Acid mine drainage and heavy metals contamination of abandoned and active mine site at Old Repas Dam in Bentong, Pahang, Malaysia

Kishan Gunasegeran¹², Md Rowshon Kamal¹, Hasfalina Che Man¹, Aimrun Wayayok¹, Syed Ali Haider²

¹Department of Biological Agricultural Engineering, Faculty of Engineering Universiti Putra Malaysia
²Department of Civil Engineering, Faculty of Engineering and Quantity Surveying, INTI International University, Negeri Sembilan, Malaysia

Email: Kishan.gunasegeran@newinti.edu.my

Abstract. Acid Mine Drainage (AMD) occurs as a result of mining activities during mineral exploration. Interaction of the minerals in the presence of atmospheric oxygen and water produces AMD as an end product. AMD can also be produced by weathering of sulphide minerals through series of process, which includes oxidation and hydrolysis. The main aim of the study is to determine the presence of Acid Mine Drainage (AMD) and contamination of the active and abandoned mining sites with heavy metals in Bentong Pahang. This study deals with the identification of heavy metal toxins traces in water bodies that result in discoloration of the water catchment, downstream of the Old Repas dam. Any discoloration of the water present proves the occurrence of AMD. In order to have better comprehension of the scenario, site reconnaissance and survey is carried. This is to examine the areas affected and thus recognising two different sampling points that have traces of AMD contamination. Water sampling and testing are carried out in the chosen sampling point using four in-situ parameters and five selected heavy metals. The chosen parameters are water pH, dissolved oxygen content, total dissolved solids and ammoniacal nitrogen. The selected heavy metals are Zinc, Lead, Tin, Mercury and Arsenic. Four samples were collected each from two sampling point on two different sampling days. In addition to that, the surface water with sediments was also collected and analysed for the presence of heavy metals. From the results, it was found that the pH of the sampling point was ranging from 5 to 7 indicating the presence of AMD, which is the major finding in this study. Based on the heavy metal analysis, it was found that the concentration of Pb, Sn, Hg, As & Zn was present in greater than the allowable standard limits for treated water by the Malaysian Ministry of Health. This concludes an urgent intervention required to treat the site to prevent any further environmental deterioration.

1. Introduction

Pahang is house of various forms of natural minerals that is been actively mined. Based on Malaysian Mining Industry report, a study on mineral exploration activity for metallic industry and energy minerals conducted by The Minerals and Geoscience Department states that Pahang remained the top producer for most minerals in the country. Apart from that, several other anomalies of iron ore and tin were also identified in Pahang. Major sources of valued minerals
such as pyrite and arsenopyrite can be still found in Pahang via mining. Due to lack of enforcement of previous mining regulations, there are several mines in Pahang have been abandoned or shut down in an inappropriate manner. One example of these poorly managed mining sites is Bukit Ibam. In order to tackle this sorts of issues, Environmental Quality Act (1974) and Mineral Development Act (1974) have been established. These acts prevent inappropriate closing down of mining site as well as contamination from mining activities in Malaysia. Corelated to aim of the act, Old Repas Dam (1925) and New Repas Dam (1963) were thus constructed to enable silt retention.

Several activities such as land development, mining and agriculture that are carried out on the upstream of the Old Repas dam in Bentong, Pahang has resulted in deterioration of water quality. The contaminated water bodies by heavy metal toxin found in wastewater (acidic water) and surface runoffs are mainly due to precipitation. Ultimately the contaminated wastewater would reach the dam which consequently affect the living of aquatic lives. The main purpose of the dam is to hold residue, dirt and silt from previous tin mining activities that has been washed down by surface runoff. Thus, dam prevents these impurities from being washed downstream as it blocks the lower part of the river which may lead to flooding. In the case where the heavy metal contaminants mixes with water, it alters the nature of water into acidic. One of the important contributing factor of acid leaching is mining activities. Besides causing destructions of watersheds, mining can also cause contamination of human water sources with compounds like sulfuric acid and heavy metal toxins.

Therefore, this study aimed to determine the presence of Acid Mine Drainage (AMD) and contamination of the active and abandoned mining sites with heavy metals in Bentong, Pahang by testing analysing the surface water sediments. This study would be beneficial to identify the source of contamination, which would be then easier to treat and manage.

