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Active Treatment of Acidic Mine Water to Minimize Environmental Impacts in a Densely Populated Downstream Area

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Highlights

- Mine water treatment minimized environmental impacts in a densely populated area
- Unacceptable high pH due to lime overdosing during low- and medium-flowing period
- Downstream transport of trace elements especially Mn, Cr, Ba and Sr still took place
- Treated mine water as an irrigation water source has advantages and disadvantages
- Suggestions to improve treatment process and assessment of environmental risk

1 **Active Treatment of Acidic Mine Water to Minimize Environmental Impacts in a Densely**
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2 **Populated Downstream Area**
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169 Declaration of Interest: None

20 **ABSTRACT**

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4 31 Field monitoring was conducted to evaluate the effects of active mine water treatment on improving
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6 32 the water quality of receiving river in a densely populated catchment. Microcosm experiment was
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8 33 also performed to assess the effects of treated mine water on the growth of the vegetable and the
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11 34 uptake of trace elements by the vegetable. The results show that the treatment process was very
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13 35 effective in terms of raising the water pH (from below 3 to above 8 at the high-flow event) and
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15 36 removing trace elements (over 99% for most of the investigated trace elements) from the mine water.
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18 37 However, overdose of acid neutralizing materials might occur during low- and medium-flowing
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20 38 period, resulting in unacceptable high pH in the river reach immediately downstream of the treatment
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23 39 facility. To improve the treatment performance, more accurate estimation of lime requirement for
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25 40 treating the mine water can be done by a real-time monitoring for titratable acidity of mine water in
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28 41 the buffer pond to guide lime-dosing. It was found that downstream transport of trace elements still
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30 42 took place, especially for elements with variable valency such as manganese and chromium. The
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33 43 addition of lime also caused elevated concentration of barium and strontium in the river water, which
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35 44 requires assessment of their potential ecotoxicity to the downstream aquatic ecosystem. The use of
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37 45 treated mine water for irrigation purpose has both advantages and disadvantages; while it served as a
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40 46 source of irrigation water and tended to reduce the uptake of arsenic by the crop plant, the acid
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42 47 materials could still be introduced into the soils with the irrigation water and adversely affected the
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45 48 growth of the vegetable. It could increase the leaching of some trace elements especially arsenic
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47 49 from the soil to the shallow aquifer and cause contamination of groundwater.
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51 **Key words:** acid mine drainage, environmental impacts, water treatment, irrigation, heavy metal
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1 Introduction

Acidic mine water is a significant source of contaminants to the receiving environments (Mayes et al., 2008; Byrne et al., 2012). This drives development of remediation technologies for treating acid mine drainage (AMD) in an attempt to correct water acidity and immobilize water-borne heavy metals/metalloids (Johnson et al., 2005; Kefeni et al., 2017). Among various treatment technologies for acidic mine water, the active treatment is one of the most commonly used methods (Neculita et al., 2006; Nleya et al., 2016). This process involves the use of alkaline materials such as lime to neutralize the water-borne acids. The elevated pH level causes hydrolysis of potentially toxic metals such as aluminium (Al), cadmium (Cd), cobalt (Co), chromium (Cr), Copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) contained in the mine water, resulting in precipitation or co-precipitation of these metals (Akcil and Koldas, 2006; Bolan et al., 2014). In particular, the hydrolysis and polymerization of Fe ions could lead to formation of secondary iron compounds such as schwertmannite, jarosite, goethite, ferrihydrite, lepidocrocite etc. (Bigham et al., 1996) that have the capacity to adsorb various heavy metals and metalloids (e.g. As, Sb etc.).

Active mine water treatment method is much more costly, as compared to passive treatments methods (Johnson and Hallberg, 2002; Neculita et al., 2006). It is frequently used where there is a legal requirement for rapid removal of potentially toxic materials contained in the mine water in order to effectively eliminating or reducing their adverse impacts on the receiving environments. While, in theory, this outcome is expected, there are many factors that could affect the effectiveness of active mine water treatment under complex field conditions. To the best of our knowledge, there has been so far no detailed scientific report examining the effects of active mine water treatment on improving the quality of receiving environments, especially in the agricultural systems that are contaminated by the mine water.

66 For the past decade, intensive investigations into the mining-related environmental degradation
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27 were carried by our research team in a mine site (the Dabaoshan Mine) with over one thousand years
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68 of acid mine drainage history (since the Song Dynasty, 960-1279 AD) in the southern China.
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69 Significant impacts of AMD on mined lands (Liu et al., 2009; Lu et al., 2010), downstream river
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70 reach (Lin et al., 2007; Lu et al., 2011; Ma et al., 2011), farmlands (Lin et al., 2005),
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171 groundwater/drinking water (Chen et al., 2007) and crops (Lin et al., 2005) have been previously
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152 reported. In 2016, the state-run Dabaoshan Mining Company Ltd. installed a mine water treatment
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173 facility immediately downstream of the mine water discharge point. This provides an opportunity to
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194 observe the geochemical changes in the river and farmlands that are affected by mine water
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225 following the operation of active mine water treatment. In this study, the water monitoring results of
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246 the affected river reach for the three different seasons are reported. The effects of the treated mine
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277 water on the irrigated soils and the growing crop plants were also evaluated. These will assist in
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298 closing the knowledge gaps mentioned above.
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32 2 Study Site and Methods 33

34 35 36 37 38 39 40 41 42 2.1 Study Site

42 The study site (Latitude: 24°31'37"N; Longitude: 113°42'49"E) is located in the northern
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90 generation, leading to acidification of soils and draining water from the mined areas. Acid mine
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21 drainage becomes a serious environmental problem to the mine site and its surrounding areas. Acidic
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92 mine water with a pH as low as 2 was directly discharged into the downstream river, destroying
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93 aquatic life in the receiving river reach. During flood events, acidic mine water could impact on the
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94 river up to a distance over 25 km from the mine water discharge point (Lin et al., 2007). The
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195 population in the downstream area affected by the mine water was roughly estimated to be 79,704
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156 people with a population density of approximately 165 people per km².

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197 A mine water treatment facility (Fig. S1 in the Supplementary Materials) immediately
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208 downstream of the mine water discharge point was constructed and has started to operate since 2016.
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299 The mine water treatment process is illustrated in Fig. 2. This involves the use of sodium
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100 hypochlorite to accelerate the oxidation of ferrous ion in the mine water, followed by application of
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101 lime to neutralize the acidity. Flocculant was also added to speed up the sedimentation of suspended
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102 materials for rapid separation of the sludge from the treated water to be discharged into the
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103 downstream river reach.

104 2.2 Water Quality Monitoring

105 In-situ measurements of pH and electrical conductivity (EC) were conducted along the mine
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107 water-affected river reaches from the mine water discharge point to a distance approximately 25 km
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109 downstream of the discharge point for three selected seasons, which represented low-flow
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111 (10/12/2016), medium-flow (25/03/2017) and high-flow (01/06/2017) conditions. Six water
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113 sampling stations were set; (a) Station 1: the mine water discharge point; (b) Station 2: lime adding
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115 point; (c) Station 3: discharge point of the mine water treatment plant; (d) Station 4: about 7 km
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117 downstream of the mine water discharge point; (e) Station 5: about 13 km downstream of the mine
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119 water discharge point; and (f) Station 6: about 25 km downstream of the mine water discharge point.
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121 At each station, a composite water sample was obtained by mixing together multiple grab samples

collected from different spots across the cross section of the river. The composite samples were transported to the laboratory within 6 hours after collection for pre-treatment and laboratory analysis.

