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Metal Distribution and Contamination of the Mamut River, Malaysia, Caused by Copper Mine Discharge

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Over the last decades, environmental contamination with heavy metals has increased drastically (Knasmuller et al., 1998). Metal-rich wastes resulting from the mining activities are one of the most important potential hazard to the environmental (Fergusson, 1990, Larsen et al., 2001). Mining activities have a considerable impact on the environment. Besides the local disturbance of the soil profile and structure, a more widespread contamination of soils, vegetation and watercourses by toxic metals and metalloids can occur (Wilmoth et al., 1991). Mining and milling operations, together with grinding, concentrating ores and disposal of tailings, provide obvious sources of contamination in the surface environment, along with mine and mill waste water (Adriano, 1986). As a result, elevated levels of heavy metals can be found in and around disused metalliferous mines due to discharge and dispersion of mine wastes into nearby agricultural soils, food crops and stream systems. Eventually, they may pose a potential health risk to residents in the vicinity of mining areas (Jung 2001).

In Malaysia, an open pit copper mine is located in the headwater of the Mamut River in the interior of Sabah, Borneo. The mine began operation in 1975 and ceased operation in 1999. This mine has known to cause a number of environmental problems and is a source of heavy metals for environmental contamination. The main source of heavy metals originates from the runoff of the mine site in addition to the floatation process used in preparing copper concentrates. A number of rivers downstream to the mine site have been reported contaminated by heavy metals (Lee et al., 1993, Lee, 1995). A study of the Mamut River by Lee and Stuebing (1990) on the effect of copper mine runoff/discharge indicated that not only the river itself is contaminated but fauna living in the riparian zone also contaminated by high level of several metals, notably copper.

The Mamut River flows through a section of the Kinabalu Park at Poring, an area of lowland tropical rainforest gazetted for conservation, recreation and tourism. During the operation of the copper mine, the Mamut River and its riparian zone were prohibited for recreational and tourism purposes because of river pollution caused by high level of heavy metals in the Mamut River and in the soil.

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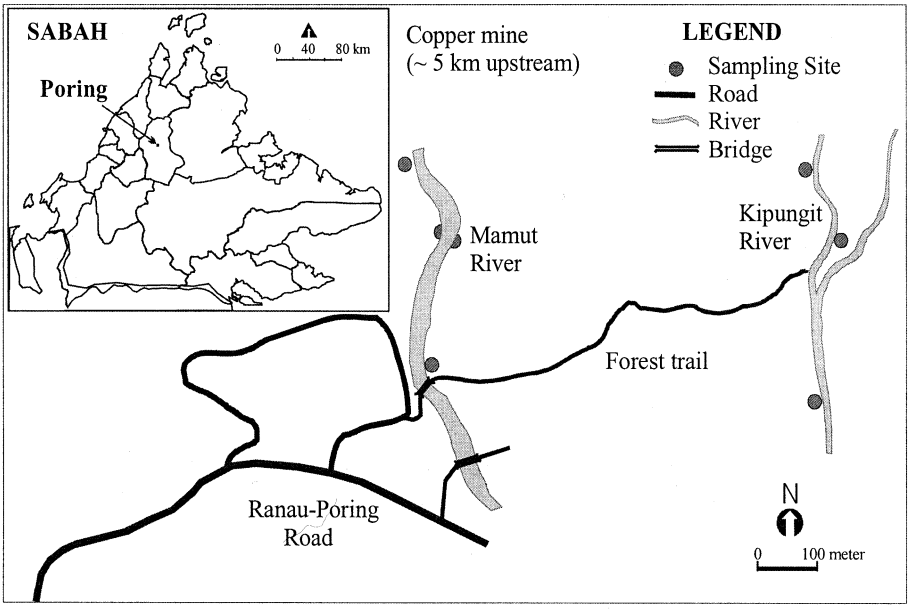

Figure 1. The location of sampling points along the Mamut and Kipunyit Rivers at Poring Park, Sabah, Malaysia.