2. Methodology and laboratory analysis
The study involves several stages in order to achieve the objective. During the initial stage, site reconnaissance and survey was carried out. This is important as it provides a clearer view on the number of samples to be taken from the location. Based on the site reconnaissance, area of study was determined at latitude 3°33’23.46"N and longitude 101°52’38.52”E [1]. The specific point of study was named as Point A, Point B, Point C and Point D. Area chosen are based on the reconnaissance results that provides probably hint that the area is highly acidic and contaminated with heavy metals. In order to confirm this assumption, two samples were taken at each sampling point on two different sampling months. Four in-situ parameters were identified for testing which include total dissolved solids (TDS), pH of water, dissolved oxygen content (DO) and ammoniacal nitrogen [1]. Sampling equipment was brought to the site for sampling purposes. Sample of water is initially collected in bottle without preservatives, and then was poured into another bottle containing preservatives. Styrofoam box filled with ice was used to preserve the samples from decay. TDS was measured using a TDS meter, pH was measured using a pH meter, DO measured using a DO meter and ammoniacal nitrogen measured using a spectrometer. Sample was taken from specific sampling points and sent to the lab for analysis. The samples collected were then analyzed for the presence of five heavy metals, which includes arsenic, mercury, lead, tin and zinc using Inductive Couples Plasma-Optical Emission Spectrometer in the laboratory. As two samples were collected from the site, each sample was collected in different High-density polyethylene (HDPE) plastic bottles in which one with preservatives and one is without preservatives. Bottle with preservative is commonly used for testing the presence of heavy metal nitric acid. Meanwhile testing of other parameters
does not require addition of preservatives. Testing of the remaining parameters are thus aided with collection of samples in a larger bottle.

3. Results and discussions

The table 1 and table 2 show average results of all samples taken on February 2018 and March 2018. The results are tabulated in table 1 and 2 for better correlation and comprehension.

**Table 1.** Average Results on February 2018.

| Sample No | Dissolved Oxygen (mg/L) | Total dissolved solids (mg/L) | pH | Ammoniacal Nitrogen (mg/L) | Arsenic (mg/L) | Mercury (mg/L) | Lead (mg/L) | Tin (mg/L) | Zinc (mg/L) |
|-----------|-------------------------|-------------------------------|----|---------------------------|---------------|---------------|-------------|------------|-------------|
| A         | 9.88                    | 17.20                         | 5.94 | 1.74                     | 0.153         | 0.000         | 0           | 0          | 0           |
| B         | 9.99                    | 28.10                         | 5.84 | 1.475                    | 0.215         | 0.003         | 0.0608      | 0.1163     | 0           |
| C         | 10.08                   | 29.40                         | 5.81 | 1.85                     | 0.131         | 0.0028        | 0.0465      | 0          | 0           |
| D         | 9.71                    | 30                             | 5.77 | 1.795                    | 0.109         | 0.003         | 0.0254      | 0          | 0           |

**Table 2.** Average Results on March 2018.

| Sample No | Dissolved Oxygen (mg/L) | Total dissolved solids (mg/L) | pH | Ammoniacal Nitrogen (mg/L) | Arsenic (mg/L) | Mercury (mg/L) | Lead (mg/L) | Tin (mg/L) | Zinc (mg/L) |
|-----------|-------------------------|-------------------------------|----|---------------------------|---------------|---------------|-------------|------------|-------------|
| A         | 10.57                   | 28.4                          | 6.35 | 1.565                    | 0.0265        | 0.0022        | 0.2245      | <0.019     | 1.4369      |
| B         | 10.43                   | 28.4                          | 6.14 | 1.540                    | 0.0645        | 0.0014        | <0.024      | <0.019     | 1.5743      |
| C         | 9.60                    | 31.1                          | 6.16 | 1.565                    | 0.0157        | 0.0009        | <0.024      | 1.727      | 1.5750      |
| D         | 10.05                   | 28.8                          | 6.05 | 1.510                    | 0.0549        | 0.0010        | <0.024      | <0.019     | 1.4944      |