2.3 Plant Growth Experiment

2.3.1 The Soil Used in the Experiment

The mine water-contaminated soil (0-20 cm) used in the plant growth experiment was collected from an agricultural land that has been irrigated with river water contaminated by trace elements discharged from the mine area (Fig. 1). After air-drying, the soil was crushed to pass a 2-mm sieve prior to use for the plant growth experiment. The major physical and chemical characteristics of the soil are given in Table S1 (Supplementary Materials).

2.3.2 The Mine Water used for Irrigation of the Soil in the Experiment

The irrigation water used for the plant growth experiment was collected monthly from a location close to the soil sampling site (refer to Fig.1). Table S1 gives the mean value of pH, Eh, EC and various heavy metals in the treated mine water.

2.3.3 Pot Experiment Design

Ipomoea aquatica was used as the test vegetable plant for the experiment. One control and one treatment were set: (a) the control: irrigated with tap water; and (b) the treatment: irrigated with the treated mine water. About 2 kg of the contaminated soil were placed in a plastic pot (top diameter: 21 cm, base diameter: 18 cm; height: 17 cm). For each pot, three seedlings were transplanted at the beginning of the experiment. The pots were randomly placed in a green house. The experiment commenced on April 15, 2017 and the plants were harvested on June 15, 2017. For irrigation, 100 mL of mine water was added to the soil 4 times each week. Leachate was collected from the bottom of the pot following irrigation and stored at -4°C after acidification with nitric acid prior to

laboratory analysis. After harvest, the plants were rinsed with deionized water and the excess moisture on the surfaces of plants was removed using absorbent paper towels prior to sample analyses.

2.4 Analytical Methods

2.4.1 Determination of Trace Elements in Mine water and the Affected River Water

In the laboratory, the water samples were filtered using Whatman filter paper with a pore size of 25 μm . This gives a measurement of trace element pool including soluble, colloidal and suspended particles with a diameter less than 25 μm . The filtered solutions were then acidified with nitric acid and stored at -4°C prior to determination of trace elements by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700).

2.4.2 Determination of Trace Elements in Soil

To determine the total trace elements in the soil, 0.15 g of the ground soil sample ($<0.15\text{ mm}$) was digested with $\text{HNO}_3\text{-HF-H}_2\text{O}_2$ in a microwave digester. The extract was then used for determination of various trace elements by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700).

2.4.3 Determination of Plant Biomass and Tissue-borne Trace Elements

The above-ground and below-ground portions of the washed plants from the same pot were separated and oven-dried at 70°C in envelopes. The dry weight of biomass for both above-ground portion and below-ground portion was then obtained by weighing.

For determination of the plant tissue-borne trace elements, 0.25 g of the ground plant sample was digested with the mixed $\text{HNO}_3\text{-H}_2\text{O}_2$ solution in a microwave digester. The extract was then

used for determination of various trace elements by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700).

2.4.4 Determination of Trace Elements in the Leachate

All the leachate samples for either the control or the treatment collected during the period of the experiment were mixed to form a composite sample. Various trace elements contained in the solution samples were determined by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7700).

2.5 Statistical analysis method

Significant difference analysis was performed using SPSS (version 22.0). The statistical significance of various soil, leachate and plant parameters in the control and treatment was determined by an independent sample t-test at the 0.05 level and 0.01 level.

3 Results and Discussion

3.1 Downstream Variations in pH and EC

The pH of mine water at the discharge point was below 3.9, for the sampling occasion on 10/12/2016, 3.0 for the sampling occasion on 25/03/2017, and 2.7 for the sampling occasion on 01/06/2017, suggesting that the acidity of mine water increased from the low-flow to medium-flow to high-flow conditions (Fig 3a). Transport of sulfide oxidation products from the mined area to the downstream areas is driven by rains. Heavy rains and the associated floods tend to remove more acidic materials and this explains the much lower water pH recorded during the high-flow season. After addition of the acid-neutralizing agent (lime), the water pH rapidly increased with a value of 12.6, 10.5 and 8.2 being recorded at the discharge point of the mine water treatment facility. This suggests that overdose of lime took place at the low-flow and medium-flow events, resulting in unacceptably higher water pH, as compared to the Chinese river water quality standard (pH 6-9). The water pH then decreased to below 9 at the location approximately 13 km downstream of the mine

180 water discharge point. For the high-flow event, the water pH was around 8 all the way from the
181 treatment facility discharge point to the farthest water monitoring station (approximately 25 km
182 downstream of the mine water discharge point), meeting the requirement set for the Chinese river
183 water quality standard.

184 The water EC showed different spatial variation patterns at the different flow events (Fig 3b).
185 At the low-flow event, the EC at the mine water discharge point was very low (0.34 dS/m),
186 indicating that a very limited amount of soluble salts contained in the mine water. The sudden
187 increase in EC at the discharge point of treatment facility was almost attributable to the introduction
188 of additives during water treatment. The EC then decreased to a very low value at the location about
189 7 km, suggesting precipitation of insoluble compounds took place. Unlike the low-flow event, the EC
190 at the high-flow event was nearly 9 dS/m, indicating a very high concentration of soluble salts
191 contained in the mine water. Introduction of the additives at the treatment facility resulted in a sharp
192 drop in EC, indicating rapid precipitation of insoluble compounds due to acid neutralization.

3.2 Downstream Variations in Trace Elements

194 Although different downstream variation patterns were observed, it is clear that most of the
195 trace elements in the water suddenly decreased to a very low level after the treatment (Figs. 4, 5 and
196 6). For arsenic (As), Co, Ni, Pb, uranium (U) and Zn, the concentration at the mine water discharge
197 point was in the following decreasing order: high-flow event > medium-flow event > low-flow event.
198 During the low-flow event, the concentration of metals was much lower, as compared to that in the
199 medium- and high-flow events (Fig. 4). This corresponds very well with the water pH, suggesting
200 strong control of pH on the concentration of these metals in mine water. Cd, Cu, molybdenum (Mo)
201 and Mn also showed a similar trend (Fig. 5). However, for Cd, Cu and Mo, the concentration was
202 very close to each other for the medium-flow event and the high-flow event (Figs. 5a, 5b and 5c)
203 while the concentration of Mn at the mine water discharge was relatively high (>2000 mg/L) (Fig.

204 5d). Manganese is a metal with variable charge and its solubility is controlled by both pH and redox
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205 potential (Gotoh and Patrick, 1972). , Due to the presence of substantial amounts of ferrous iron
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206 (Fe^{2+}) in the mine water, Mn was likely to be reduced to Mn^{2+} , which is water-soluble irrespective of
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207 pH (Patrick and Verloo, 1998; Piszcz-Karaś et al., 2016).
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208 While the water-borne Cr at the medium- and high-flow events also showed a sudden decrease
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209 after neutralization treatment, the concentration of Cr in water at the low-flow event increased after
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210 treatment, suggesting introduction of Cr into the water from the additives used for the water
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211 treatment (Fig 6b). Unlike other trace elements, only less than 70% of Cr was removed from the
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212 mine water after the neutralization treatment. Since chromium might be present in anionic forms
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213 CrO_4^{2-} or Cr_2O_7 , which is not pH-dependent, acid neutralization did not necessarily result in the
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214 immobilization of water-borne Cr. This explains the restricted removal of water-borne Cr even after
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215 neutralization treatment. There was a marked increase in barium (Ba) and strontium (Sr) after
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216 neutralization treatment except for Ba at the low-flow event (Fig 6a and 6c). Ba and Sr are frequently
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217 associated with limestone (Kim et al., 1999), the feedstock for producing lime. It is interesting to
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218 note that mercury (Hg) at the mine water discharge point was higher at the low-flow event than at the
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219 medium-flow and high-flow events when only a trace amount of Hg was recorded (Gill and Bruland,
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220 1999; Holley et al., 2007; Richard et al., 2016).
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221 The current treatment method heavily relied on the use of lime for acid neutralization of the
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222 mine water, which was associated with a risk of overdosing to raise the pH of the treated mine water
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223 to a level exceeding the river water quality standard. To improve the treatment performance, it may
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224 be worthwhile to consider incorporating the uses of nanocomposites (Zou et al., 2016; Zhao et al.,
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225 2018) into the treatment process to more efficiently remove the water-borne heavy metals while the
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226 lime can be more conservatively used to reduce the risk of lime overdose.
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227 3.3 Effects of the Treated Mine Water on Soil, Leachate and Plants

