative village is nationally known due to extremely high mortality rate that has been attributed by the local people to contamination of their land by acidic mine water discharged from the Dabaoshan Mine, which has attracted great attention from the media. In this area, a truck canal was constructed to connect the AMD-affected stream water (at a location approximately 5 km downstream of the mine water discharge point) with the irrigation ditch system within the Shangba floodplain (refer to Fig. 1).

## 3. Research methods

### 3.1. Field methods

#### 3.1.1. Mine water sampling

As part of the stream water monitoring program, water samples were collected from a location near the entry point of irrigation water during the period from July 2005 to June 2006.

#### 3.1.2. Well water sampling

There are nine natural villages scattered within the Shangba floodpain: (1) Xiaba (XB), (2) Xinxi (XX), (3) Liangwu (LW), (4) Qiaotou (QT), (5) Caoshi (CS), (6) Qunlou (QO), (7) Qunlian (QL), (8) Shangzhang (SZ) and (9) Qunzhang (QZ) (refer to Fig. 1). Number of wells selected for investigation was 29 for XB, 10 for XX, 14 for LW, 5 for CS, 6 for QT, 10 for QO, 13 for QL, 12 for SZ and 13 for QZ. Therefore, there were 112 wells selected for this study. For all the selected wells, water samples were collected on July 15, 2005 (representing the wet season) and January 11, 2006 (representing the dry season) for measuring *in situ* pH.

For more detailed chemical analysis, six wells (marked as A, B, C, D, E and F; refer to Fig. 1) were further selected for long-term monitoring of water quality. Wells A, B and C were located in QL where the well water had the lowest average pH, as measured on July 15, 2005. Wells D, E and F were located in QZ, QO and XX, respectively. These three wells form a north–south transect running across the floodplain. Water samples from the six selected wells were collected monthly.

### 3.2. Laboratory methods

#### 3.2.1. Water analysis

pH and EC of the water samples were measured on site using a portable pH and EC meters, respectively. Water samples were stored in a fridge before being analyzed. Cu, Pb, Zn, Cd, Fe and Mn were measured by graphite furnace atomic absorption spectrometry. Al was measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

#### 3.2.2. Toxicity testing

Water samples collected from Wells A, D, E and F on January 11, 2006 were used for toxicity assessment using *Daphnia carinata* as a test organism. Prior to tests, neonates (2-d-old) from the individual cultures were transferred from the individual culture into a beaker containing ISO standard water ($T_{ISO\ water}$) and allowed to swim for 15 min to be cleaned up. This procedure was repeated in the second and the third $T_{ISO\ water}$ (*i.e.* the animals were cleaned up with ISO standard water three times; each for 15 min). Ten cleaned animals were then placed in each 150 ml beaker containing 100 ml test solution. 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. The 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), respectively. All treatments were in six replicates.

### 3.3. Statistical methods

Analysis on statistical significance of difference between means was performed using Pearson Correlation (SPSS 13.0 for Windows).

## 4. Results and discussion

### 4.1. Chemistry of stream water used as a source of irrigation water

Table 1 gives the monitoring results of the AMD-affected stream water, which has been used as a source of irrigation water for farmlands in the Shangba floodplain for many years. The results show that each chemical parameter was variable during the monitoring period. On average, pH was $2.9 \pm 0.3$, which indicates that the acidity was more than 600 times higher than the permit limit set in the Chinese National Standards for Irrigation Water Quality (GB5084-1992). As a result, concentration of various metals of potential toxicity was also extremely high. Among the investigated four metals, the concentration was in the following decreasing order: Zn > Cu > Pb > Cd. The concentration of the metals in the water was 1.6, 21, 1.76 and 13 times higher than the irrigation water permit limits (GB5084-1992) for Zn, Cu, Pb and Cd, respectively.

### 4.2. Well water chemistry

#### 4.2.1. Spatial variation on well water pH

The average pH of well water at each of the nine natural villages was all below 7 on all the two sampling occasions (refer to Fig. 1). There was variation in the mean pH of well water with QL having the lowest mean pH among the nine natural villages. These results suggest that the groundwater in the Shangba floodplain might have been affected by the acidic irrigation water and the lowest pH recorded in QL is attributable to its closest proximity to the inflowing irrigation water of AMD origin.