**Figure 1.** Dissolved Oxygen (DO) concentration.

Figure 1 shows that the DO concentration measured on the February 2018 and March 2018 of sampling. The highest DO measured on the February 2018 was 10.08 mg/L from sampling point C. This followed by sampling point A, B and point D with DO concentration of 9.99 mg/L, 9.88 mg/L and 9.71 mg/L. In contrast, on the March 2018, point A measured the highest DO concentration of 10.57 mg/L. this was followed by point B, D and C with value of 10.43 mg/L, 10.05 mg/L and 9.60 mg/L. Based on the graph, it was found that the DO concentration obtained on March 2018 was higher than the DO concentration on February 2018 for all the
samples except sample C. DO concentration was higher on March 2018 was because of the heavy precipitation that occurred few hours prior to the sampling. Due to high amount of precipitation, the water flow was rapid. This resulted in normal water level when sampling was carried out. Due to this rapid flow of water, the water particles were well aerated allowing more oxygen to be dissolved in the water. This is similar to a study conducted in Florida [2], whereby the paper concludes that rate of aeration increases with rainfall intensity. Despite good aeration, point C is seemed to have poor DO concentration.

Figure 2. pH Value.

From figure 2, the pH value obtained during the February 2018 sampling in point A, B, C and D is 5.94, 5.84, 5.81 and 5.77 respectively. Similarly, the measured pH on the second (March 2018) in point A, B, C and D is 6.35, 6.14, 6.16 and 6.05 respectively. It was observed that pH value for both the sampling month (February 2018 and March 2018) was quite similar when compared. pH value for both sampling lies within the range of 5 to 7 which shows that the pH value was acidic on both. The samples taken on the February 2018 sampling were more acidic as compared to the March 2018 sampling. These acidic pH values show the occurrence of AMD (Acid Mine Drainage) and this is in accordance to the study conducted in Portugal whereby surface water revealed that low pH value leading teratological forms of aquatic organisms. The low pH was contributed by presence of AMD as result of poor infrastructure maintenance in an abandoned mine [3].

Figure 3. Total Dissolved Solids (TDS) Concentration.
Based on the figure, sample from point D measured to have the highest TDS concentration of 30 mg/L on the February 2018 sampling visit. This is followed by point C, B and A with TDS concentration of 29.40 mg/L, 28.10 mg/L and 17.20 mg/L. In contrast, point C is measured to have highest TDS concentration of 31.1 mg/L on the March 2018 sampling visit. This is followed by sampling point D, A and B with TDS concentration of 28.8 mg/L, 28.4 mg/L and 28.4 mg/L respectively. Based on the analysis, TDS concentration measured in the March 2018 sampling visit seemed to be higher in overall. This can be explained with presence of heavy rainfall that occurred few hours prior to sample collection. The rainfall caused the runoff water to wash out the sediments into the water, thus raising the concentration of TDS. This is on par with the study in Japan as rain events are on the contributing factor in transporting and dispersing the dissolved particles in river watershed and marine environment [4].

According to figure 4, the result on February 2018 sampling day, point C is proven to have highest NH₃-N concentration with measured value of 1.85 mg/L, followed by point D, A and B with value of 1.795 mg/L, 1.74 mg/L and 1.475 mg/L. The highest concentration of NH₃-N obtained on March 2018 sampling is 1.565 mg/L which is similar in both point A and C. This is followed by point B and D with NH₃-N concentration of 1.540 mg/L and 1.510 mg/L respectively. This shows that the concentration of NH₃-N in point C remain high on February 2018 and March 2018 sampling. Greater NH₃-N concentration indicates that the presence of traces of AMD contamination, which are nitrogen and sulphate, is a serious environmental problem [5].

**Figure 4.** Ammonia Nitrogen (NH₃-N) Concentration.
Figure 5. Heavy Metal Comparison.

From the figure 5, Arsenic concentration on the February 2018 sampling was highest in point B with concentration of 0.215 mg/L. This is followed by point A, C and D with concentration of 0.153 mg/L, 0.131 mg/L and 0.109 mg/L. Similarly, point B also measured to have highest Arsenic concentration on the March 2018 sampling with value of 0.0645 mg/L, followed by point D, A and C with value of 0.0549 mg/L, 0.0265 mg/L and 0.0157 mg/L respectively. Arsenic had a higher concentration during the February 2018 sampling compared to March 2018 sampling. This is due to the heavy rain prior to the sampling causing the surface runoff. Sediments were deposited from the surface to the water carrying heavy metal toxins along the way therefore increasing the arsenic concentrations. High concentration of Arsenic on the first sampling day indicates the occurrence of AMD. In fact acid mine drainage is often accompanied with elevated concentrations of arsenic due to the high affinity of arsenic for sulfide mineral ores [6].