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228 When the treated mine water was used as irrigation water for the plant growth, it still caused
 1 soil acidification with the pH significantly decreasing from 4.97 (the control) to 4.20 (the treatment)
 229 3 and the exchangeable acidity significantly increasing from 1.63 cmol/kg (the control) to 2.38
 4 230 6 and the exchangeable acidity significantly increasing from 1.63 cmol/kg (the control) to 2.38
 231 8 cmol/kg (the treatment). The EC value also significantly increased from 0.41 dS/m (the control) to
 9 232 10 0.78 dS/m (the treatment). These suggests that acid materials were introduced into the soil from the
 11 233 13 treated mine water. Although the treated mine water had a pH >7 when it was collected. It was
 14 234 15 observed that the pH of the treated mine water decreased over time (data not shown). It might be due
 16 235 18 to the oxidation of ferrous iron (Fe²⁺) contained in the treated mine water and the subsequent
 19 236 20 hydrolysis of Fe³⁺, which generate H⁺, as shown in the following chemical equations



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30 239 31 The irrigation water also resulted in an increase in soil Cu and Cd but a decrease in As and Ni.
 32 240 33 The soil under treatment had a high concentration of As, Cd, Cr, Pb and Ni but a low concentration
 34 241 35 of Cu and Zn. The lower soil-borne As and Ni in the treatment than in the control may therefore be
 36 242 38 attributed to the enhanced leaching of these elements from the soil during the period of the
 39 243 40 experiment.

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42
43 244 44 The biomass was higher in the control than in the treatment, suggesting that the use of the
 45 245 46 treated mine water disfavour the growth of the crop. In terms of accumulation of trace elements in
 47 246 49 the plant tissue, there was no significant difference between the control and the treatment except for
 50 247 51 Cd in the root portion and As in both root and shoot portions. It is clear that the use of the treated
 52 248 54 mine water as irrigation water tended to reduce the uptake of As by the crop plant, which may be
 55 249 56 attributable to the reduced availability of As due to enhanced leaching of As from the soil.

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59 250 **4 Conclusion and Recommendations**

251 Active treatment of the acidic mine water was very effective in terms of raising the water pH
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252 and removing trace elements from the mine water. However, overdose of acid neutralizing materials
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253 might occur during the low- and medium-flowing period, resulting in unacceptable high pH in the
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254 river reach immediately downstream of the treatment facility. It is therefore necessary to more
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255 accurately estimate the lime requirement for the treated mine water. This requires real-time
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256 monitoring for titratable acidity of mine water in the buffer pond to guide lime-dosing. The inability
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257 to completely immobilizing elements with variable valency such as Mn and Cr means that these trace
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258 elements could still be transported downstream to an extended distance, potentially affecting the
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259 aquatic ecosystem. The elevated concentration of Ba and Sr in the river water as a result of water
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260 treatment may also adversely affect the downstream environment. Therefore, their potential
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261 ecotoxicity needs to be assessed.
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262 There are advantages and disadvantages for the use of the treated mine water as a source of
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303 irrigation water. Acid materials could still be introduced into the soils and thus adversely affected the
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334 growth of the vegetable. It could also enhance the leaching of some trace elements especially arsenic
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265 from the soil to the shallow aquifer, causing contamination of groundwater. Since the local people no
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366 longer use the well water as the source of drinking water, the direct human health impact is not
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267 significant. As a result of trace element leaching, soil-borne As tended to decrease, which effectively
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268 reduced the uptake of As by the vegetable, especially in the edible portion.
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269 **Acknowledgements**

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272 (201804010313).
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273 **References**

57
58
59
60
61
62
63
64
65

-
- 274 Akcil, A., Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. J.
1
275 Clean. Prod. 14, 1139-1145.
2
3
4
5
276 Bolan, N., Kunhikrishnan, A., Thangarajan, R., Kumpiene, J., Park, J., Makino, T., Kirkham, M.B.,
7
277 Scheckel, K., 2014. Remediation of heavy metal(loid)s contaminated soils - To mobilize or to
9
278 immobilize? J. Hazard. Mater. 266, 141-166.
10
11
12
13
279 Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L., Wolf, M., 1996. Schwertmannite and
15
280 the chemical modeling of iron in acid sulfate waters. Geochim. Cosmochim. Ac. 60(12), 2111-
16
281 2121.
17
18
19
20
21
22
282 Byrne, P., Wood, P.J., Reid, I., 2012. The impairment of river systems by metal mine contamination:
23
24 a review including remediation options. Crit. Rev. Env. Sci. Tec. 42, 2017-2077.
25
26
27
28
284 Chen, A., Lin, C., Lu, W., Wu, Y., Ma, Y., Li, J. Zhu, L., 2007. Well water contaminated by acidic
29
30 mine water from the Dabaoshan Mine, South China: chemistry and toxicity. Chemosphere, 70,
31
32 248-255.
33
34
35
36
387 Fu, W.C., Pan, H.B., Kang, Z.Q., 2014. Studies on the composition characteristics of pyrite from
38
388 Dabaoshan polymetallic ore deposit, Northern Guangdong Province. Adv. Mater. Res. 904, 180-
39
40 183.
41
42
43
44
450 Gill, G.A., Bruland, K.W., 1990. Mercury speciation in surface freshwater systems in California and
46
47 other areas. Environ. Sci. Technol. 24, 1392-1400.
48
49
50
502 Gotoh, S., Patrick, W.H., 1972. Transformation of Manganese in a Waterlogged Soil as Affected by
51
52 Redox Potential and pH¹. Soil. Sci. Soc. Amer. Proc. 36, 738-742.
53
54
55
56
594 Johnson, D.B., Hallberg, K.B., 2002. Pitfalls of passive mine water treatment Rev. Environ. Sci. Bio.
57
58 1, 335-343.
59
60
61
62
63
64
65