Several years after the closure of the mine, there is now interest to allow the River to be used for recreation and tourism. We have recently carried out a study on the along the river bank to ascertain whether the river is safe for human recreational activities after the cessation of mining. The results reported here not only useful for assessing the process of recovery from heavy metal pollution of a riverine environment in the tropics, it also allows the evaluation of possible impact on human health if the riparian zone of the Mamut River at Poring is to be used for recreational purposes.

MATERIALS AND METHODS

Three sampling sites along the Mamut River, which are accessible and may be used for recreational activities were selected. At each site apart from water samples, soil samples were also collected at riverbanks where flooding occurs during wet season in which deposition of mine wastes from the river occurred. For comparison purpose, three other sites were selected from the Kipungit River situated within approximately 600 m from the Mamut River but not affected by the discharge from the copper mine. The location of the rivers and sampling stations are shown in Fig 1.

Composite soil samples were collected up to a depth of 20cm at 0, 5, and 10 m from the edge of the river. The heavy metals were extracted from the soil samples using USEPA methods (1979). Ten grams of soil samples were extracted with 50 mL of 1M HCl for 24 hours. The extract was then filtered through a 45 μm membrane filter (Millipore) and analyzed for 10 metals (As, Cd, Cu, Pb, Zn, Cr,

Table 1. The recovery and reproducibility of the analytical procedure used for the determination of heavy metals and As in soil samples.

Metal	Metal spiked (mg/kg)	Recovery (%)	Reproducibility RSD (%)
As	0.12	81.2	0.8
Cd	0.025	84.0	2.1
Co	2	82.7	8.6
Cr	3	81.2	9.0
Cu	40	90.6	3.1
Mn	50	83.3	2.3
Ni	20	87.8	7.4
Pb	10	84.7	7.3
Zn	0.40	89.3	1.0

Ni, Fe, Mn and Co) using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 4300 DV).

For water samples, pH, total dissolved solid (TDS), electric conductivity (EC) and temperature were measured in the field using a Myron portable meter. Dissolved oxygen (DO) was measured with a YSI oxygen meter. Before analysis, water samples were filtered with 0.45 μm filters (Millipore) and then acidified to pH< 2 with nitric acid (APHA, 1995). Water samples were analyzed for 10 metals (Cu, As, Cr, Co, Mn, Ni, Pb, Zn, Fe and Cd.) with ICP–OES. All samples were analyzed in five replicates. Reproducibility and recovery studies on the analytical procedures were also carried out. The t-test was used to compare heavy metals concentrations in soil and water samples from the Mamut River and Kipungit River with P values <0.05.

RESULTS AND DISCUSSION

The recovery and reproducibility of the metal analysis in soil samples spiked with appropriate amounts of metals and As are shown in Table 1.

The recovery of the procedure for soil metal analysis yielded 81 – 90 % recoveries for all metals. This implies that the extraction procedure used is satisfactory in extracting acid soluble metal compounds from the soil. Furthermore, the analysis of five replicates of each soil samples demonstrated relative standard errors (RSD) below 10% in general. Therefore, the procedure is reliable for metal determination in soil.

The levels of metal in soil samples from the riverbank of the Mamut River at various distances from the river are included in Table 2. Compared with the Kipungit River, which is not contaminated by copper mine wastes, soil samples from the riverbank of the Mamut River have higher average contents of all metals analyzed. In general, the levels of heavy metals and As in soils from Mamut River

Table 2. Heavy metals content** (mg/kg) of soil samples from Mamut and Kipungit riverbanks.

