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Acid mine drainage and heavy metals contamination at abandoned and active mine sites in Pahang

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Abstract — Active and abandoned mine sites in Pahang have been investigated recently to find out the occurrence of acid mine drainage and heavy metals contamination. Acid mine drainage (or also popularly known as AMD), which is a product of weathering (oxidation and hydrolysis) on sulphide minerals has been a major concern in mining industry. Seven mine and quarry sites in Pahang were visited, namely Bukit Botol, Bukit Ibam, Panching quarry, Sg Lembing, Kota Gelanggi, Padang Piol and Kg Awah. *In-situ* water quality parameters such as pH, dissolved oxygen and electrical conductivity were measured. Some surface water samples were also collected and analysed for heavy metals. After the first screening test on these sites, the abandoned tin mine of Sg. Lembing (underground mining) was chosen for further examination. Detailed study at Sg. Lembing involved sampling of surface water and mine tailings. The study has revealed that arsenic (As) concentrations in surface water ranges from 0.003-16.20 mg/L and in mine tailings 755-74475 mg/kg. The arsenic level measured in surface water and mine tailings at Sg Lembing Mine are higher than the environmental standard for effluents (Standard A) in Environmental Quality Act (1974) and contaminated soil standard by ICRCL (1987). The concentrations of other heavy metals such as Cu, Fe, Mn, Pb, and Zn are also exceeding the limit allowed by EQA (1974) and ICRCL (1987). The study concludes that there is an urgency to regulate the better closure of abandoned mine sites. Pulverised mine tailings which is very rich in sulphide minerals must be kept away from contact with water and oxygen to avoid reactions that will produce acidic water and harmful chemicals.

Keywords: acid mine drainage, heavy metal contamination, abandoned mine, active mine, Pahang

INTRODUCTION

Acid mine drainage (AMD) is produced by the exposure of certain sulphide minerals, most commonly pyrite and arsenopyrite, to air and water, resulting in the production of acid and elevated concentrations of metals and sulphate (Sengupta, 1992). Metal-bearing minerals such as arsenopyrite, pyrite, and chalcopyrite are abundant in finely ground mine tailings or pulverised by-product from mining activities. Tailings with 5% pyrite and arsenopyrite are high enough to produce acid in mine drainage (Bodenan *et al*., 2004). The chemical reactions (i.e. hydrolysis and oxidation) can transform sulphide minerals to sulphuric acid that will decrease the pH of water at active or abandoned mines sites. Such waters usually pose an additional risk to the environment by the fact that they often contain elevated concentrations of toxic metals including Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Zn (May *et al*., 2001). Oxidation and hydrolysis of arsenopyrite (FeAsS) to generate acid, arsenic and sulphate in AMD can be described by the reaction as follows:

$$4FeAsS + 13O_2 + 6H_2O = 4Fe^{2+} + 4AsSO_4^{3-} + 4SO_4^{2-} + 12H^+$$

Pahang has many kinds of mineral resources that have been actively mined, such as tin, iron, and gold. As a result of heavy mining in this state, there are several mines that are now abandoned without proper manner of closure due to poor enforcement of previous mining regulations. Currently, Environmental Quality Act (1974) and Mineral Development Act (1994) have been established to avoid abandonment and contaminations from mine activities in Malaysia. Abandoned mine is characterised by huge hole or man-made lake, very steep and rough topography, with large deposition of mining waste (i.e. tailings). The study was conducted to investigate the AMD phenomenon at several active and abandoned mines in Pahang. Sg Lembing ex-mining site was selected to examine the effects of acid mine drainage on the quality of surface water and soil. This ex-mine is very rich in sulphide minerals that have been pulverised and exposed to water and air. Mining activities during the last decades have generated huge quantity of mine waste materials, which were left without proper treatment. The total concentrations of heavy metals in surface water and mine tailings were determined; therefore the pollution assessment of this mine can be made.

