HEAVY METALS CONCENTRATION IN SURFACE WATER AND SEDIMENT FROM TIN MINE EFFLUENTS AT KEPAYANG RIVER, PERAK, MALAYSIA

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ABSTRACT

A preliminary study on physico-chemical properties and heavy metals concentrations (Al, As, Ba, Be, Cd, Co, Cu, Cr, Fe, Mn, Ni, Pb, Se, and Zn) was conducted at the nearest point of tin mine effluent in Kepayang River, Perak. Composite samples of water and sediment were analysed using ICP-MS and data were compared with the raw water of MOH and industrial soil of CCME guidelines. The concentration of Fe and As in both water and sediment were found to have exceeded the MOH and CCME guidelines. The output from this study will present the background report on metals concentration of tin mine effluent and be useful for future monitoring works.

Keywords: Effluent, heavy metals, sediment, tin mine, water.

INTRODUCTION

Tin mining is one of the oldest industries in Malaysia. Malaysia was once a leading country in the world's tin production and has contributed a lot to the national socio-economy. The exploitation of tin ore due to demand has led to uncontrolled mining activities during the late 19th and early 20th centuries [1]. These have caused serious environmental problems such as deterioration of mining land and river water quality. The processes of dredging and extracting tin ore have attributed to the formation of mine tailings that are toxic to the environment. These tailings are then washed into the river by surface runoff, thus polluting the river with toxic metals. Previous studies in Malaysia showed mining as the major source of heavy metal contaminations in the water [2-6].

These toxic metals may affect human health either through direct contact with the polluted water or indirectly through the consumption of fish, invertebrates and plants from the polluted river. However, these problems have lessened with the existence of legislation used to control discharge from mines, which remain in force today. As time passes by, tin ore mining activities in Malaysia have declined and are limited to a few areas due to land availability and environmental issues. Rahman Hydraulic Tin Sdn. Bhd. (RHT) is known to be the largest tin mining company in Malaysia that has been operating in the upper stream area of Kepayang River, Perak since 1907 and is still active [7]. However, over the last few years, lower water quality was reported downstream, which has caused a decline in fish caught in the connected Rui River [8, 9].

Although there are laws applicable to a mining operation, they have been seldom enforced strictly [1]. Elevated levels of heavy metals due to mining have been reported to pollute the natural aquatic environments in Malaysia [10-12]. Most of the studies on tin mines in Malaysia have only focused on ex-mining areas [2-5] and very rarely to cover active mines. Data on raw water quality, especially the levels of heavy metals from the discharge point of active mines are lacking, and those available only focus on selected places and important metal elements [6, 13]. Therefore, this preliminary study attempts to provide data on the metal content in mine effluent from RHT that has been released into the Kepayang River so that appropriate action or research can be taken to monitor any hazardous effects on the water and biodiversity downstream.

METHODOLOGY

Rahman Hydraulic Tin Sdn. Bhd. (RHT) is located at the upper stream of Kepayang River in Klian Intan, Perak, in the northen part of Peninsular Malaysia (Figure 1). Kepayang River is one of the small tributaries of Rui River responsible for transporting any waste or pollutants from the RHT mine into the main Perak River. Composite samples of surface water and sediment were collected in May 2016 at the point of 300 m from the RHT's settling pond located at N 5° 35.876′ and E 101° 3.625′ (Figure 1). The water sample was stored in an acid-washed polyethylene bottle and acidified with concentrated HNO_3 to a pH < 2. Meanwhile, the sediment sample was collected using a plastic scoop and stored in an acid-washed polyethylene bag. Both samples were then transported to the laboratory at 4 °C until analyses.

The in situ water quality parameters such as pH, temperature (Temp), electrical conductivity (EC), salinity, dissolved oxygen (DO), and turbidity were measured on site using Thermo Orion pH portable, Thermo Orion conductivity portable, YSI 52 DO meter and Hach 2100P Turbidimeter, respectively. For metals analysis, the water samples were filtered through a 0.45 µm cellulose acetate membrane filter and analysed for total dissolved metals (Aluminum - Al, Arsenic - As, Barium - Ba, Cadmium - Cd, Cobalt - Co, Copper - Cu, Chromium - Cr, Iron - Fe, Manganese - Mn, Nickel - Ni, Lead - Pb, Selenium - Se, Zinc - Zn) using inductively coupled plasma mass spectrometry (ICP-MS, Perkin Elmer, ELAN DRC-e).