	Mamut River (4 samples)			Kipungit River (3 samples)
Metal	0 m	5 m	10 m	Average
As	0.16 ± 0.08	0.12 ± 0.09	0.03± 0.04	0.01 ± 0.01
Cd	0.024± 0.004	0.02 ± 0.01	0.01 ± 0.01	0.001 ± 0.002
Co	1.45 ± 0.17	0.93 ±0.48	0.83 ± 0.37	0.39 ± 0.22
Cr	3.09 ± 1.37	4.13 ± 1.15	2.18 ± 1.62	0.26 ± 0.13
Cu	41.77 ± 18.01	52.5 ± 17.0	16.6 ± 13.7	0.28 ± 0.10
Fe	1118.9 ± 457.2	1271.3 ±347.6	502.8 ± 171.2	294.6 ± 105.1
Mn	89.53 ± 26.2	48.75 ± 39.06	35.6 ± 19.40	0.39 ± 0.22
Ni	27.78 ± 13.42	21.13 ± 9.22	7.33 ± 6.92	1.95 ± 1.10
Pb	11.83 ± 8.28	9.18 ± 3.75	3.65 ± 2.12	0.38 ± 0.09
Zn	6.70 ± 1.00	4.08 ± 2.96	2.93 ± 2.36	0.83 ± 0.31

**Average of 4 – 9 analyses

were 10-100 times higher than the levels found in Kipunyit River (Table 2). The soil samples from Mamut riverbank have significantly higher levels of As, Cd, Cu, Pb, Zn, Cr, Ni, Fe, Mn and Co relative to samples from Kipungit riverbank ($P<0.05$). In the Mamut riverbank, the heavy metal concentrations of the soil were observed to decrease gradually from the edge of the river towards the forest at the riparian zone.

This clearly shows that there is deposition of sediments originated from mine wastes at the riverbank from flooding during tropical storms, which contributes to the elevated amount of metal in the soil at the riparian forest found along the river. The impact appears to extend up to 10 meters at the riverbank into the forested areas.

The degree of contamination by some metals in the soils near to the Mamut River may be compared with contamination by mining activities elsewhere. Contamination of soils by several heavy metals in the surrounding of a Au-Ag mine (Jung, 2001) showed 0.07-0.38 mg/kg Cd, 0.30-6.57 mg/kg Cu, 13.6-32.3 mg/kg Pb and 6.2-39.9 mg/kg Zn in soil samples extracted by 0.1 N HCl. For Cd, Cu, Pb and Zn, the reported world average values in soils were 0.35, 30, 35 and 90 mg/kg respectively (Jung, 2001). Metal enrichment factors (EFs) for the soil samples may be calculated by assuming that the metal content of the Kipungit soil is the natural level of the study area. The EF is thus (Manta et al. 2002):

EF = Metal concentration in Mamut soil / Metal concentration in Kipungit soil

From Table 3, all EF values were greater than 1 and this is an indication that the Mamut soils were enriched with heavy metals. Highest enrichment of metal was

Table 3. The EF values of soils from the Mamut River bank with reference to that from Kipungit River bank.

Metals	EF values of Mamut soils
As	12
Cd	20
Cr	12
Co	2.7
Cu	132
Fe	3.3
Mn	148
Ni	9.6
Pb	21.8
Zn	5.5

observed for Cu and Mn (EF = 132 and 148 respectively), this is followed by As, Cd, Cr, and Pb (EF = 10 – 21) and Co, Fe, Ni, and Zn (EF = 1 – 10). Thus, the most obvious contamination through the deposition of sediment at the riverbank from the Mamut River is Cu and Mn. But the risk of contamination by the toxic metals, e.g. Cd, Pb and As is also high since the soils at the Mamut River are clearly enriched by these metals. The soil samples from the Mamut River area is relatively high in Cu content, especially for samples collected at 0 m. Thus, this indicates that Cu is one of the main pollutant.

Apart from examining the heavy metal contents of the soil at the riverbank, information regarding the contamination of the Mamut River may be obtained from the river water. However, river water will only indicate the current situation of contamination and unlike soil samples, which can demonstrate the 'history' of contamination. Some water quality data and heavy metal contents of the Mamut and Kipungit River water are depicted in Table 4.