-
- 296 Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. *Sci. Total.*
1
297 *Environ.* 338, 3-14.
3
4
5
298 Holley, E.A., McQuillan, A.J., Craw, D., Kim, J.P., Sander, S.G., 2007. Mercury mobilization by
7
299 oxidative dissolution of cinnabar (α -HgS) and metacinnabar (β -HgS). *Chem. Geol.* 240, 313-
9
300 325.
10
11
12
13
301 Kefeni, K.K., Msagati, T.A.M., Mamba, B.B., 2017. Acid mine drainage: prevention, treatment
15
302 options, and resource recovery: a review. *J. Clean. Prod.* 151, 475-493.
16
17
18
19
303 Kim, G., Yang, H.S., Church, T.M., 1999. Geochemistry of alkaline earth elements (Mg, Ca, Sr, Ba)
21
304 in the surface sediments of the Yellow Sea. *Chem. Geol.* 153, 1-10.
22
23
24
25
305 Li, C.Y., Zhang, H., Wang, F.Y., Liu, J.Q., Sun, Y.L., Hao, X.L., Li, Y.L., Sun, W.D., 2012. The
27
306 formation of the Dabaoshan porphyry molybdenum deposit induced by slab rollback. *Lithos.*
28
29
30
307 150, 101-110.
31
32
33
308 Lin, C., Lu, W., Wu, Y., 2005. Agricultural soils irrigated with acidic mine water: acidity, heavy
34
35
36
309 metals, and crop contamination. *Aust. J. Soil. Res.* 43, 819-826.
37
38
39
40 Lin, C., Wu, Y., Lu, W., Chen, A., Liu, Y., 2007. Water chemistry and ecotoxicity of an acid mine
41
42
43 drainage-affected stream in subtropical China during a major flood event. *J. Hazard. Mater.* 142,
44
45
46 199-207.
47
48
49
50
51 Liu, Y., Lin, C., Ma, Y., Lu W., Wu, Y., Huang, S., Zhu, L., Li, J., Chen, A., 2009. Toxic effects of
52
53 two acid sulfate soils from the Dabaoshan Mine on *Corymbia citridora var. variegata* and
54
55
56
57
58
59
60
61
62
63
64
65

-
- 316 Lu, W., Lin, C., Ma, Y., Huang, S., Si, C., Liu, Y., Li, J., 2010. Characteristics and potential
1 environmental consequence of weathered materials in the surface layer of a spontaneously
317 3 environmental consequence of weathered materials in the surface layer of a spontaneously
3 3
4
318 4 combusting mine spoil stockpile. *Appl. Geochem.* 25, 496-501.
6
7
319 Lu, W., Ma, Y., Lin, C., 2011. Status of aluminium in environmental compartments contaminated by
9 acidic mine water. *J. Hazard. Mater.* 189, 700-709.
10
320 10
321 11
12
13
321 Ma, Y., Lu, W., Lin, C., 2011. Downstream patterns of bed sediment-borne metals, minerals and
15 organic matter in a stream system receiving acidic mine effluent: A preliminary study. *J.*
16
322 16
323 17
18
323 18
20
21
22
324 22 Mao, W., Rusk, B., Yang, F.C., Zhang, M.J., 2017. Physical and chemical evolution of the
23 23
24
325 24 Dabaoshan porphyry mo deposit, South China: insights from fluid inclusions,
26
326 25
327 26
28
29
30
327 30 Mayes, W.M., Gozzard, E., Potter, H.A.B., Jarvis, A.P., 2008. Quantifying the importance of diffuse
32 minewater pollution in a historically heavily coal mined catchment. *Environ. Pollut.* 151, 165-
33 33
34 34
35
329 35 175.
37
38
330 38 Neculita, C.M., Zagury. G.J., 2006. Passive treatment of acid mine drainage in bioreactors using
40 sulfate-reducing bacteria. *J. Environ. Qual.* 36, 1-16.
41
42 41
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

337 Piszcz-Karaś, K., Łuczak, J., Hupka, J., 2016. Release of selected chemical elements from shale drill
 1 cuttings to aqueous solutions of different pH. *Appl. Geochem.* 72, 136-145.
 338
 3
 4
 5
 339 Richard, J.H., Bischoff, C., Ahrens, C.G.M., Biester, H., 2016. Mercury (II) reduction and co-
 7 precipitation of metallic mercury on hydrous ferric oxide in contaminated groundwater. *Sci.*
 340
 9
 10
 341 *Total. Environ.* 539, 36-44.
 12
 13
 342 Zhao, G., Huang, X., Tang, Z., Huang, Q., Niu F., Wang, X. 2018. Polymer-based nanocomposites
 15 for heavy metal ions removal from aqueous solution: a review. *Polym. Chem.* 9, 3562-3582.
 343
 16
 17
 18
 19
 344 Zou, Y., Wang, X., Khan, A., Wang, P., Liu, Y., Alsaedi, A., Hayat, T., Wang, X. 2016.
 21
 22
 345 Environmental remediation and application of nanoscale zero-valent iron and its composites for
 23 the removal of heavy metal ions: a review. *Environ. Sci. Technol.* 50(14), 7290-7304.
 24
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347 **Figure Captions**
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348 Fig 1 Location map showing the Dabaoshan Mine and the water monitoring stations along the
 33 affected river reaches
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350 Fig. 2 A schematic diagram showing the mine water treatment process
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351 Fig 3 Spatial variations in (a) water pH and (b) water EC from the mine water discharge point to the
 41 farthest monitoring station
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353 Fig. 4 Downstream variation in water-borne (a) As, (b) Co, (c) Ni, (d) Pb, (e) U and (f) Zn at the
 47 low-flow, medium flow and high-flow events
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355 Fig. 5 Downstream variation in water-borne (a) Cd, (b) Cu, (c) Mo and (d) Mn at the low-flow,
 52 medium flow and high-flow events
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357 Fig. 6 Downstream variation in water-borne (a) Ba, (b) Cr, (c) Sr and (d) Hg at the low-flow,
 58 medium flow and high-flow events
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359 **Table 1 Comparison of various soil, leachate and plant parameters between the control and the**
 360 **treatment**

Parameter	Control	Treatment
Soil		
pH	4.97±0.18	4.20±0.00*
EC (dS/m)	0.41±0.01	0.78±0.02**
Exchangeable acidity (cmol/kg)	1.63±0.00	2.38±0.07**
As (mg/kg)	23.0±1.66	15.9±0.41*
Cd (mg/kg)	0.23±0.02	0.53±0.07*
Cr (mg/kg)	25.4±3.20	24.9±4.08
Cu (mg/kg)	97.0±0.89	105±1.65*
Zn (mg/kg)	81.7±1.57	83.6±1.54
Pb (mg/kg)	50.1±3.76	43.2±4.95
Ni (mg/kg)	7.55±0.24	5.58±0.14**
Leachate		
As (µg/L)	13.2±1.35	40.1±0.34**
Cd (µg/L)	19.7±1.67	42.6±0.34**
Cr (µg/L)	28.5±0.99	46.3±0.21**
Cu (µg/L)	139±4.49	87.7±0.59**
Zn (µg/L)	134±3.77	91.6±1.02**
Pb (µg/L)	65.6±3.75	83.2±0.43*
Ni (µg/L)	18.5±1.12	41.9±0.26**
Shoot		
Dry biomass (g)	2.57±0.15	1.65±0.04**
As (mg/kg)	1.42±0.09	0.43±0.08*
Cd (mg/kg)	0.87±0.20	0.96±0.07
Cr (mg/kg)	25.2±0.47	22.2±1.73
Cu (mg/kg)	46.6±4.26	52.8±1.63
Zn (mg/kg)	125±13.7	146±7.14
Pb (mg/kg)	6.98±0.37	7.90±0.24
Ni (mg/kg)	5.27±0.90	3.68±0.21
Root		
Dry biomass (g)	0.90±0.09	0.64±0.03*
As (mg/kg)	5.43±0.08	4.83±0.16*
Cd (mg/kg)	0.94±0.01	0.59±0.06**
Cr (mg/kg)	19.9±1.39	27.1±3.21
Cu (mg/kg)	177±11.0	226±16.7
Zn (mg/kg)	140±2.40	153±13.8
Pb (mg/kg)	17.3±0.55	18.4±0.75
Ni (mg/kg)	7.63±1.25	9.85±0.42

361 The significant difference between the control and the treatment for each soil parameter was
 50
 362 determined by an independent sample t-test at the 0.05 level (an asterisk) and at the 0.01 level (two
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 363 asterisks).