MATERIALS AND METHODS

The study was conducted at two active mines and five abandoned mine sites in Pahang, which is the largest state in Peninsular Malaysia (Figure 1). The quarries and mines visited were Kuari Kg Awah, Padang Piol iron mine, Kota Gelanggi Limestone quarry, Bukit Pancing Limestone quarry, Sg Lembing ex-tin mine, Bukit Botol ex-mine, and finally Bukit Ibam (Table 1). Contaminated soil (or tailings) and surface water were collected at these sites and were taken back to the laboratory for chemical analyses. Soils were air-dried at room temperature for several days, pulverised into a fine powder using agate-mortar and digested using microwave digestion technique with a concentrated acid mixture (HNO_3, $HClO_4$, and HF). Only 0.1 g of soil was

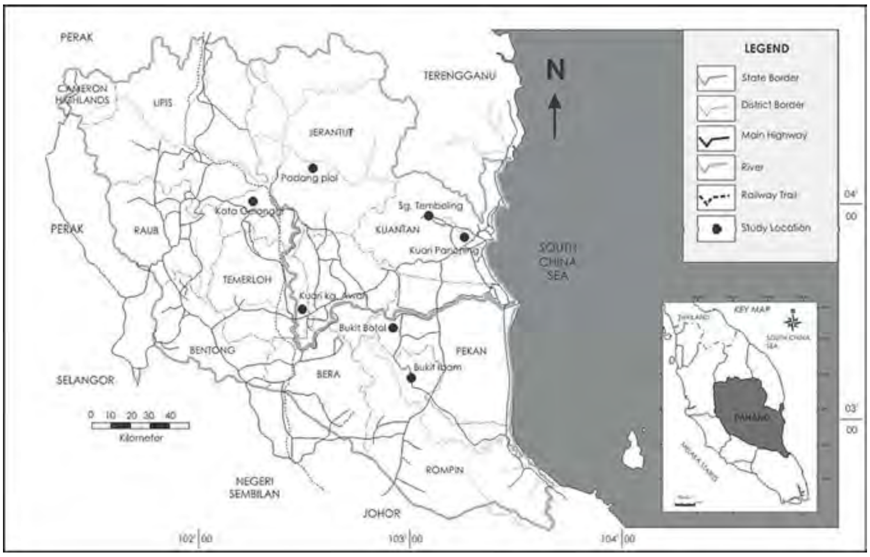

Figure 1: The location of sampling stations in Pahang, Malaysia.

used in digestion technique. Water samples were collected with great care to prevent cross contamination. The water samples were preserved by adding ultra-pure acid (1% or 2% by volume). The samples were filtered upon arrival in the laboratory. Filtered water samples and digested solutions produced from acid digestions technique were analysed using inductively coupled plasma mass spectrometry (ICPMS) for heavy metals, such as Pb, Cu, Ni, Zn, As, etc. Some *in-situ* parameters such as pH, electrical conductivity, salinity, temperature and turbidity were also measured on site using portable water quality meter (YSI 656). The meter probe was immersed in the surface water on-site and readings of various parameters were recorded. Next step of the study involved detail investigation which was specifically conducted at Sg. Lembing ex-tin mine. The investigation conducted at Sg Lembing involved mapping (i.e. traverse) to map the locations of mine tailings and surface water sampling stations. Figure 2 shows the locations of sampling stations for mine tailings and surface water. Ten sampling stations were used to collect surface water and five stations for mine tailings. Surface water was sampled from surface drainage, abandoned ponds, streams, and river. Contaminated soil and/or mine tailings were collected from the surface, where the tailings were left exposed in the gunny sacks. The location C is located very close the mine adits on top of the hill, while locations A and L are located on the mine ex-processing plant (Figure 2). Locations S and J are rather far from the others, i.e. located at the river bank of the main river in this area (Sg. Kenau).

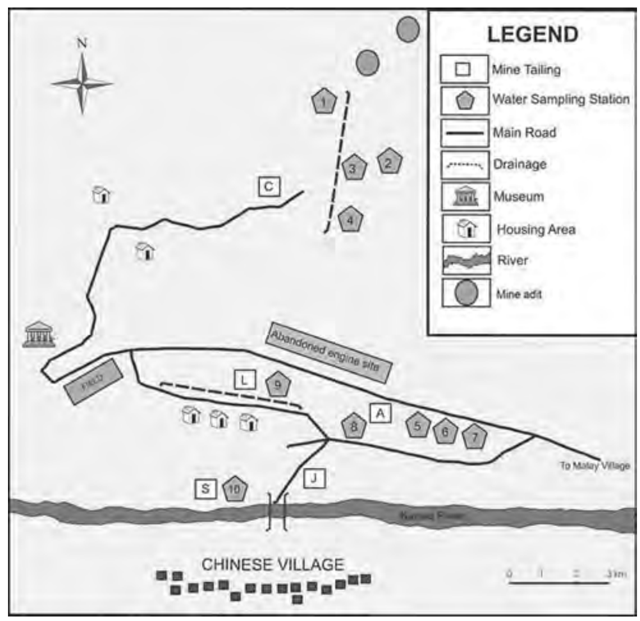

Figure 2: Map of the sampling stations around abandoned mine of Sg Lembing.