Table 1
Chemical characteristics of the AMD-affected stream water used for irrigation of farmlands in the Shangba Village (data derived from chemical analyses of water samples collected on 7 occasions during the period from July 15, 2005 to June 9, 2006)

| Parameter | 15/7/05 | 6/8/05 | 19/10/05 | 15/11/05 | 23/2/06 | 3/4/06 | 9/6/06 | Mean ± SD | GB |
|---|---|---|---|---|---|---|---|---|---|
| pH | 2.7 | 2.6 | 2.8 | 2.6 | 3.1 | 3.0 | 3.2 | 2.9 ± 0.2 | 5.5 |
| EC (dS $m^{-1}$) | 1.97 | 2.44 | 3.47 | 3.33 | 2.98 | 2.08 | 0.72 | 2.43 ± 0.95 | – |
| Cu (mg $l^{-1}$) | 3.19 | 3.36 | 1.29 | 3.52 | 1.09 | 3.63 | 2.10 | 2.60 ± 1.09 | 1.0 |
| Pb (mg $l^{-1}$) | 1.17 | 1.25 | 0.73 | 0.72 | 0.44 | 0.44 | 10.63 | 2.20 ± 3.73 | 0.1 |
| Zn (mg $l^{-1}$) | 11.49 | 17.45 | 38.00 | 32.56 | 42.82 | 35.40 | 0.92 | 25.52 ± 15.65 | 2.0 |
| Cd (mg $l^{-1}$) | 0.06 | 0.07 | 0.09 | 0.09 | 0.06 | 0.08 | 0.03 | 0.07 ± 0.02 | 0.005 |
| Fe (mg $l^{-1}$) | 4.77 | 8.64 | 107.90 | 29.50 | 230.07 | 103.79 | 15.49 | 71.45 ± 82.48 | – |
| Mn (mg $l^{-1}$) | 9.41 | 11.25 | 41.25 | 48.69 | 47.92 | 28.91 | 6.74 | 27.74 ± 18.61 | – |
| Al (mg $l^{-1}$) | | | 97.32 | 97.25 | | | 29.24 | 74.60 ± 39.29 | – |

GB: Chinese Standards for irrigation water quality (GB5084-1992).

*4.2.2. Chemical characteristics of groundwater collected from the six selected wells*

Water pH of the three wells (A, B and C) in QL was all below 5. There is a trend that well water pH increased from QL (Wells A, B and C) to QZ (Well D) to QO (Well E) to XX (Well F) (Table 2), suggesting that the impacts of acidic irrigation water on groundwater decreased southwards. The Chinese National Standards for Drinking Water (GB 5749-85) set a very low permit limit (0.002 mg $l^{-1}$) for Zn, which does not appear reasonable. World Health Organization (WHO) considers Zn "not of health concern at concentrations normally observed in drinking-water" and did not establish a guideline value in its third edition of the Guidelines for Drinking-water Quality (WHO, 2004). In the earlier version of the WHO Guidelines for Drinking-water Quality (WHO, 1993), the permit limit for Zn was 3 mg $l^{-1}$. Therefore, in this study Zn in the well water is not compared with its permit limit set in the Chinese National Standards for Drinking Water (GB 5749-85). Concentrations of Cu, Pb and Cd were not in excess of the permit limits set in the Chinese National Standards for Drinking Water (GB 5749-85) for Wells E (Cd was marginally exceeded the limit) and F; Pb was all below the limit for all the investigated wells; water Cu and Cd in Wells A, B, C and D were all exceeded the limits except for Cu in water from Well D, which was marginally below the limit.

WHO (2004) applied a guideline value of 0.003 mg $l^{-1}$ for Cd in drinking water, which is much lower than the permit limit (0.01 mg $l^{-1}$) for Cd set in the Chinese National Standards for Drinking Water (GB 5749-85). Water in most wells located in QL village had Cd concentration almost 10 times as high as the WHO standard.