The pH of sediment was measured according to Mclean [14] by using distilled water with 1:2.5; solid/liquid ratio, shaken for 4 h at 175 rpm and then read with a pH meter. The sediment EC was measured by using a conductivity meter in a mixture of distilled water with 1:1; the solid/liquid ratio [15]. For metals, the sediment samples were oven-dried at 60 °C for 48 – 72 hours, then meshed and sieved (63 µm). About 1 g of the dried sediment was digested in a 10-ml solution of a mixture of HNO_3 and $HClO_4$ in the ratio of 4:1 (v/v) into a block digester at a low temperature (40 °C) for 1 h and then at 140 °C for 3 h [16]. The digested sample was then diluted to 100 ml with Milli-Q (Millipore, USA) water and filtered through a 0.45 µm cellulose acetate membrane filter before measured by using ICP-MS.

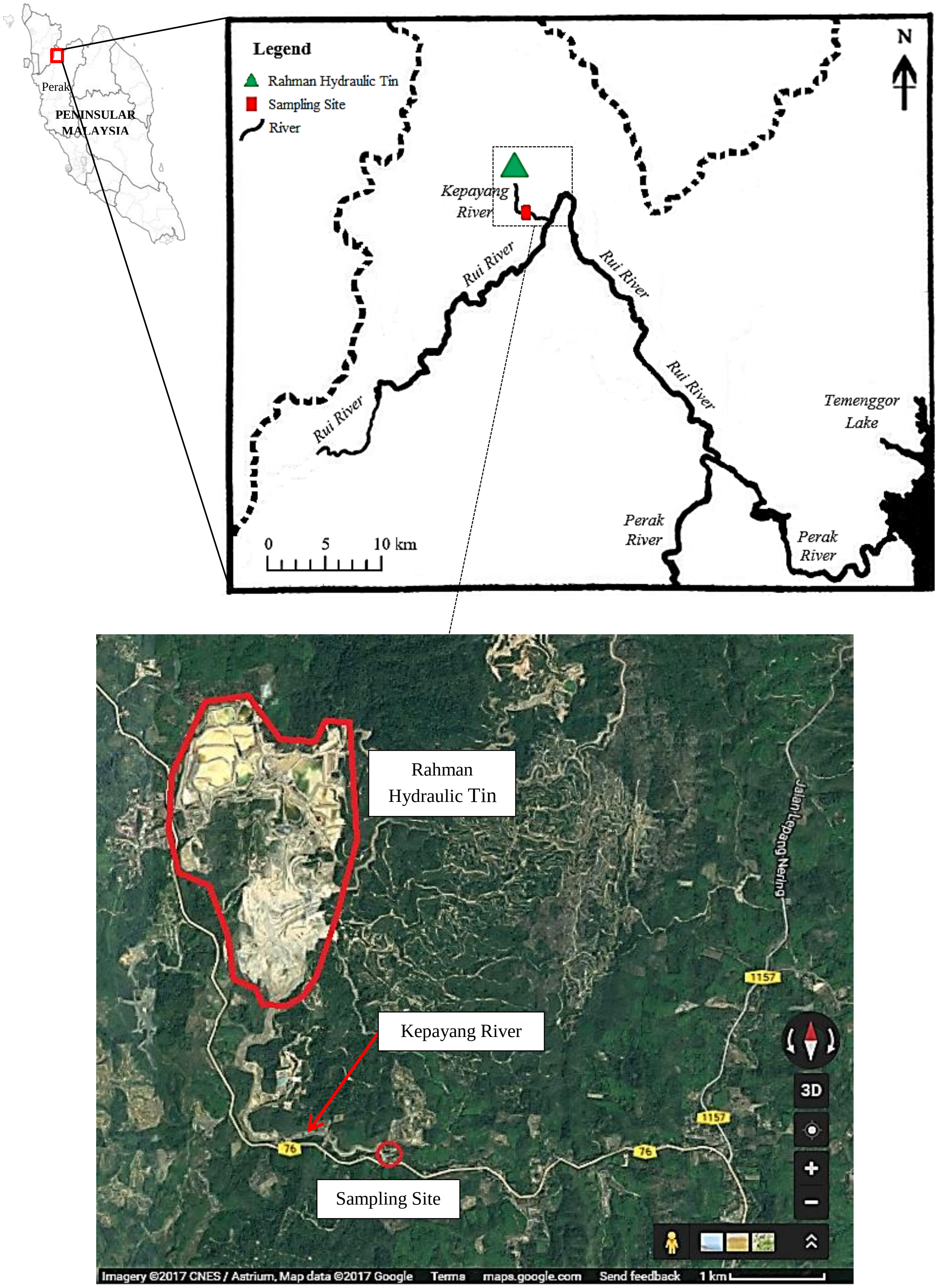

Figure 1 Study area showing the sampling site

For quality assurance and control, reagents used in the present study were of analytical grade. All apparatus and glassware were soaked in 10 % HNO_3 for at least 24 h and rinsed with distilled water. Triplicate samples were tested for each composite sample. A blank was used to ascertain background correction. A series of standard solutions was prepared from a stock solution (ICP-MS III, Perkin Elmer) to ensure precision and accuracy. Statistical analysis was conducted using SPSS (version 17, SPSS Inc.). Data on both water and sediment were compared to guidelines from the Ministry of Health (MOH) Malaysia for raw water and Canadian Council of Ministers of the Environment (CCME) for industrial soil, respectively.

RESULTS AND DISCUSSION

Based on the results (Table 1), the pH of both water and sediment were within the range values of the MOH and CCME guidelines. Previous studies showed that water draining from mining activities are usually in an acidic condition [17, 18]. However, in this present study, the pH values of both water and sediment were nearly neutral which may be due to the limestone treatment applied to the settling pond upstream on the same day of sampling. According to Edokpayi et al. [19], mining activities can also attribute to the high levels of EC which greater than 700 µS/cm may possess negative impacts on aquatic organisms. Therefore, the EC of water in the present study was considered high with a value of 945 ± 2.65 µS/cm. The higher water temperature (32.33 ± 0.12 °C) and DO (6.99 ± 0.20 mg/l) recorded in the present study might be influenced by the river characteristics of the sampling site which is shallow (0.18 m deep) and flowing.