RESULTS AND DISCUSSIONS

Results of in-situ parameter measurements, such as electrical conductivity (EC), pH, dissolved oxygen (DO), and salinity are presented in Table 2. The pH values show that Bukit Botol, Bukit Ibam and Sg Lembing ex-mines are extremely acidic with the pH values ranging from 2.38 to 4.75. The pH values recorded at these sites would give an indication that the acid mine drainage was formed at these three areas. The pH values measured at Kuari Panching, Kuari Kg Awah, Kota Gelanggi, and Padang Piol are alkaline, with the pH values above 7.0. The results indicate that there is no formation of AMD at these sites, probably due to non-existence of sulphide minerals or the AMD formation is controlled by the limestone formation, as a dominant rock at these areas. It is interesting to note that at Kuari Kg Awah, which is underlain by andesite and limestone, is also alkaline. Although sulphide minerals such as pyrite and chalcopyrite are present in this area to generate AMD, its formation is probably neutralised by limestone that is highly capable of controlling the acid formation. It is also interesting to see high pH measured at Padang Piol iron mine (active hardrock mining). Observation on site revealed that pyrite mineral is dominant, but due to the immature age of this mine, the formation of acid mine drainage is not properly completed (i.e. still at an early stage). More time is required for water in Padang Piol mine to turn acidic. It is also interesting to observe that the pH also influences other parameters especially the electrical conductivity and salinity (excluding DO). The electrical conductivity and salinity increase with a decreasing pH, while the DO values decreased.

The results in Table 2 show that there are several sites with AMD problems, namely Sg Lembing, Bukit Ibam and Bukit Botol. They are all abandoned mines. We have decided to conduct detail investigation at Sg Lembing ex-tin mine. The study involved mapping the mine area, sampling of surface water and mine tailings. Table 3 shows the average values of heavy metals from five surface water samples collected at eight mines and quarries. The average concentrations of heavy metals are higher at ore/mineral mine sites as compared to rock quarries. This is due to the formation of AMD at these sites. The concentration values are compared with parameter limits of effluents of Standard A from Environmental Quality Act 1974. Most of the heavy metals especially at abandoned mine sites such as Bukit Ibam, Bukit Botol and Sg Lembing are higher than the environmental standard from EQA (1974). For example the Pb, concentrations at Bukit Ibam, Bukit Botol and Sg Lembing mines are up to 15 times higher than the environmental standard. Lower than environmental standard was observed at other mines/quarries except at Kuari Kota Gelanggi, which is slightly higher than the standard (5 times higher). Arsenic (As) concentrations at all mines are below the environmental standard (<0.05 mg/L). Cu and Zn average concentrations at three abandoned mine sites (Bukit Ibam, Bukit Botol and Sg Lembing) are 1 to 30 times higher than the environmental standard. Other heavy metals such as Ba, Sr, Ni, Co and Cr are not too critical where their values are below 1 mg/L. The comparison of Ba, Sr, and Co with environmental standard could not be made because these values are not included in the current effluent Standard A from EQA (1974).

Further investigation was carried out at Sg Lembing, where the selection of Sg Lembing was based on the results presented earlier in Table 2 and 3 and also because Sg Lembing is considered as highly polluted compared to other mine areas. Therefore, the priority for environmental assessment is more important at Sg lembing mine. The study at Sg Lembing involved more sampling of surface water and tailings. The results in Table 4 shows the *in-situ* parameters of surface water measured at ten sampling stations at Sg Lembing mine area. It is interesting to note that there are five stations that have lower pH (less than 3.06), and these stations are located at the main ex-ore processing plant of the mine (stations 5, 6, 7, 8, and 9 - Figure 2). The pH of surface water at locations near the mine entrance (adit), symbol as 1, 2, 3, and 4 on the map in Figure 2, is nearly alkaline (very weak acid) with pH values ranging from 5.26 to 6.79. The results indicate that the formation of AMD is not from the abandoned adits of the former mine, but takes place where tailings were deposited and left to expose to water and air.