*4.2.3. Temporal variation on water chemistry of Well A*

As mentioned above, well water in QL village had the lowest average pH and highest mean concentration of Cd among the investigated nine natural villages. Well A located in QL is selected to demonstrate the temporal variation on water quality parameters during the monitoring period from July 2005 to June 2006 (Fig. 2). Except for in February 2006, pH in the well water remained little change. Variation in EC was also minor except for in June 2006. There was observable variation on concentrations of various heavy metals during the one year monitoring period, particularly for Cu and Pb. It is interesting to note that concentration of various heavy metals in the well water was consistently the lowest on February 22, 2006 among the 12 sampling occasions. This corresponds very well with the highest pH recorded in the well water collected at the same time, suggesting that pH had an important control on the concentration of heavy metals in the well water.

*4.2.4. Correlation between various chemical parameters of the well water*

Data obtained from the chemical analysis of 72 well water samples (12 samples per year × 6 wells) were used to establish relationships among the six selected chemical parameters (pH, EC, Cu, Pb, Zn and Cd). Correlation matrix showing coefficients for variables is given in Table 3. Except for Pb, all chemical parameters were all significantly interrelated at 0.01 level. Cu, Zn and Cd were all negatively related with pH, indicating the control of $H^+$ activity on the concentrations of these metals in the well water. The poor relationship between Pb and other

Table 2
Chemical characteristics of the six selected wells in comparison with the guideline values set in the China National Standards for drinking water (GB 5749-85)

| Parameter | A | B | C | D | E | F | GB |
|---|---|---|---|---|---|---|---|
| pH | 4.6 ± 0.4 | 4.7 ± 0.2 | 4.9 ± 0.4 | 5.2 ± 0.3 | 5.8 ± 0.4 | 6.7 ± 0.2 | 6.5 |
| EC (dS $m^{-1}$) | 0.79 ± 0.13 | 0.79 ± 0.16 | 0.80 ± 0.14 | 0.89 ± 0.15 | 0.76 ± 0.15 | 0.39 ± 0.83 | – |
| Cu (mg $l^{-1}$) | 1.89 ± 0.76 | 1.93 ± 0.59 | 1.71 ± 0.74 | 0.94 ± 0.26 | 0.02 ± 0.06 | BDl | 1.0 |
| Pb (mg $l^{-1}$) | BDL | BDL | BDL | BDL | BDL | BDL | 0.05 |
| Zn (mg $l^{-1}$) | 3.81 ± 1.09 | 3.87 ± 1.12 | 4.03 ± 1.56 | 3.04 ± 0.78 | 1.22 ± 0.90 | BDL | – |
| Cd (mg $l^{-1}$) | 0.03 ± 0.01 | 0.03 ± 0.01 | 0.03 ± 0.01 | 0.02 ± 0.00 | 0.01 ± 0.01 | BDL | 0.01 |

