

# Hydrogeochemical assessment of mine-impacted water and sediment of iron ore mining

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**Abstract.** This study was carried out to evaluate the hydrogeochemical behaviour of mine-impacted water and sediment of a former iron ore mining area. Sampling of mine water and sediment were carried out at selected locations within the mine including the former mining ponds, mine tailings and the nearby stream. The water samples were analysed for their hydrochemical facies, major and trace elements including heavy metals. The water in the mining ponds and the mine tailings was characterised as highly acidic (pH 2.54-3.07), but has near-neutral pH in the nearby stream. Results indicated that Fe and Mn in water have exceeded the recommended guidelines values and was also supported by the results of geochemical modelling. The results also indicated that sediments in the mining area were contaminated with Cd and As as shown by the potential ecological risk index values. The total risk index of heavy metals in the sediment were ranked in the order of Cd>As>Pb>Cu>Zn>Cr. Overall, the extent of potential ecological risks of the mining area were categorised as having low to moderate ecological risk.

## 1. Introduction

Metal mining can be associated with some environmental degradation despite being an important source for mineral exploration in the country. This can be related with the impact on water and soil quality due to water acidification and impact of heavy metals [1,2]. During the excavation process of mining for instance, exposure of soil minerals may leach metals and acidity into the water. When exposed to the environment, the contaminants can be released to the surface water or seep into the groundwater system and into soil. The environmental impact not only visible in an active mining site, but also long after the sites are abandoned [3]. Acidic discharge water that is enriched with metals can be a common feature, thereby causing acidification and heavy metal pollution.

The impact of acid mine drainage (AMD) can be particularly significant in both active and abandoned mining sites [4]. AMD occurs when water flows over the sulphur-bearing materials forming net acidity solutions. AMD which is a product of weathering of sulphide has been a major concern in mining industry [5]. AMD is a major environmental problem as it involves the release of acidic, sulphate and metal-containing water into the environment [6]. It usually has low pH, which is acidic, contains toxic



and non-biodegradable pollutants such as heavy metals, e.g. lead, aluminium, copper, iron, manganese and zinc. Mining impact on sediment quality may also be significant. Sediments can accumulate heavy metals from overlying waters. The enrichment of heavy metals in sediments can be the indicator of the contamination status [7].

Therefore, the study was carried out to provide an assessment on the hydrogeochemical behaviour of the mine-impacted water and sediment of the abandoned iron ore mining site. Such an assessment would be useful to understand the impact of metal mining activities on its surrounding environment and for future mitigation measures.

## 2. Materials and method

### 2.1 Study site

The study was carried out near a former iron ore mine, in Bukit Besi, Terengganu. The mine was a productive area for iron ore mining in Malaysia and was once known as one of the world's largest iron ore producers in Southeast Asia. The Bukit Besi iron ore has the highest quality among the iron ores in Malaysia. Geologically, the major minerals in this area are magnetite, quartz, and goethite. However, the mining operation has ceased in the early 1970's. Previous iron ore extraction in Bukit Besi involves the smelting, digging as well as metal processing activities that have caused the perturbation of the metal cycle.

### 2.2 Mine water sampling

The sampling was conducted at selected locations within the area of the former mine. The water samples were collected from the mining ponds (S1, S2), mine tailings (S3) and the nearby stream (S4). In-situ field measurements included the measurements of pH, temperature, conductivity, redox potential (Eh) and total dissolved solids (TDS) using Myron L Ultrameter 6P. On-site alkalinity measurement was taken using a HACH alkalinity kit, turbidity was measured using a turbidity meter and dissolved oxygen (DO) was measured using a DO meter. For laboratory analysis, all the samples were kept cool and transported back to the laboratory. The samples were stored at 4°C upon reaching the laboratory.