Table 1 Mean concentrations (± SD) of physico-chemical properties and heavy metals in surface water (mg/l) and sediment (mg/kg, dry weight) of tin mine effluent at Kepayang River

	Water	Sediment	MOH – Raw Water (2010)	CCME – Industrial Soil (2015)
pH	7.13 ± 0.18	6.50 ± 0.09	5.50-9.00	6.0-8.0
EC (µS/cm)	945 ± 2.65	301 ± 2.65	NA	4000
Salinity (ppt)	0.50 ± 0.00	0.10 ± 0.00	NA	NA
Temp (°C)	32.33 ± 0.12	NA	NA	NA
Turbidity (NTU)	65.47 ± 3.42	NA	1000	NA
DO (mg/l)	6.99 ± 0.20	NA	NA	NA
Al	2.750 ± 0.070	4844.29 ± 36.10	NA	NA
As	0.288 ± 0.002	1038.10 ± 3.49	0.01	12
Ba	0.111 ± 0.001	223.41 ± 1.14	NA	2000
Cd	0.001 ± 0.000	0.48 ± 0.01	0.003	22
Co	0.089 ± 0.001	20.34 ± 0.13	NA	NA
Cr	ND	7.40 ± 0.12	0.05	87
Cu	0.102 ± 0.002	94.48 ± 0.40	1.00	91
Fe	5.679 ± 0.126	14526.73 ± 55.03	1.00	300
Mn	4.673 ± 0.122	289.34 ± 1.37	0.20	NA
Ni	0.106 ± 0.001	19.91 ± 0.17	NA	89
Pb	0.001 ± 0.000	149.34 ± 0.73	0.05	600
Se	0.001 ± 0.000	1.44 ± 0.02	0.01	NA
Zn	0.057 ± 0.001	39.78 ± 0.13	3.00	360

Notes: MOH = Ministry of Health, Malaysia; CCME = Canadian Council of Ministers of the Environment; NA = no available standard/data; ND = not detected; SD = standard deviation

This study found that Fe, Mn and As concentrations have exceeded the recommended MOH guidelines for untreated raw water with mean concentrations of 5.679 ± 0.126, 4.673 ± 0.122 and 0.288 ± 0.002 mg/l respectively. Meanwhile, in the sediment sample, the mean concentrations of Fe, As and Cu were found to exceed the recommended CCME guidelines with values of 14526.73 ± 55.03, 1038.10 ± 3.49 and 94.48 ± 0.40 mg/kg respectively. Although there is no available standard for Al of both MOH and CCME guidelines (Table 1), its concentration in the water in the present study was very high (2.750 ± 0.070 mg/l), exceeding the Al standard (0.200 mg/l) for MOH drinking water guideline. Overall, the tin mine effluent was responsible for the elevated concentration of As and Fe in both water and sediment of the Kepayang River. This result is supported by Johnson and Hallberg [18] who stated that elevated concentrations of metals such as Al, As, Fe and Mn are related to acid mine drainage from mining activities. Although both water and sediment pH in the present study were not acidic, the concentrations of those metals were at dangerous levels and can be more toxic when the pH decreases due to rainwater or untreated mine drainage.