The concentrations of the heavy metals (Cd, Cu, Fe, Mn, Ni, Zn) of water samples from the Mamut were higher than that of Kipungit River and *t*-test results indicate that such differences are significant at $P<0.05$. For most metals, the concentrations are approximately 3 – 10 times higher in the water of the Mamut River compared with Kipungit River. Mn, Ni and Co concentrations in the Mamut River are from 10 to several hundred times higher. Obviously, the contamination of the Mamut River by metals still occurs even though the copper mine has ceased operation several years ago.

The contamination of the Mamut River is further confirmed by the electrical conductivity and total dissolved solids of the Mamut River, which is almost 10 times higher than that of the Kipungit River (Table 4). Therefore, water from the Mamut River still contains a relatively high loading of dissolved substance come from the mine wastes. Nevertheless, Except for Mn, the levels of metals in the water of the Mamut River are still very much below safe standards recommended

Table 4. The metals contents and physical parameters of water samples from the river studied as compared to Malaysian and FAO standards.

	Mamut	Kipungit	[a]Malaysian standards	[b]FAO standards
As (µg/L)	2.56±0.43 (2.1 – 3.28)	*nd – 3.36	50	100
Cd (µg/L)	0.37±0.22 (0.13 - 0.83)	0.15±0.15 (0.11– 0.35)	5	10
Co (µg/L)	2.86±0.54 (2.02 - 4.04)	nd	-	-
Cr (µg/L)	0.71±0.70 (0.27 - 3.33)	nd – 0.52	50	-
Cu (µg/L)	13.6±3.0 (10.6 - 17.1)	1.39±2.18 (0.42 – 6.20)	1000	200
Fe (µg/L)	14.85±6.25 (5.36 - 22.4)	3.91±1.69 (2.33 – 5.48)	1000	5000
Ni (µg/L)	24.5±3.0 (21.7 - 33.8)	0.80±1.02 (0.50 – 1.98)	-	200
Pb (µg/L)	2.08±1.42 (1.03 - 4.83)	nd – 2.14	100	500
Zn (µg/L)	21.8±9.8 (10.1 - 45.2)	6.01±2.31 (2.86 – 9.39)	1500	2000
Mn (µg/L)	406±32 (368 - 472)	0.38±0.39 (0.101– 1.24)	200	200
EC (µS/cm)	318.5±6.0	40.2±1.6	-	
pH	6.15±0.43	7.30±0.90	5.5-9.0	
TDS (mg/L)	208.0±3.0	25.8±1.1	1500	
DO (mg/L)	7.7±0.3	7.5±0.2	-	

[a] Ministry of Health, Malaysia (1990). Recommended raw water criteria. [b] FAO irrigation water standard (Kamra et al., 2002). * nd : not detected. Detection limit (µg/L): As <2; Co<2; Cd<2; Pb<1.

by Malaysia and FAO (Kamra, 2002) (Table 4). The data for several metals in water may be compared with similar studies from a Au-Ag mine (Jung, 2001), which reported the highest level of Cd, Cu, Pb and Zn as 10, 20, 10 and 60 µg/L respectively. These levels of heavy metals are higher than those found in the Mamut River (Table 4).

The effect of cessation of copper mine operation on the water quality and metal contents of the Mamut River may be assessed by comparing data of some metals reported for the river since 1980 (Table 5). There is a very clear reduction of the As and several other heavy metals in the water of the Mamut River from 1980 to

Table 5. The variation of metal contents and some water quality parameters of the Mamut River from 1980-2003.

	[a]1980	1982	1984	2003 (This work)
As (μg/L)	15	-	-	2.56
Cd (μg/L)	8	10	-	0.37
Cr (μg/L)	15	48	10	0.71
Cu (μg/L)	330	718	720	13.6
Mn (μg/L)	488	240	790	407.5
Pb (μg/L)	55	-	140	2.08
EC (μS/cm)	1000	494.8	174	318.5
pH	6.5 – 8.5	6.5 – 8.5	5.5 - 8.5	6.15

[a]Data source for 1980-1984: Department of Environment, Malaysia (1992).