Samples for major and trace elements were collected in pre-washed polypropylene bottles. For analysis of cations and heavy metals, the samples were acidified with 1% v/v of concentrated HNO<sub>3</sub>. The samples were then analysed using Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) for cations (Ca, Mg, Na, K) and heavy metals (Fe, Pb, Cr, Cd, Zn, Cu, Mn, Sr and metalloid As).

### 2.3. Sediment sampling

The surface sediments were collected using a scoop according to the accessibility of the sampling locations. About 500 g of surface sediment samples were collected to perform the analysis. The samples were kept in an icebox <4°C and transported to laboratory for further analysis. Sediments were maintained at room temperature, air-dried and homogenized by using mortars and pestles. Then, they were sieved through 2 mm sieve for physicochemical analyses.

Acid digestion method was used for extraction of heavy metal in the samples. In this study, HNO<sub>3</sub> and HCl matrix was used to extract the heavy metal from the sediment samples. The HNO<sub>3</sub> and HCl were used with the ratio of 3:1. Approximately 1 g of sample was transferred into the digestion tube for acid digestion process. 9 mL of HNO<sub>3</sub> and 3 mL of HCl were added into the tube and were digested overnight. Samples were analysed using ICP-OES to determine the concentration of the metals.

### 2.4 Hydrochemical facies and geochemical modelling

The water hydrochemical facies were determined by identifying the dominant cations and anions in the water based on the percentage of total meq/L of each. The predominant cation and anion were determined from the highest percentage of each category in unit meq/L rather than mg/L. On the other

hand, geochemical modelling of the hydrochemical data was performed using PHREEQC v2.15 geochemical software to calculate saturation indices (SI) of selected mineral phases.

### 2.5 Potential ecological risk index

Ecological risk index was also considered in the assessment of the levels of heavy metal level in the sediment that incorporates ecological and environmental effects with the toxicological effect. The potential ecological risk index, RI of the multi-elements was computed using the following equations:

$$C_r^i = C_s^i / C_n^i \tag{1}$$

$$E_r^i = C_r^i \times T_r^i \tag{2}$$

$$RI = \sum E_r^i = \sum T_r^i (C_s^i / C_n^i) \tag{3}$$

where  $C_s^i$  is the present concentration of heavy metal in the sediment;  $C_n^i$  is the reference value of heavy metal in the sediment;  $T_r^i$  is the toxic response factor for a single heavy metal contamination;  $E_r^i$  is the potential ecological risk index for single heavy metal. Classification of potential ecological risk is given in table 1.

**Table 1.** Classification of potential ecological risk coefficient ( $E_r^i$ ) and risk index (RI)

$E_r^i$	Risk classification	RI	Risk classification
$E_r^i < 40$	Low Risk	$RI < 50$	Low Risk
$40 \leq E_r^i < 80$	Moderate Risk	$50 \leq RI < 200$	Moderate Risk
$80 \leq E_r^i < 160$	Considerable Risk	$200 \leq RI < 300$	Considerable Risk
$160 \leq E_r^i < 320$	High Risk	$RI \geq 300$	High Risk
$E_r^i \geq 320$	Very High Risk		

Adapted from [8]

## 3. Results and discussion

### 3.1 Hydrochemical facies in water

The hydrochemical facies of the water in mining ponds (S1-S3) were indicated by a Ca-SO<sub>4</sub> water type, showing the dominance of calcium (cation) and sulphate (anion), which contributes to about 80% of the total percentage of the compositions. This might be attributed to the occurrence of gypsum-bearing sedimentary materials affected by oxidation of pyrite and other sulphide minerals. The dominance of SO<sub>4</sub> can be associated with pyrite weathering and oxidation of other minerals such as Zn, Pb and Cu sulphides in the water. Meanwhile, S4 shows a Ca-HCO<sub>3</sub> water type. The dominance of bicarbonate in the water originates from the dissolution of carbonate minerals from the host rocks, and the bicarbonate-rich surface runoff entering the stream. It also suggested the likely input of buffering minerals within its surroundings. The increase of pH in S4 was also signified by the high ratio of HCO<sub>3</sub><sup>-</sup>/(HCO<sub>3</sub><sup>-</sup>+SO<sub>4</sub><sup>2-</sup>) of > 0.5 in the stream, indicating the contribution of carbonic acid weathering producing bicarbonate alkalinity.