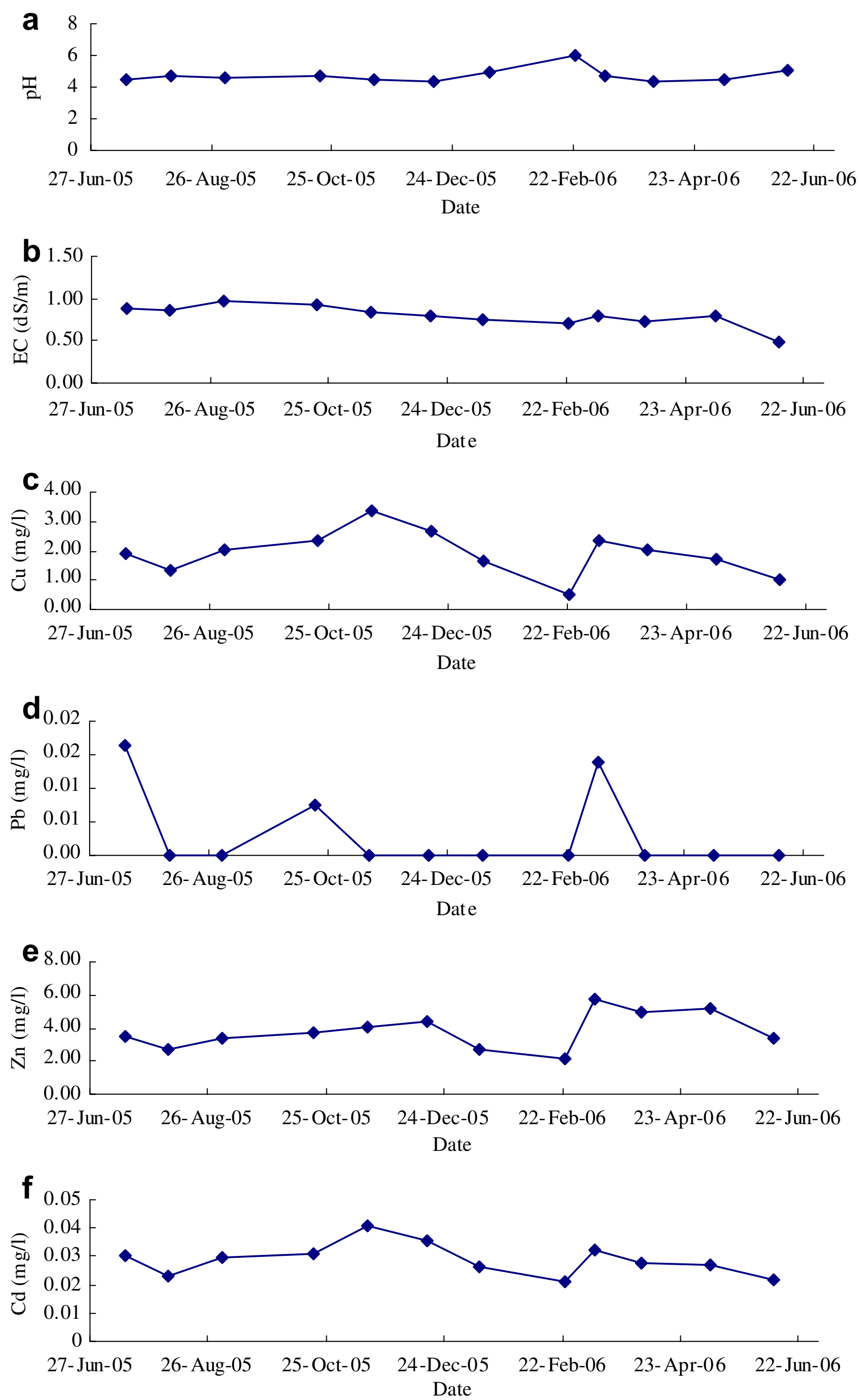



Fig. 2. Temporal variation in (a) pH, (b) EC, (c) Cu, (d) Pb, (e) Zn and (f) Cd in the water samples collected from Well A during the period of water quality monitoring.

parameters is attributable to the extremely low solubility of Pb under the pH range encountered in the well water.

### *4.3. Relationship of chemical parameters between irrigation source water and well water*

As demonstrated previously, well water in QL was most affected by the acidic mine water among the investigated natural villages. The mean of chemical parameters obtained from the monitoring results of three wells (A, B and C) was used to represent the well water quality in QL. These data were then plotted against the same chemical parameters measured from the irrigation source water on the same day (Fig. 3). Regression analysis indicates that certain relationships existed between irrigation source water and well water for a few chemical parameters: Cu had the highest $R^2$ value (0.8935), followed by Cd ($R^2 = 0.8255$), EC ($R^2 = 0.5978$) and pH ($R^2 = 0.4357$).

Table 3
Correlation matrix showing coefficients for variables (pH, EC, Cu, Pb, Zn and Cd in well water)

| | pH | EC | Cu | Pb | Zn | Cd |
|---|---|---|---|---|---|---|
| pH | 1 | −0.730** | −0.851** | 0.037 | −0.884** | −0.907** |
| EC | | 1 | 0.528** | 0.134 | 0.572** | 0.638** |
| Cu | | | 1 | −0.031 | 0.822** | 0.910** |
| Pb | | | | 1 | −0.099 | −0.030 |
| Zn | | | | | 1 | 0.905** |
| Cd | | | | | | 1 |

** Correlation is statistically significant at the 0.01 level.

No commendable relationships between irrigation source water and well water were observed for Zn and Pb. pH was much higher in the well water than in the irrigation source water while EC was much lower in the well water than in the irrigation source water. This indicates that much of the dissolved solids contained in the irrigation water were retained by the soils when the irrigation water infiltrated through the soil column.