Iron and manganese are essential micronutrients for the biological activities in plant and fish especially in cellular respiration, protein and enzyme activities [20, 21]. However, excess iron and manganese can generate reactive oxygen species (ROS) and induce oxidative stress [22]. Aluminum, on the other hand, has been associated with apoptosis and necrosis on fish gills and can be lethal if excessive. Arsenic is carcinogenic to humans. Long-term exposure to high As may cause skin and lung cancers to humans [23]. Although there is less human activity at the Kepayang River in the present study, the toxic metals from the mine effluent are carried down to the Rui River, which is important for human activities especially fishing. Many studies have reported high concentrations of metals in fish tissues due to mining activities that exceed the permissible levels for human consumption [24-26].

Many studies have identified that metals are generally not present in water-soluble forms but are alternately associated with sediment load and suspended particles [24,27]. This can be associated with the present study where the metal concentrations were higher in the sediment than in the water. These metals would also be transported along the river and accumulated in the sediment downstream. Therefore, further detailed analysis of heavy metals needs to be done downstream along the Rui River and Perak River on its impact on human, aquatic organisms, and the ecosystem.

CONCLUSION

This study has revealed that As and Fe are the major metal contaminants in the Kepayang River coming from a tin mine company located at the upper stream of the river. Although the mining company has set up a settling pond together with a limestone treatment, the concentrations of these metals still exceed the water and sediment quality guidelines. Therefore, future monitoring works and treatment should be taken by the mining company and government in order to protect the environment.

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REFERENCES

[1] Balamurugan, G. (1991). Tin mining and sediment supply in Peninsular Malaysia with special reference to the Kelang River Basin. *The Environmentalist*, *11*(4), 281–291.

[2] Ashraf, M. A., Maah, M. J., & Yusoff, I. Bin. (2010). Study of Water Quality and Heavy Metals in Soil & Water of Ex-Mining Area Bestari Jaya , Peninsular Malaysia. *International Journal of Basic & Applied Sciences*, *10*(3), 7–23.

[3] Ahmad, A. K., & Sarah, A. A.-M. (2014). Assessment of Abandoned Mine Impacts on Concentrations and Distribution of Heavy Metals in Surface Sediments of Catchments Around Sungai Lembing Abandoned Tin Mine. *Iranica Journal of Energy & Environment*, *5*(4), 453–460.

[4] Aris, A., & Kusin, F. M. (2014). Anoxic Limestone Drain for Treatment of Highly Acidic Water. In *From Sources to Solution Proceedings of the International Conference on Environmental Forensics*, 181–186.

[5] Orji, K. U., Sapari, N. B., Yusof, K. W., Robabeh, A., & Olisa, E. (2014). Water Quality Assessment of Ex-Mining Lakes in Perak, Malaysia as Alternative Source of Water Supply. *Applied Mechanics and Materials*, 567, 177–182.

[6] Abdullah, N. H., Mohamed, N., Sulaiman, L. H., Zakaria, T. A., & Abdul Rahim, D. (2016). Potential health impacts of bauxite mining in Kuantan. *Malaysian Journal of Medical Sciences*, *23*(3), 1–8.

[7] PHDC (Pengkalan Hulu District Council). (2016). *Rahman Hydraulic Tin Ore Mine*. Pengkalan Hulu District Council. Available from: http://www.mdph.gov.my/en/visitors/places-interest/rahman-hydraulic-tin-ore-mine [Accessed on 27th December 2016].

[8] Bernama. (2015, September 22). *Ikan loma diancam sisa perlombongan*. Sinar Harian, Kuala Lumpur, Malaysia. Available from: http://www.sinarharian.com.my/rencana/ikan-loma-diancam-sisa-perlombongan-1.433647 [Accessed on 11th April 2016].

[9] Abd Manap, A.H. (2016, December 27). *Dapat induk dengan menjala di Lenggong*. Harian Metro, Kuala Lumpur, Malaysia. Available from: http:// http://www.hmetro.com.my/node/191930 [Accessed on 27th December 2016]

[10] Kamaruzzaman, Y., Siti, W. A., Ong, M. C., & Joseph, B. (2010). Spatial distribution of lead and copper in the bottom sediments of Pahang river estuary, Pahang, Malaysia. *Sains Malaysiana*, *39*(4), 543–547.