Table 1: List of mines that were examined in this study.

Study area	GPS reading	Type of mineral deposit	Status
Bukit Ibam	N03°11.54’ E103°01.54’	Iron	Abandoned
Bukit Botol	N03°22.64’ E102°55.66’	Iron, barite	Abandoned
Kuari Panching	N03°53.43’ E103°08.43’	Limestone	Abandoned
Kuari Kampung Awah	N03°29.87’ E102°32.54’	Andesite	Active
Kuari Kota Gelanggi	N03°53.14’ E102°28.7’	Limestone	Abandoned
Padang Piol	N04°00.43’ E102°18.60’	Iron	Active
Sungai Lembing	N03°54.59’ E103°01.83’	Tin	Abandoned

Table 2: Measurements of in-situ parameters in surface water at eight mines and quarries in Pahang.

Station	EC (mS/cm)	pH	DO (mg/L)	Salinity (ppt)
Bukit Ibam 1	0.623	4.75	3.78	0.30
Bukit Ibam 2	0.124	4.02	5.68	0.06
Bukit Botol	1.536	2.38	3.23	0.76
Kuari Panching	0.261	7.54	5.74	0.12
Sg. Lembing	0.116	3.82	5.51	0.08
Kuari Kg. Awah	0.322	8.41	7.00	0.15
Kota gelanggi	0.321	7.90	5.90	0.15
Padang Piol	0.859	7.85	5.08	0.42

EC = electrical conductivity; DO = dissolved oxygen

The electrical conductivity values are higher at these five stations (except for station 9), due to high quantity of total dissolved solids in the water. There are some stations with high dissolved oxygen (DO) such as station 1, 3, 9, and 10. High DO (>5 mg/L) at these sites are mainly attributed to the slow flow in drainage that aerated the water. Other stations show lower DO values (<5mg/L), indicating that the quality of surface water is so poor and cannot support an aquatic life.

Table 5 shows the concentrations of nine heavy metals measured in surface water at ten different stations in the Sg Lembing Mine. The results show that there is very serious contamination of heavy metals at certain locations of the site, especially at locations 5, 6, 7, 8 and 9. Arsenic (As) concentrations measured at ten sites are varied, the highest As recorded is at station 8, with the concentration of 16.2 mg/L (320 times over the environmental standard EQA, 1974). Williams *et al*. (1996) analysed surface-water from ex-tin mine in Thailand and have confirmed the presence of dissolved As at concentrations exceeding WHO potable water guidelines by up to a factor of 500 (WHO limits for As is 0.01 mg/L). Station 8 is a small monsoon drain that has eroded a pile of exposed mine tailings. High Cu concentration was measured at stations 6 and 7, with the values of 165 and 169 mg/L, respectively. High Zn concentration was recorded

Table 3: Analytical results of surface water at eight mines and quarries in Pahang (average values of five samples, n = 5).

mg/L	Bkt Ibam 1	Bkt Ibam 2	Bukit Botol	Kuari Panching	Sg. Lembing	Kuari Kg. Awah	Kuari Kota Gelanggi	Pdg Piol	EQA (1974)
Pb	0.48	0.15	1.55	0.01	0.04	0.02	0.54	0.03	0.1
As	0.02	0.02	0.06	0.00	0.04	0.01	0.08	0.01	0.05
Cu	0.77	0.28	6.00	0.01	5.07	0.57	0.21	0.01	0.2
Zn	2.01	0.25	9.86	0.00	5.30	0.04	0.03	0.27	2.0
Ba	0.07	0.14	0.10	0.06	0.04	0.04	0.04	0.04	NA
Sr	0.17	0.02	0.01	0.16	0.11	0.61	0.09	0.39	NA
Ni	0.02	0.01	0.02	0.00	0.06	0.01	0.01	0.00	0.2
Co	0.03	0.02	0.06	0.00	0.25	0.00	0.00	0.00	NA
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05

NA = not available; EQA (1947) : Environmental Quality Act, 1974. Parameter Limits of Effluent of Standard A

at station 9, Fe at station 5 and 6, Mn and Pb at station 9. Apart from that, the concentrations of other heavy metals (i.e. Ni, Cr, and Cd) are not too critical except at certain stations such station 9 for Ni (1.12 mg/L), stations 7 and 9 for Cd (1.2 and 1.88 mg/L respectively). The graphical plots of the heavy metals at their sampling stations are presented in Figure 3.