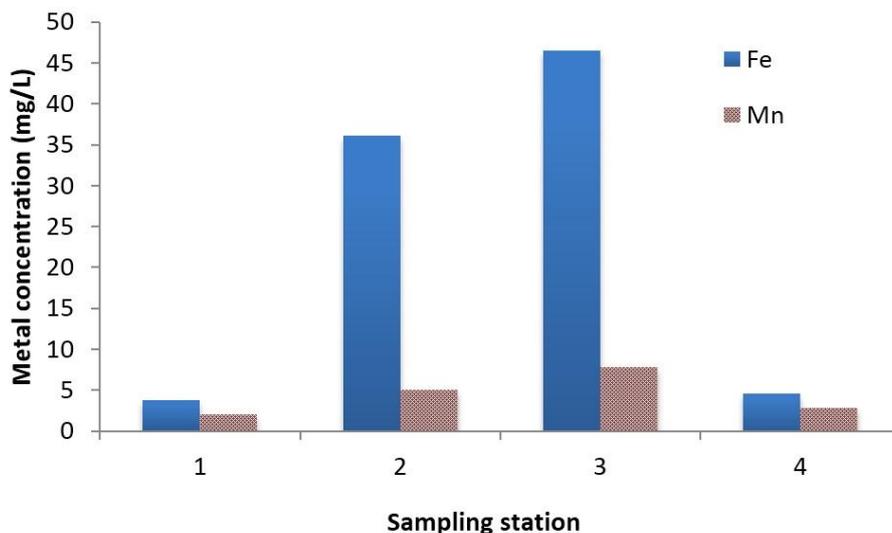
### 3.2 Major and trace elements in water

Major compositions such as Ca, Mg, Na, K, SO<sub>4</sub> and Cl were found to be within the acceptable range of the Ministry of Health (MOH) recommended values for untreated water. Metal elements including Zn, Pb, As, Cd, Cr, Cu and Sr were also found to be within the recommended guidelines values for all

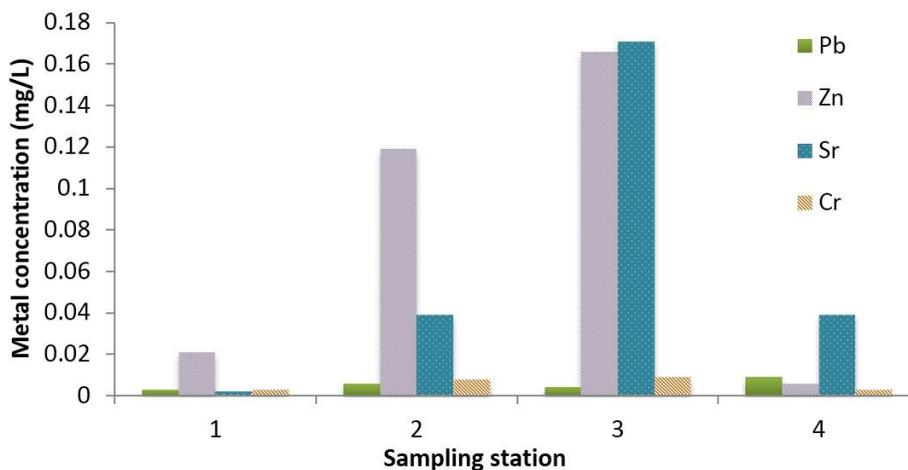
sampling stations. However, the concentrations of Mn and Fe were found above the MOH recommended guideline values at all locations. The concentrations of heavy metals in the sampling area are as depicted in figure 1 and figure 2.