[11] Ashraf, M. A., Maah, M. J., Yusoff, I., Wajid, A., & Mahmood, K. (2011). Sand mining effects, causes and concerns: A case study from Bestari Jaya, Selangor, Peninsular Malaysia. *Scientific Research and Essays*, *6*(6), 1216–1231.

[12] Kusin, F. M., Rahman, M. S. A., Madzin, Z., Jusop, S., Mohamat-Yusuff, F., Ariffin, M., & Z, M. S. M. (2016). The occurrence and potential ecological risk assessment of bauxite mine-impacted water and sediments in Kuantan, Pahang,Malaysia. *Environmental Science and Pollution Research*, (October), 1–16.

[13] Madzin, Z., Shai-in, M. F., & Kusin, F. M. (2015). Comparing Heavy Metal Mobility in Active and Abandoned Mining Sites at Bestari Jaya, Selangor. *Procedia Environmental Sciences*, 30, 232–237.

[14] McLean, E. O. (1982). Soil pH and lime requirement. *Methods of soil analysis. Part 2. Chemical and Microbiological Properties*, 199-224.

[15] Eigenberg, R. A., Doran, J. W., Nienaber, J. A., Ferguson, R. B., & Woodbury, B. L. (2002). Electrical conductivity monitoring of soil condition and available N with animal manure and a cover crop. *Agriculture, Ecosystems & Environment*, *88*(2), 183-193.

[16] Ismail, A. (1993). Heavy metal concentrations in sediments off Bintulu, Malaysia. *Marine Pollution Bulletin*, *26*(12), 706-707.

[17] Salomons, W. (1995). Environmental impact of metals derived from mining activities: Processes, predictions, prevention. *Journal of Geochemical Exploration*, *52*(1–2), 5–23.

[18] Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: A review. *Science of the Total Environment*, *338*(1–2 SPEC. ISS.), 3–14.

[19] Edokpayi, J. N., Odiyo, J. O., & Shikwambana, P. P. (2016). Seasonal variation of the impact of mining activities on Ga-Selati River in Limpopo Province, South Africa. *International Journal of Environmental, Chemical, Ecological, Geological and Geophysical Engineering*, *10*(2), 156–161.

[20] Millaleo, R., Reyes- Diaz, M., Ivanov, A. G., Mora, M. L., & Alberdi, M. (2010). Manganese As Essential and Toxic Element for Plants: Transport, Accumulation and Resistance Mechanisms. *Journal of Soil Science and Plant Nutrition*, *10*, 470–481.

[21] Debnath, M., Saha, R. K., Kamilya, D., Saikia, D., & Saha, H. (2012). Effects of water borne iron on spawn of Indian major carps (Catla catla (Ham.), Labeo rohita (Ham.) and Cirrhinus mrigala (Ham). *Bulletin of Environmental Contamination and Toxicology*, *89*(6), 1170–1174.

[22] Sevcikova, M., Modra, H., Slaninova, A., & Svobodova, Z. (2011). Metals as a cause of oxidative stress in fish: a review. *Veterinarni Medicina*, *56*(11), 537–546.

[23] ATSDR. (2007). Toxicological profile for Arsenic. Available from: https://www.atsdr.cdc.gov/toxprofiles/tp2.pdf [Accessed on 30th March 2017].

[24] Tarras-Wahlberg, N. H., Flachier, A., Lane, S. N., & Sangfors, O. (2001). Environmental impacts and metal exposure of aquatic ecosystems in rivers contaminated by small scale gold mining: The Puyango River basin, southern Ecuador. *Science of the Total Environment*, *278*(1–3), 239–261.

[25] Zhu, F., Qu, L., Fan, W., Wang, A., Hao, H., Li, X., & Yao, S. (2015). Study on heavy metal levels and its health risk assessment in some edible fishes from Nansi Lake, China. *Environmental Monitoring and Assessment*, *187*(4), 161.

[26] Squadrone, S., Burioli, E., Monaco, G., Koya, M. K., Prearo, M., Gennero, S., … Abete, M. C. (2016). Human exposure to metals due to consumption of fish from an artificial lake basin close to an active mining area in Katanga (D.R. Congo). *Science of the Total Environment*, *568*(May), 679–684.

[27] Mol, J. H., & Ouboter, P. E. (2004). Downstream Effects of Erosion from Small-Scale Gold Mining on the Instream Habitat and Fish Community of a Small Neotropical Rainforest Stream. *Conservation Biology*, *18*(1), 201–214.