Table 6 shows the average concentrations of heavy metals in mine tailing deposits at five stations in Sg Lembing mine. These values are compared with the environmental standard of ICRCL (1987) and DOEQ (1989), due to the fact that Malaysia does not have its own standard for contaminated land. ICRCL (1987) is a comprehensive standard; however it does not include Co, Fe and Mn. The standard concentration values for Co and Mn from DOEQ (1989) was adopted as replacement (as shown inTable 6). It is interesting to note that at location C, which is a pile of mine waste that was dumped near the mine entrance (i.e. mine adits), has high elevated concentrations of heavy metals such as Cu, Zn, Fe, Pb and As. The concentration of As at location C is the highest measured in this area with the average value of 74475 mg/kg (i.e. 1000 times exceeded the action value of ICRCL, 1987). These values are extremely high compared to As concentration in contaminated sediment measured to be up to 900 mg/kg (Bhattacharya *et al*., 2006). The concentrations of Fe in all stations are also extremely high, ranging from 124300 to 643300 mg/kg. The concentrations of Cr and Ni at all stations are below the ICRCL (1987) standard of 664 and 376 mg/kg, respectively. The results presented in Table 6 are considered as extremely contaminated and immediate action must be taken into consideration to remediate the site. To date, all mine tailings were remediated (i.e. either removed or covered) to prevent leaching of heavy metals especially Cu, Fe, Pb and As into soil, surface water and groundwater. The average concentrations of metals were presented in graphical form as shown in Figure 4. The total metal concentration of heavy metals is useful in identifying the pollution source and the potential contamination (Zhou *et al*., 2007). Total metal concentrations in surface water (Table 5) and mine tailings (Table 6) showed that the Sg Lembing ex-mining site is highly contaminated with heavy

Table 4: Average values of in-situ parameters of surface water measured at 10 stations at Sg Lembing mine (No of readings per station, n = 3).

Station	EC (mS/cm)	pH	DO (mg/L)	Salinity (ppt)
1	0.029	5.79	7.25	0.01
2	0.085	6.79	3.74	0.04
3	0.055	5.26	5.86	0.02
4	0.06	6.59	1.99	0.3
5	1.076	2.97	2.23	0.92
6	0.772	3.06	4.46	0.38
7	2.776	2.67	2.83	1.43
8	0.773	2.27	3.35	1.23
9	0.008	2.68	8.34	0
10	0.029	5.67	6.3	0.02

EC = electrical conductivity; DO = dissolved oxygen

metals. The pollution source deduced from the study is not from the inside of the mine but from the pile of mining waste that was left exposed at this site. Concas *et al*. (2006) stated that the main sources of contamination are from the mine tailings stored in mine tunnels at their study area. At Sg Lembing however, the surface water from the drainage that flows out of the mine's adit has relatively low concentration of heavy metals and merely over the environmental standard for some elements. The pH of the water is also near to alkaline (pH 5-6) which is not considered as a product of AMD. Bhattaacharya *et al*. (2006) reported that acid mine drainage at their study area was characterised by very low pH (pH 2-4).

CONCLUSIONS

The study at abandoned and active mines and quarries in Pahang revealed that acid mine drainage occurs only at the place where sulphide-bearing minerals were exposed to the environment. At some localities, limestone formation is a good neutraliser to prevent acid mine formation. This has been proven at Kuari Kg Awah, where sulphide-minerals in andesite exist together with limestone. The formation of AMD at abandoned mine of Sg Lembing is not from the derelict mine adits, but from the exposed mine wastes or tailings. The tailings have produced acidic water and