## 4.4. Toxicity of well water

Table 4 shows that when the water collected from Well A was diluted with aerated tap water with a dilution factor of 51, the MP of the tested animals was 82%, 84%, 86% and 92% at 24 h, 48 h, 72 h and 96 h, respectively. For the water collected from Well D, when it is diluted with aerated tap water with a dilution factor of 31.2, the MP of the tested animals was 86%, 98%, 98% and 98% at 24 h, 48 h, 72 h and 96 h, respectively. Only the undiluted water from Well E showed certain toxicity to the test organism after 96 h, while there was no acute toxicity that was observed even for the undiluted water from Well F. Guilhermino et al. (2000) suggested that acute toxicity test with *Daphnia* can

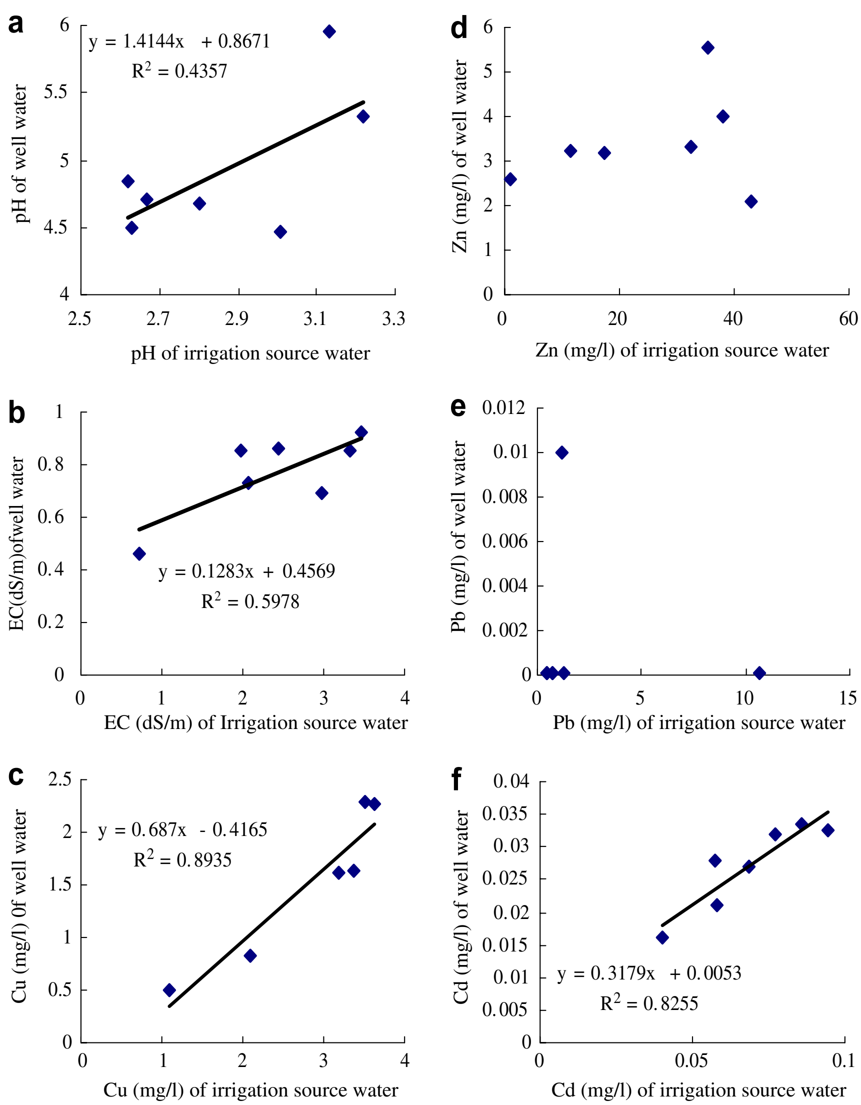



Fig. 3. Relationships of (a) pH, (b) EC, (c) Cu, (d) Zn, (e) Pb and (f) Cd between the irrigation source water and the well water collected from Qunlian (QL).