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Figure 1

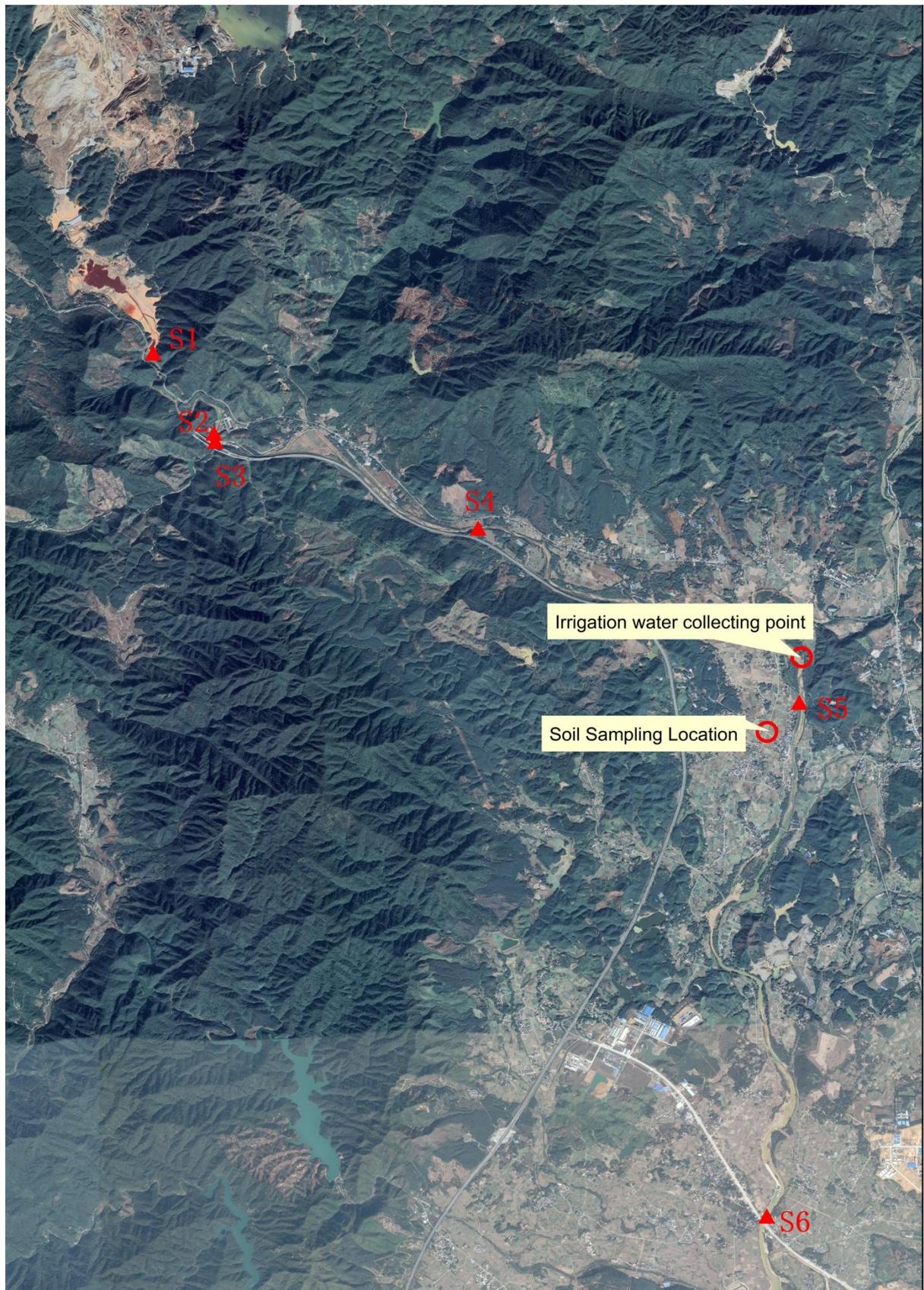


Fig 1 Location map showing the Dabaoshan Mine and the water monitoring stations along the affected river reaches