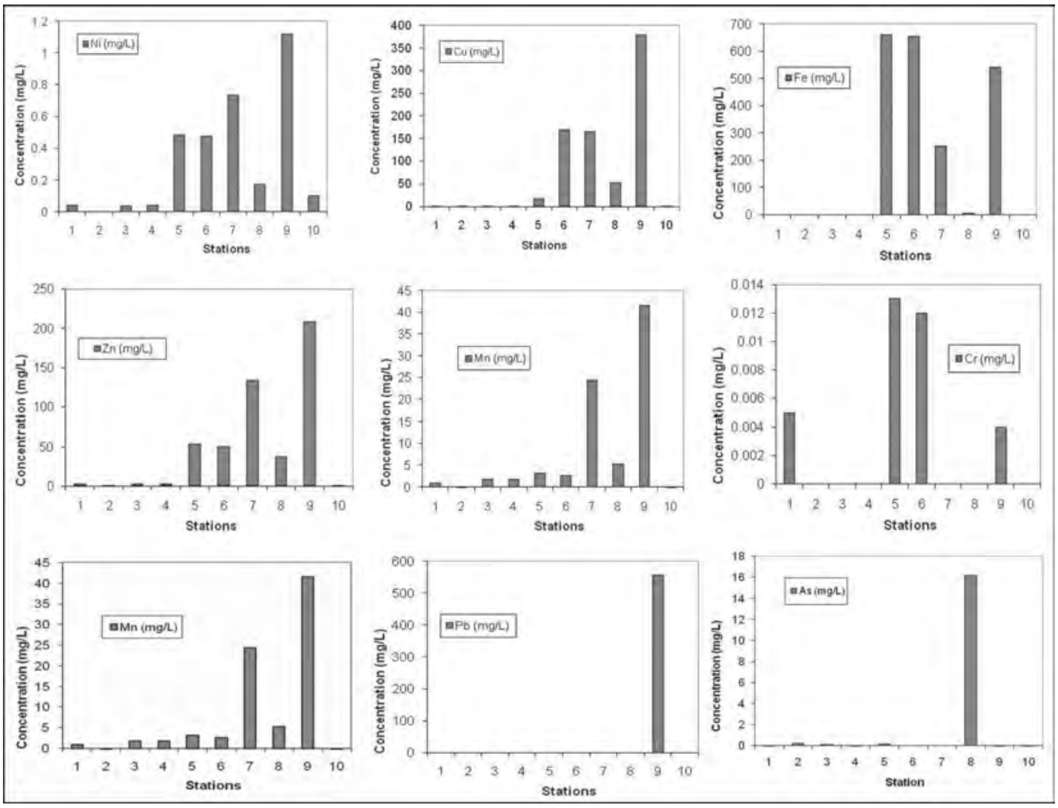

Figure 3: Concentration of heavy metals in surface water at Sg. Lembing Mine.