Table 4
Toxicity of water collected from various wells to *Daphnia carinata*

| Well No. | Dilution factor | Mortality percentage (MP) | | | |
|---|---|---|---|---|---|
| | | 24 h | 48 h | 72 h | 96 h |
| A | Control | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 1000 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 4.00 ± 2.45 |
| | 512 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 6.00 ± 2.45 |
| | 312 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 178 | 2.00 ± 2.00 | 4.00 ± 2.45 | 4.00 ± 2.45 | 4.00 ± 2.45 |
| | 100 | 38.00 ± 6.63 | 40.00 ± 8.37 | 42.00 ± 8.00 | 48.00 ± 5.83 |
| | 51 | 82.00 ± 8.60 | 84.00 ± 9.27 | 86.00 ± 7.48 | 92.00 ± 3.74 |
| D | Control | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 178 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 100 | 4.00 ± 2.45 | 4.00 ± 2.45 | 4.00 ± 2.45 | 10.00 ± 3.16 |
| | 51 | 24.00 ± 2.45 | 26.00 ± 4.00 | 28.00 ± 3.74 | 28.00 ± 3.74 |
| | 31.2 | 86.00 ± 6.00 | 98.00 ± 2.00 | 98.00 ± 2.00 | 98.00 ± 2.00 |
| | 17.8 | 100.00 ± 0.00 | 100.00 ± 0.00 | 100.00 ± 0.00 | 100.00 ± 0.00 |
| | 10 | 100.00 ± 0.00 | 100.00 ± 0.00 | 100.00 ± 0.00 | 100.00 ± 0.00 |
| E | Control | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 17.8 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 6.00 ± 4.00 |
| | 10 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 4.00 ± 2.45 |
| | 5.12 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 6.00 ± 2.45 |
| | 3.12 | 0.00 ± 0.00 | 0.00 ± 0.00 | 2.00 ± 2.00 | 22.00 ± 8.60 |
| | 1.78 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 12.00 ± 3.74 |
| | 1 | 0.00 ± 0.00 | 2.00 ± 2.00 | 28.00 ± 4.90 | 64.00 ± 5.10 |
| F | Control | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 |
| | 1 | 0.00 ± 0.00 | 0.00 ± 0.00 | 2.00 ± 2.00 | 2.00 ± 2.00 |

be used as an alternative to mammals in the prescreening of chemical toxicity. The current study confirms that part of the well water in the Shangba Village was severely contaminated. However, it must be realized that the drinking water-borne heavy metal is not the only source of heavy metal that has been intaken by the poisoned local people. Other possible pathways of heavy metal intake include soil ingestion and consumption of agricultural products derived from the contaminated soils (Zhou et al., 2004; Lin et al., 2005). It is likely that the potential health hazards that the local people face are caused by a combined intake of both drinking water-borne and contaminated food-borne heavy metals.

## 5. Conclusion

Results from this investigation indicate that the downstream land system has been severely contaminated by the acidic mine water draining from the Dabaoshan Mine. There is a trend that well water pH increased southwards, suggesting that the impacts of acidic irrigation water on groundwater decreased with increasing distance to the entry point of acidic irrigation water. Water quality monitoring results from selected wells show that Cu and Cd in the water exceeded the limits set in the National Standards for Drinking Water (GB 5749-85) for the wells close to the irrigation water source. Toxicity testing results reveal that the test organism (*Daphnia carinata*) had strong toxic response to the well water collected from locations close to the irrigation water source. The biotoxicity results here were in good agreement with the chemical data *i.e.* well water with lower pH and higher concentrations of heavy metals was more toxic to the test organism. The presence of excessive amounts of heavy metals, particularly Cd in the drinking well water is likely to be at least partly responsible for the reported high mortality rate in the study area.

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