Figure 2

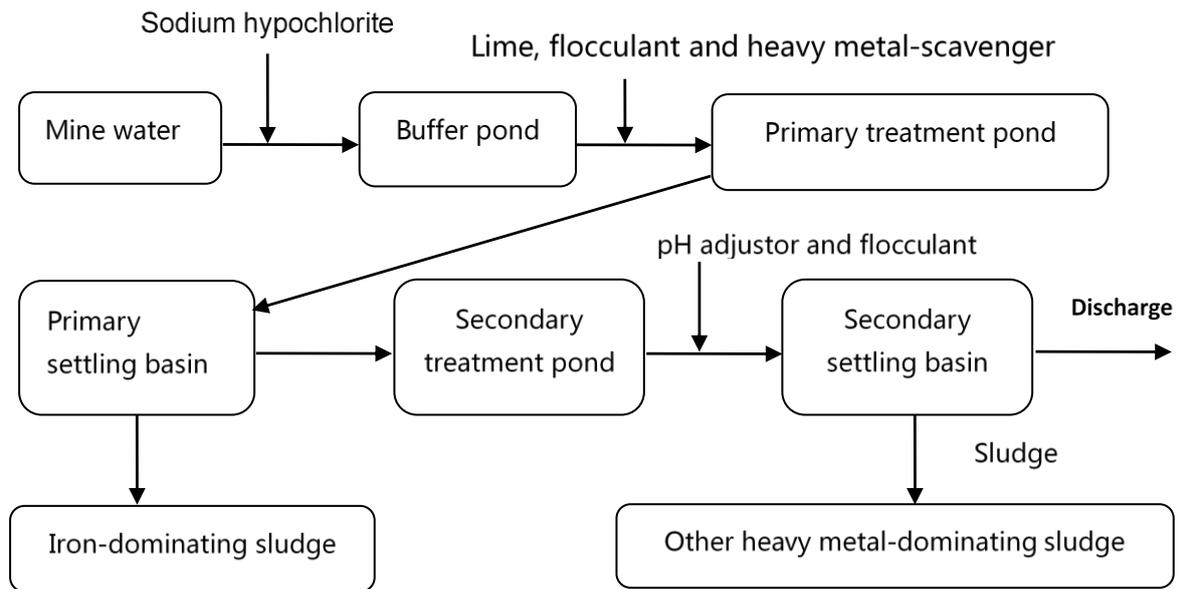


Fig. 2 A schematic diagram showing the mine water treatment process

Figure 3

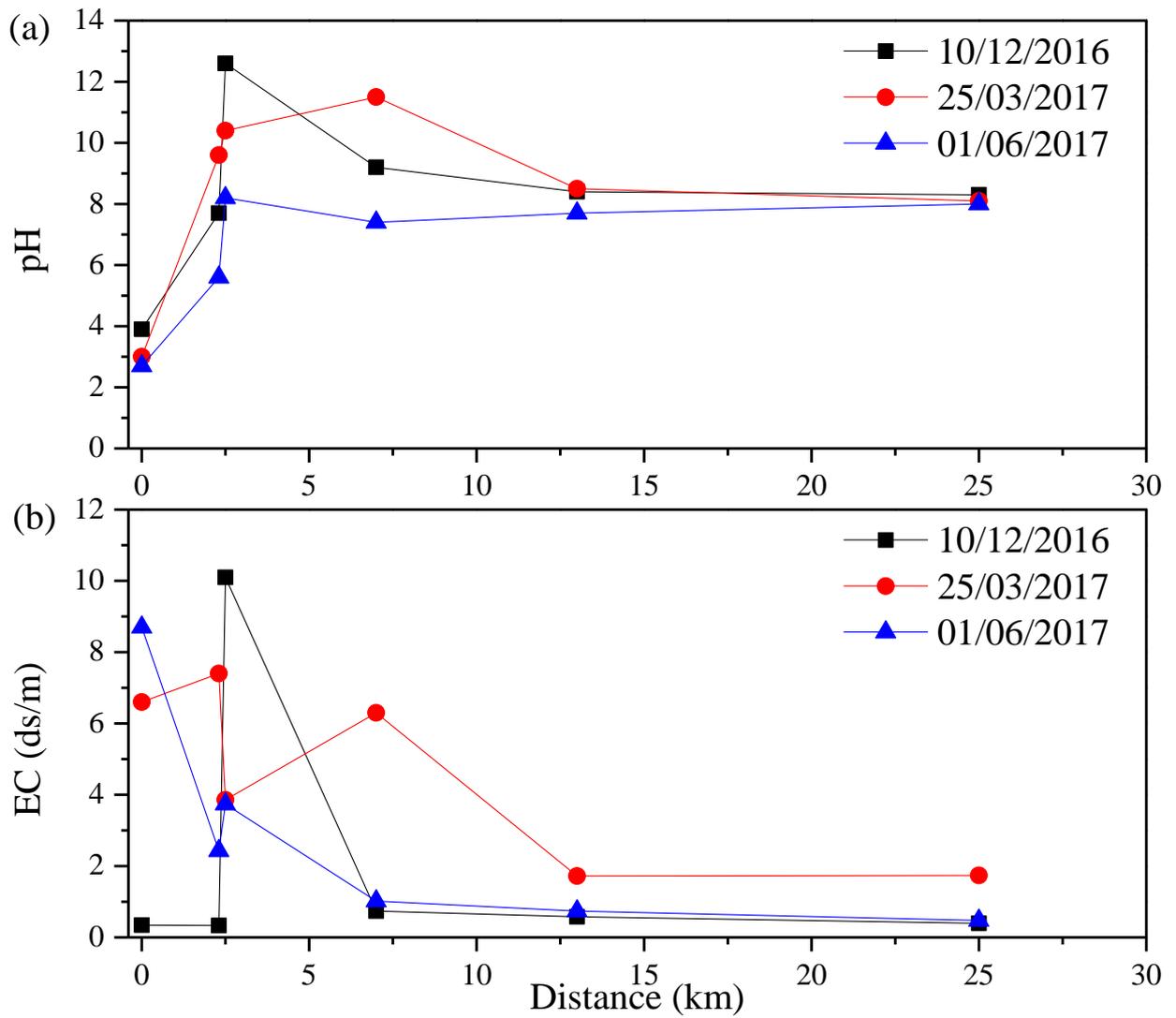


Fig 3 Spatial variations in (a) water pH and (b) water EC from the mine water discharge point to the farthest monitoring station

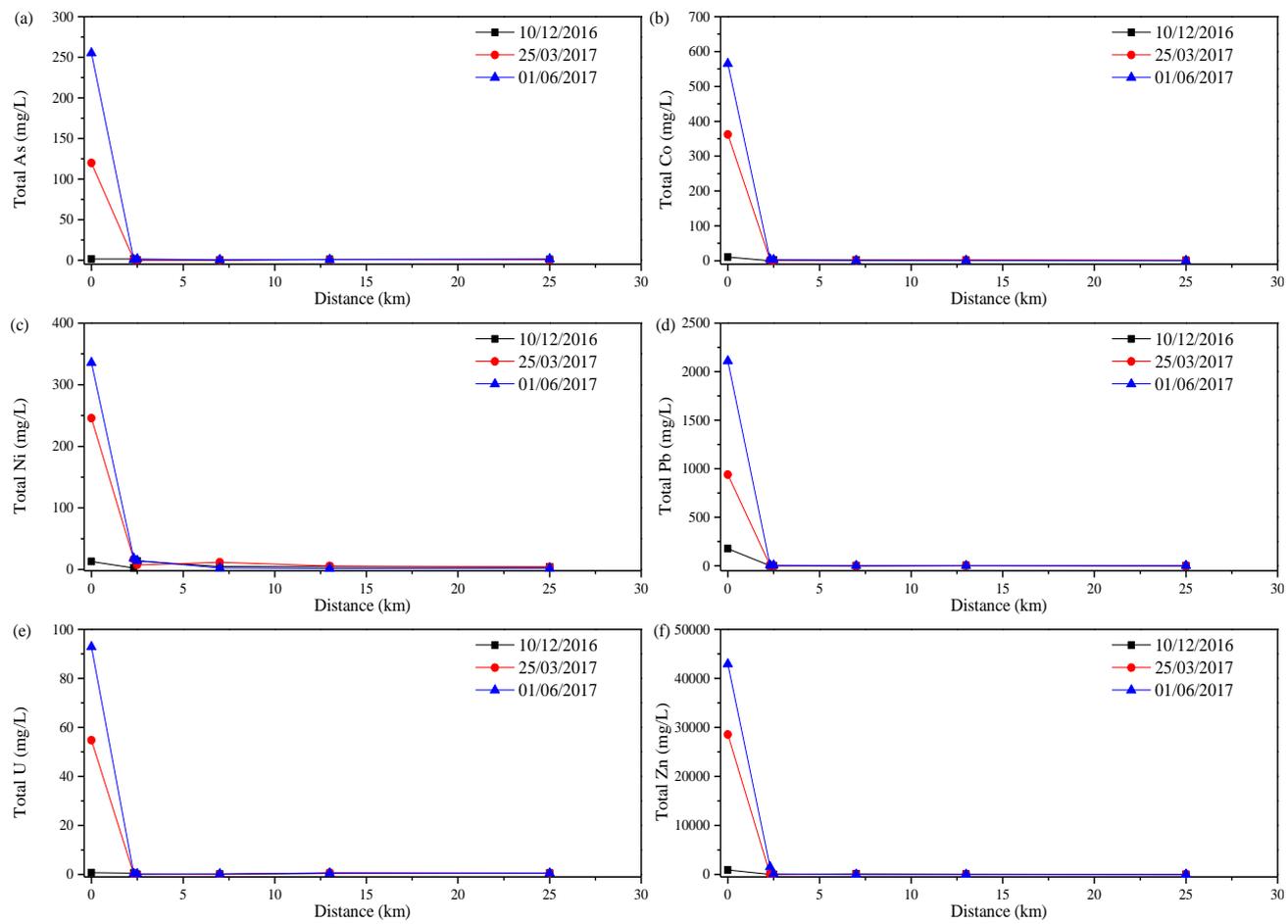


Fig. 4 Downstream variation in water-borne (a) As, (b) Co, (c) Ni, (d) Pb, (e) U and (f) Zn at the low-flow, medium flow and high-flow events