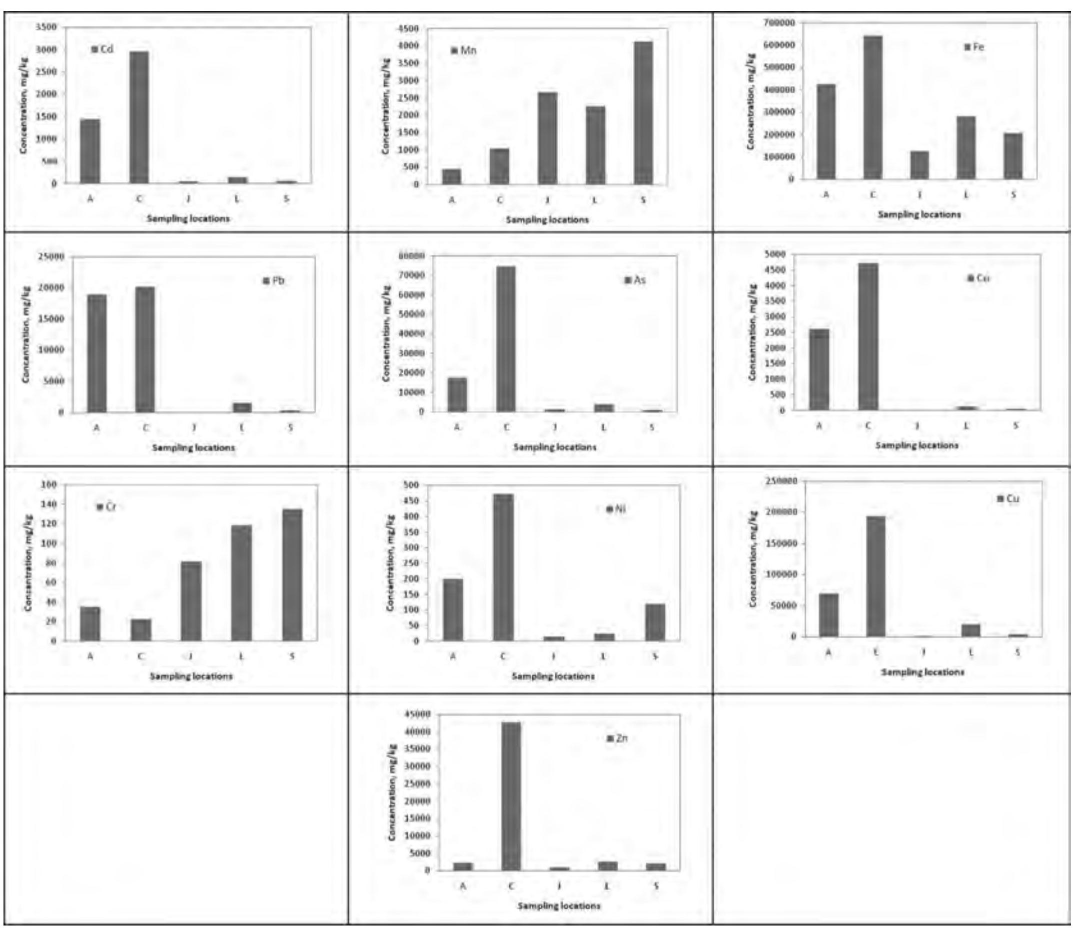

Figure 4: Concentrations of heavy metals in mine tailing deposits around Sg. Lembing Mine.

Table 5: Analytical results of surface water at 10 stations around Sg Lembing Mine.

Station	As (mg/L)	Cu (mg/L)	Zn (mg/L)	Ni (mg/L)	Fe (mg/L)	Mn (mg/L)	Cr (mg/L)	Cd (mg/L)	Pb (mg/L)
1	0.00294	0.117	2.33	0.041	0.021	0.949	0.005	0.029	0.015
2	0.212	0.014	0.054	0	0.058	0.018	0	0.005	0.064
3	0.0868	0.17	2.53	0.038	0.016	1.78	0	0.024	0.042
4	0.0167	0.417	2.42	0.04	0.038	1.81	0	0.028	0.015
5	0.174	17.3	52.7	0.485	659	3.22	0.013	0.979	0.774
6	0	169	49.8	0.475	655	2.72	0.012	0.954	0.774
7	0	165	133	0.734	251	24.4	0	1.2	0.293
8	16.2	52.3	36.8	0.173	6.75	5.29	0	0.293	0.107
9	0.0292	379	208	1.12	540	41.5	0.004	1.88	556
10	0.0031	0.209	0.153	0.098	0.868	0.074	0	0.003	0.016
EQA (1974)	0.05	0.20	2.00	0.20	1.00	0.20	0.20	0.01	0.10

EQA (1947): Environmental Quality Act, 1974. Parameter Limits of Effluent of Standard A

Table 6: Analytical results of heavy metals at five mine tailings deposits at Sg Lembing Mine.

Stations	No. of samples	Average concentration (mg/kg)									
		Cu	Zn	Ni	Co	Fe	Mn	Cr	Cd	Pb	As
A	n=3	69393	2218	199	2618	425333	446	35	1438	18887	17410
C	n=3	193533	42567	473	4727	643333	1048	23	2960	20167	74475
J	n=3	1293	917	16	26	124333	2667	82	49	73	1097
L	n=2	19430	2530	24	133	281000	2260	119	140	1529	3830
S	n=4	3968	2025	120	62	205500	4125	135	67	331	755
ICRCL(1987)		423	1665	376	NA	NA	NA	664	15	813	69
DOEQ (1989)					2-70*		500**				

NA = not available ; ICRCL (1987): action values; DOEQ (1989) - *background level ** environmental investigation level

increased the level of heavy metals in surface water and soils. To date, the site has not been cleaned up and the levels of contaminations to the environment especially groundwater and surface water are expected to increase. Therefore, the contamination of groundwater due the AMD is of great concern at Sg Lembing ex-mining site and immediate study and care must be carried out as soon as possible.

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