2003 indicating the diminishing level of contamination by metals. However, for Mn, its level remains high and comparable to values reported in the 1980's. Therefore, since the mine operation stopped in 1999, the negative impact of mining on the Mamut River appears to diminish.

This study has shown that contamination of the Mamut River by copper mine located upstream still occurs even after the mine operation ceased in 1999. The soil of the forest area along the riverbank remain highly contaminated especially by copper and other toxic metals whilst the river water still contained elevated levels of most metals although there is a trend of reduction in metal contents. The heavy metals and As contents of the riverine environment remain high, and this may be a health hazard if the site is used for recreation purposes. This is because the accumulation of non-essential elements such as Pb and Cd can occur and this may magnify their toxicity (Abo-Elseoud et al., 1994). Therefore, the impact of the contaminated site on the surrounding biota needs to be known before any attempt to reopen the site for recreational purposes.

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REFERENCES

Abo-Elseoud MA, Abdel- Shafy HI (1994). Environmental studies of plants grown in soil polluted with cobalt and nickel. J. Environ. Manage. & Health 5:16-21.

Adriano DC (1986). Trace elements in the terrestrial environment, Springer-Verlag, New York.

American Public Health Association (APHA) (1995). Standard methods for the examination of water and wastewater (19th Edn), APHA, Washington, DC.

Department of Environment, Ministry of Science, Technology and environment, Malaysia (1992) Development of Water Quality Criteria and Stndards - Phase IV (River Classification), Kuala Lumpur, Malaysia.

Fergusson JE (1990). The Heavy Elements: Chemistry, Environmental Impact and Health Effects. Pergamon Press, Oxford.

Jung MC (2001). Heavy metals contamination of soils and waters in and around Imcheon Au-Ag mine, Korea. J. Appl. Geochem. 16:1369-1375.

Kamra SK, Khajanchi L, Singh OP, and Boonstra J (2002). Effect of pumping on temporal changes in groundwater quality, J. Agri. Wat. Manage. 56: 169-178.

Knasmuller S, Gottman E, Steinkellner H, Fomin A, Pickl C, Paschke A, God R, Kundi M (1998). Detection of genotoxic effects of heavy metal contaminated soils with plant bioassays. J. Mut. Res. Genet. Toxicol. Environ. Mutagen. 420: 37–48.

Larsen TS, Kristensen JA, Asmund G, Bjerregaard P (2001). Lead and zinc in sediments and biota from Maarmorilik, West Greenland: an assessment of the environmental impact of mining wastes on an Arctic fjord system. Environ. Pollut. 114: 275–283.

Lee YH, Stuebing RB (1990). Heavy metals Contamination in the river Toad, *Bufo jutasper* (Inger), Near a Copper Mine in East Malaysia. Bull. Environ. Contam. Toxicol. 45: 272-279.

Lee Y.H. (1992). Development of Water Quality Criteria and Standards – Phase IV (River Classification).Volume VI, River Classification – Sg. Sugut. Ministry of Science, Technology and Environment, Kuala Lumpur, Malaysia.

Lee Y.H. (1996). Effects of land use on the water quality of rivers in the Ranau-Kundasang area, Sabah. In Low K.S. (ed). Control of Water Pollution Caused by Mining Activities in Southeast Asia, UNEP, 50-80.

Manta DS, Angelone M, Bellanca A, Neri R, Sprovieri M (2002). Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. Sci. Tot. Environ. 300:229-243.

Ministry of Health, Malysia (1990). Recommended raw water quality criteria and drinking water quality standards, Kuala Lumpur, Malaysia.

U.S. Environmental Protection Agency (1979). Methods for Chemical Analysis of Water and Wastes. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio.

Wilmoth RC, Hubbard SJ, Burckle JO, Martin JF (1991). Production and processing of metals: their disposal and future risks. In Merian, E. editor. Metals and their compound s in the environment. Occurrence, analysis and biological relevance. Verlagsgesellschaft mbH, Weinheim, Germany, 19-65.