As for mercury, the concentration was seen highest point B and D with concentration of 0.003 mg/L in the February 2018. This followed by point C with concentration of 0.0028 mg/L.
However, there were no traces of mercury found in point A. During the March 2018, point A was found to have the highest concentration of mercury with value of 0.0022 mg/L, followed by point B, D and C with value of 0.0014 mg/L, 0.0010 mg/L and 0.0009 mg/L respectively. In overall, mercury concentration was present during sampling in majority of sampling points. Presence of mercury in the water indicates occurrence of AMD as release of mercury in AMD result from oxidative dissolution of pyrite in coal, which only occur during activities such mine processing, waste management as well as large construction [7].

The concentration of lead was seen highest in point B during the February 2018 with value of 0.0608 mg/L based on figure 5. This is followed by point C and D with value of 0.0465 mg/L and 0.0254 mg/L. There was no any measured value of lead seen in point A. On the March 2018 sampling, point A was measured to have the highest concentration of lead with value of 0.2245 mg/L. The concentration of lead was below allowable limit in remaining points. This difference in concentration of lead higher in February 2018 can be explained by the occurrence of heavy rain prior to March 2018 sampling. Despite the heavy rain, sample from point A contain high amount of lead concentration, which indicates the presence of AMD. The result obtained somehow on par with a previous study conducted in Pahang, Malaysia, which shows that presence of lead beyond the allowable limit is a clear indication of AMD [8].

On figure 5, tin was only present in sampling point B with value of 0.1163 mg/L. In contrast, tin concentration was seen elevated in sampling point C with value of 1.727 mg/L during the March 2018 sampling. The concentration of tin in the remaining sampling points was within the allowable limit of less than 0.019 mg/L. Presence of any amount of tin beyond the allowable limit is hazardous and indicate occurrence of AMD. It is known that the site of sampling was a previous tin mining area. The main mined ore mineral for tin is oxide cassiterite (SnO₂), which is chemically stable and hence effectively locked within the mineral itself [9]. It is highly hazardous as this chemical compound is unlikely to change over time if it is present in water. Thus, interventions are required to manage the elevated level of tin found in the sample.

On the February 2018, there was no traces of zinc found in all sampling point based on figure 5. However, on the March 2018 sampling, the concentration of zinc was found raised in all the sampling points. It was found highest in point C with concentration of 1.5750 mg/L. This was followed by point B, D and A with concentration of 1.5743 mg/L, 1.4944 mg/L and 1.4369 mg/L respectively. The raised concentration of zinc in the March 2018 sampling indicates the presence of zinc contamination in water, hence proves the occurrence of AMD. This elevation of zinc concentration is parallel to a study conducted in South West Spain whereby during autumn rain, the maximum sulphate compound of zinc was seen due to precipitation [10].

4. Conclusion and recommendations
Based on the results, almost all the in situ parameters were seen elevated on the March 2018 sampling. Beginning with DO concentration, it was found greater in majority of sampling point on the March 2018 sampling. The heavy rain caused the water to flow rapidly due to surface runoff from the upstream of the dam into the sampling points. The water particles were well aerated which then contributed to a high DO concentration. This somehow proves that rain factor is vital in process of aeration, which thus increase the DO level. As the pH level comparison, it was found that the pH was acidic in all the sites during sampling. A point to note to that the acidity was higher on the February 2018 sampling as compared to March 2018 sampling. This is due to the rain that caused a dilutional effect of the pH. However, a lower pH reveals that there is occurrence of AMD in all the sampling points. Commonly it is seen in poorly maintained infrastructure. As for the TDS concentration, it was found that the value was
higher on the March 2018 sampling in majority of the sampling point. This is mainly due to important effect of rain in dispersing the dissolved particles in river watershed and marine environment. The concentration of NH3-N was seen elevated in majority of sampling points in the February 2018 sampling itself. In fact, the smell of ammonia gas was very strong from the sampling points. This specific pungent smell also proves that the locality is contaminated with level of NH3-N. Raised levels of NH3-N indicate the presence of AMD in water, which is lethal for all living organism. Based on the analysis for the five selected heavy metals, it is observed that there were presence of heavy metals such as Arsenic (As), Zinc (Zn) and tin (Sn) at very high concentrations in the samples. This raised level of heavy metals concentration can be classified as class IV or Class V as per National Water Quality Standard (NWQS) in Malaysia. Zinc was present at a very high concentration of 1.545 mg/L on the March 2018 sampling in sampling point C. Those give an impression that point C could be the discharging site of zinc itself. High concentration of zinc indicates the occurrence of the AMD on these sampling points as it gets accumulated due to heavy metal contamination.