Fe and Mn can be found naturally occurring in most rocks and soils. The concentrations of Mn were found exceeding the recommended guideline values in all sampling locations. Mn is a common contaminant in many mine waters and is not as toxic as Fe, Al, and Zn [9]. However, it has undesirable effects such as can cause corrosion, staining, and unpleasant taste in drinking water. In most mine water, Mn is usually not removed from mine water when ferrous iron is present at concentration  $> 1$  mg/L [10]. Mn in the mine water tends to be in dissolved state as  $Mn^{2+}$  according to the Eh-pH condition of the water [11]. This was also supported through the geochemical modelling that predicts none of the Mn species will form their precipitates in the water (i.e. saturation index  $< 0$ ).

The concentrations of Fe were also found above the recommended guideline values at all sampling stations. It is noticeable that Fe were found very high at the mining pond, S2 and the mine tailings, S3, but has greatly reduced in the stream, S4. According to the Eh-pH diagram for Fe, within acidic pH of between 2.54-2.72 and Eh values of 562-711 mV as in S2 and S3, based on the Eh-pH conditions of the water, Fe tends to be in dissolved aqueous state as  $Fe^{2+}$ , however as the pH increased in S4, Fe can be found in solid mineral phase. This was also supported through the geochemical modelling that predicts some Fe species such as  $Fe(OH)_3$ , goethite  $FeO(OH)$  and hematite ( $Fe_2O_3$ ), that are formed in the stream ( $SI > 0$ ) (table 2). In addition, significant correlations were also found between Fe and Mn, Zn and Cr, suggesting Fe association with the metals most likely in the form of their sulphides.



**Figure 1.** Concentrations of Fe and Mn in mine-impacted water



**Figure 2.** Concentrations of Pb, Zn, Sr and Cr in mine-impacted water

**Table 2.** Saturation index of the solid mineral phases

Species	Anhydrite CaSO <sub>4</sub>	Fe(OH) <sub>3</sub>	Goethite FeOOH	Gypsum CaSO <sub>4</sub>	Hausmannite Mn <sub>3</sub> O <sub>4</sub>	Hematite Fe <sub>2</sub> O <sub>3</sub>	Manganite MnOOH	Melanterite FeSO <sub>4</sub>	Pyrolusite MnO <sub>2</sub>
S.I	-0.29	3	9.33	-0.13	-7.11	20.73	-4.9	-3.29	-8.47

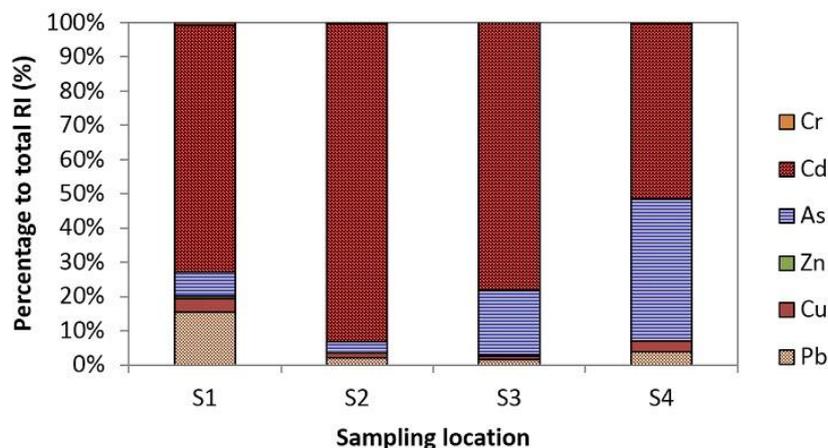
### 3.3 Heavy metal composition in sediment

It was found that almost all the heavy metals in the sediment of the sampling locations were within the recommended acceptable range except for Cd. The concentration of Cd in the mine tailings, S3 showed the highest value compared to other stations. The concentration of Cd in S3 was 0.64 mg/kg, which was slightly higher than the permissible level of the Canadian Council of Ministers of the Environment, CCME and the UK Environment Agency guidelines, i.e. 0.60 mg/kg. Meanwhile, the concentration of As was found high at some locations which is close to the recommended value, i.e. 5.18 mg/kg in S1 compared to 5.9 mg/kg of the CCME recommended value. The highest value of heavy metal element in the sediment was Fe, which was between 6665-15595 mg/kg, followed by Mn that was found in the range of 30-52 mg/kg. However, Fe and Mn were usually found in high concentration in sediment and soil because they are among the major elements in most soils [12].