Figure 5

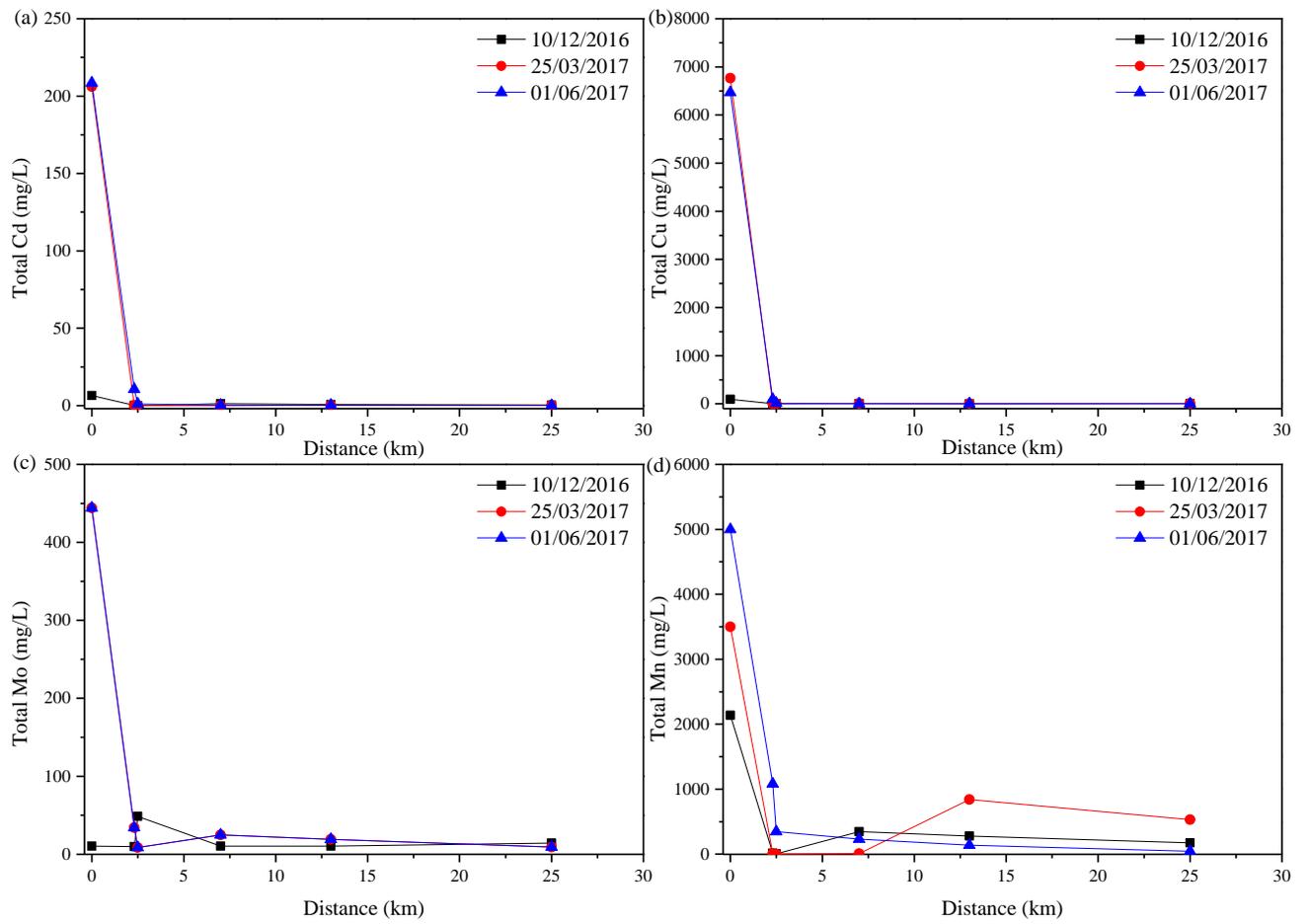


Fig. 5 Downstream variation in water-borne (a) Cd, (b) Cu, (c) Mo and (d) Mn at the low-flow, medium flow and high-flow events

Figure 6

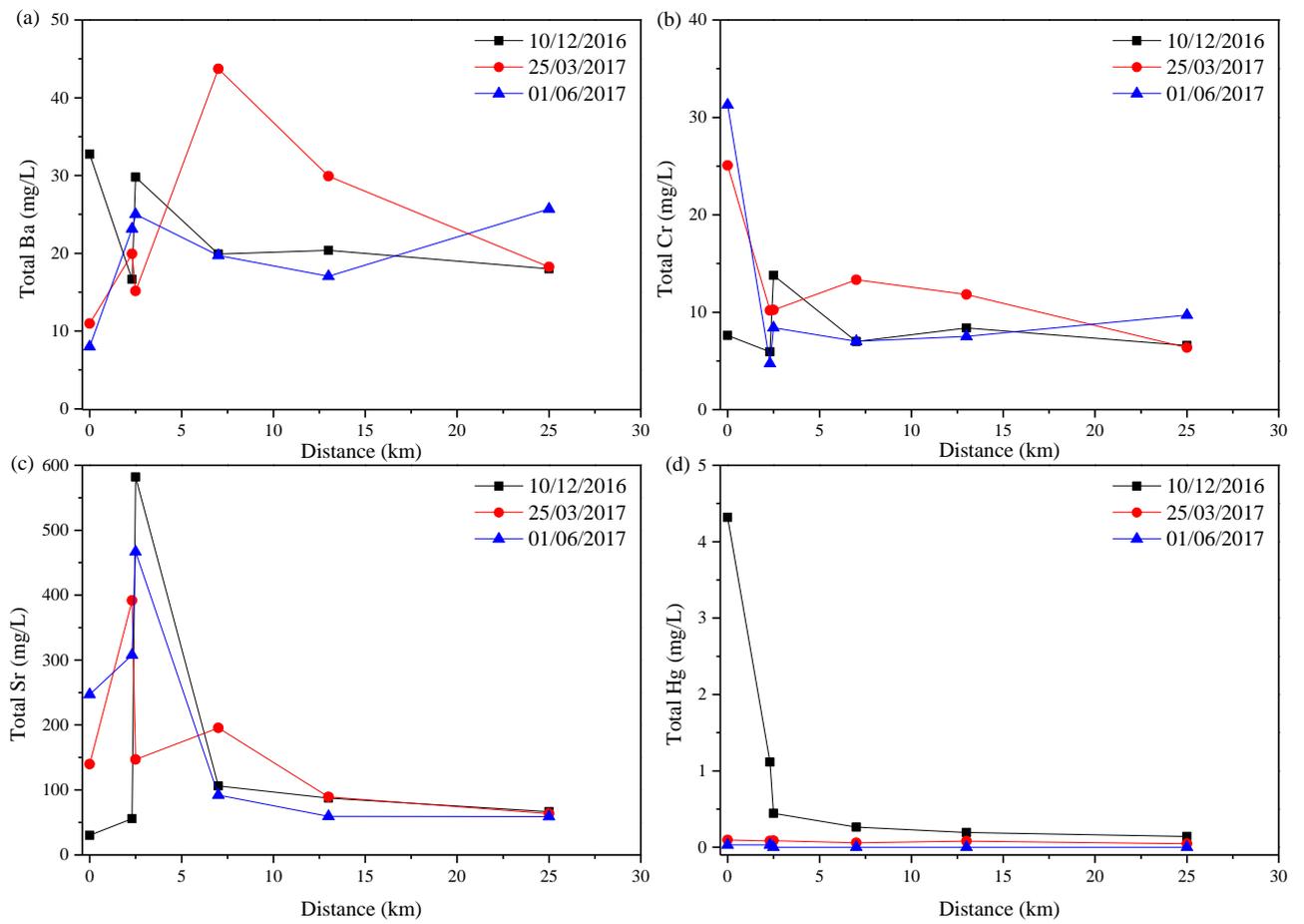


Fig. 6 Downstream variation in water-borne (a) Ba, (b) Cr, (c) Sr and (d) Hg at the low-flow, medium flow and high-flow events