Besides that, the heavy metal arsenic was also seen at high concentration on the February 2018 sampling. It measured about 0.215 mg/L in sampling point B, which is beyond the limit level of arsenic. This indicates the occurrence of AMD as the concentration measured was greater than the allowable limit. In addition to that, it was also found that sampling point C had the highest concentration of tin. The highest concentration of 1.727 mg/L was obtained on the March 2018 sampling. Thus it is categorized as class V as per National Water Quality Standard (NWQS) in Malaysia. This is crucial finding, as high level of tin is injurious to all living organism. As for mercury, it was present during February 2018 and March 2018 sampling in majority of sampling points. Presence of mercury in the water is extremely important as it indicates the occurrence of AMD. Even a lose dose of mercury can cause impact on various human system such as renal, cardiovascular and immune systems. Based on the results obtained it is likely proven that all the sampling point is affected with acid mine drainage. The effect is somehow worst in sampling point C as compared to the rest of the sampling point with high values of heavy metals. This polluted water can be very dangerous for the aquatic biodiversity as well as human beings who utilize the water for their basic needs. Hence, there is an urgent need of monitoring these water catchments areas to improve the water quality.

As for the water catchment area in sampling point C, a proper drainage should be installed to assist the flow of water. The drain should be deep enough to prevent heavy metals from contaminating the water. On these discolored areas of the sampling point C, further investigations must be carried out to determine for any negative effect on the ecological cycle. This study revealed that the water quality is in a bad state and remedial measures should be taken to improve the quality of water in the area. Proper precautions and treatment methods should be implemented with immediate effect.

References
[1] Noa G 2017 Water Quality Investigation of the Old Repas Dam in Bentong, Pahang (Nilai: INTI International University & Colleges)
[2] Belanger T V and Korzun E A 1990 Rainfall-reaeration affects J. Irrig. Drain. Eng. 116 pp 582-587
[3] Ana T, Paula T and Salome F 2011 Chemical and Diatom Characterization of metal-contaminated Stream Sediments and Surface Water Sci. Total Environ. 409 pp 4312-4325
[4] Nagao S, Kanamori M, Ochial S, Tomihara S, Fukushi K and Yamamoto M 2013 Export of $^{134}$Cs and $^{137}$Cs in Fukushima river systems at heavy rains by Typhoon Roke in September 2011 Biogeosciences 10

[5] Gerald J, Viktors I and Carmen M 2006 Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine-drainage treatment Chemosphere 64 pp. 944-954

[6] Hefa C, Yuanan H, Jian L, Bin X and Jianfu Z 2009 Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems J. Hazard. Mater. 1-3 pp. 13-26

[7] Alain M, Margarita M, Magdalena M and Valentina B 2018 Chemical forms of mercury in pyrite: implications for predicting mercury releases in acid mine drainage settings Environ. Sci. Technol. 52 pp 10286-10296

[8] Wan Z, Nur S and Hazwani A 2009 Acid mine drainage and heavy metals contamination at abandoned and active mine sites in Pahang Bul. - Geol. Soc. Malays. 55

[9] Muhammad A A 2012 Morphology, Geology and Water Quality Assessment of Former Tin Mining Catchment Sci. World J.

[10] Olias P, Nieto J M and Sarmiento A M 2004 Seasonal water quality variations in a river affected by acid mine drainage: the Odiel River Sci. Total Environ. 333 1-3, pp. 267-281