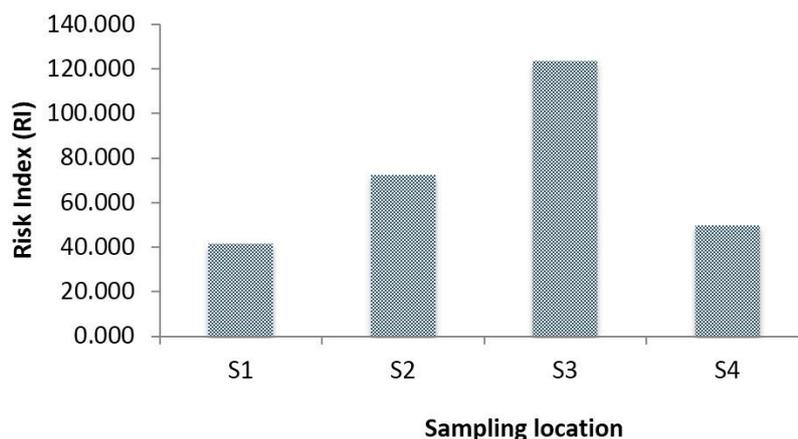
There were significant correlations found for Pb-Cu, Zn, Fe, As, Cr; Cu-Zn, Fe, As, Cr; Zn-Fe, As, Cr; Mn-Cd, Sr; Fe-As, Cr; and As-Cr. The correlations between the heavy metal content in sediment can be an indicator of whether the source of heavy metal was the same. The highly significant correlations demonstrate that the metal elements associate in their parent materials [13], indicating similar geochemical behaviour during weathering processes.

### 3.4 Potential ecological risk index (PERI)

The contribution from each metal element to the total risk index, RI is presented in figure 3. Cd is the biggest contributor to the total RI for each station as indicated by the  $E_{ir}$  values. The  $E_{ir}$  for Cd were 67 and 96 for S2 and S3, respectively indicating moderate risk level. The second highest contributor of the total RI was As, but the  $E_{ir}$  values were still categorized as having low ecological risk. It was found that the total risk index of heavy metals in the sediment were ranked in the order of Cd>As>Pb>Cu>Zn>Cr. Based on figure 4, the RI values show that S3 is having the highest potential ecological value. Both S2 and S3 were categorised as having moderate risk. Cd was found to be higher than its typical background level in most sediments, indicating possible anthropogenic sources of the metal and has been found to constitute large proportions in the potential ecological risk assessment from mining activities [14,15].



**Figure 3.** Percentage of risk index of each metal



**Figure 4.** Risk index (RI) of each sampling location

#### 4. Conclusions

The hydrogeochemical behaviour of a former iron ore mining site in Bukit Besi, Terengganu has been investigated. The former mining ponds and the mine tailings were found to be highly acidic while the nearby stream has near-neutral pH condition. The concentration of Mn and Fe were found to exceed the recommended guideline values for all the sampling locations. The water samples from the sampling locations were also signified by the different hydrochemical facies mostly dominated by a Ca-SO<sub>4</sub> water type. The sediments of the mining impacted area were contaminated by Cd and As at some locations, i.e. S3 and S1, as indicated by the potential ecological risk index values of the metal elements. Overall, the total risk index indicated that the potential ecological risk due to the presence of heavy metal in sediment can be categorised as having low to moderate ecological risk. Such assessment would be useful for current and future mitigation measures as a result of mining activities.

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