Table 1 Comparison of various soil, leachate and plant parameters between the control and the treatment

Parameter	Control	Treatment
Soil		
pH	4.97±0.18	4.20±0.00*
EC (dS/m)	0.41±0.01	0.78±0.02**
Exchangeable acidity (cmol/kg)	1.63±0.00	2.38±0.07**
As (mg/kg)	23.0±1.66	15.9±0.41*
Cd (mg/kg)	0.23±0.02	0.53±0.07*
Cr (mg/kg)	25.4±3.20	24.9±4.08
Cu (mg/kg)	97.0±0.89	105±1.65*
Zn (mg/kg)	81.7±1.57	83.6±1.54
Pb (mg/kg)	50.1±3.76	43.2±4.95
Ni (mg/kg)	7.55±0.24	5.58±0.14**
Leachate		
As (µg/L)	13.2±1.35	40.1±0.34**
Cd (µg/L)	19.7±1.67	42.6±0.34**
Cr (µg/L)	28.5±0.99	46.3±0.21**
Cu (µg/L)	139±4.49	87.7±0.59**
Zn (µg/L)	134±3.77	91.6±1.02**
Pb (µg/L)	65.6±3.75	83.2±0.43*
Ni (µg/L)	18.5±1.12	41.9±0.26**
Shoot		
Dry biomass (g)	2.57±0.15	1.65±0.04**
As (mg/kg)	1.42±0.09	0.43±0.08*
Cd (mg/kg)	0.87±0.20	0.96±0.07
Cr (mg/kg)	25.2±0.47	22.2±1.73
Cu (mg/kg)	46.6±4.26	52.8±1.63
Zn (mg/kg)	125±13.7	146±7.14
Pb (mg/kg)	6.98±0.37	7.90±0.24
Ni (mg/kg)	5.27±0.90	3.68±0.21
Root		
Dry biomass (g)	0.90±0.09	0.64±0.03*
As (mg/kg)	5.43±0.08	4.83±0.16*
Cd (mg/kg)	0.94±0.01	0.59±0.06**
Cr (mg/kg)	19.9±1.39	27.1±3.21
Cu (mg/kg)	177±11.0	226±16.7
Zn (mg/kg)	140±2.40	153±13.8
Pb (mg/kg)	17.3±0.55	18.4±0.75
Ni (mg/kg)	7.63±1.25	9.85±0.42

The significant difference between the control and the treatment for each soil parameter was determined by an independent sample t-test at the 0.05 level (an asterisk) and at the 0.01 level (two asterisks).

Supplementary Materials

1. Supplementary Tables

Table S1 Some major characteristics of the soil and irrigation water (treated mine water) used in the experiment

Parameter	Soil	Treated mine water
pH	4.30	8.10
Eh (mV)	439	317
EC (dS/m)	0.72	1.23
Organic matter (g/kg)	24.65	
Total N (g/kg)	1.72	
Available P (mg/kg)	0.018	
Available K (mg/kg)	22.27	
Pb (mg/kg)	104	
Cd (mg/kg)	0.49	
As (mg/kg)	48.60	
Cr (mg/kg)	58.70	
Cu (mg/kg)	149.7	
Zn (mg/kg)	124.6	
Ni (mg/kg)	12.21	
Hg (mg/kg)	0.23	
Pb ($\mu\text{g/L}$)		12.34
Cd ($\mu\text{g/L}$)		1.10
As ($\mu\text{g/L}$)		1.38
Cr ($\mu\text{g/L}$)		13.33
Cu ($\mu\text{g/L}$)		5.72
Zn ($\mu\text{g/L}$)		42.50
Ni ($\mu\text{g/L}$)		11.51
Hg ($\mu\text{g/L}$)		0.27

2. Supplementary Figures

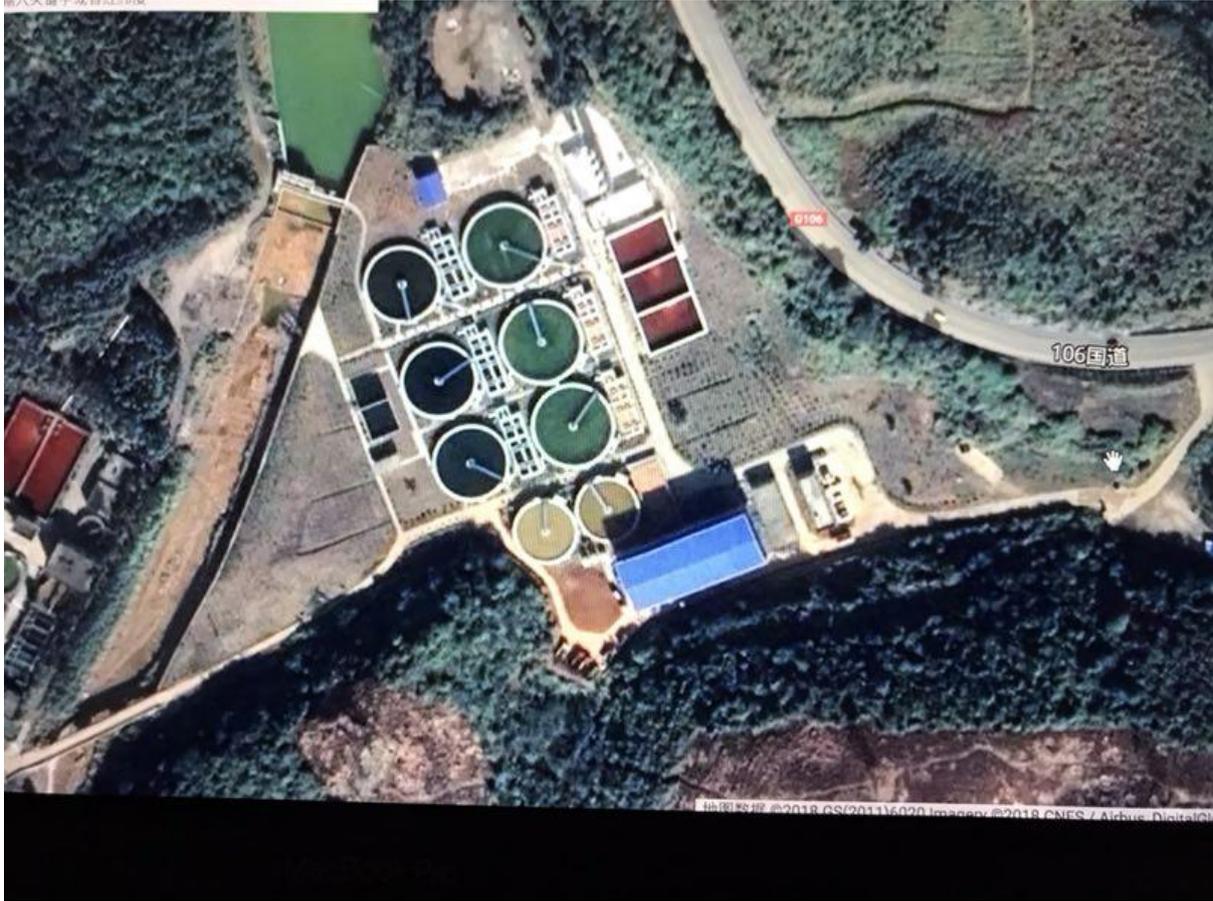


Figure S1 Google map image showing the mine water treatment facility