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Assessment of heavy metals contamination in Mamut river sediments using sediment quality guidelines and geochemical indices

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Abstract This paper describes the concentration of selected heavy metals (Co, Cu, Ni, Pb, and Zn) in the Mamut river sediments and evaluate the degree of contamination of the river polluted by a disused copper mine. Based on the analytical results, copper showed the highest concentration in most of the river samples. A comparison with Interim Canadian Sediment Quality Guidelines (ICSQG) and Germany Sediment Quality Guidelines (GSQG) indicated that the sediment samples in all the sampling stations, except Mamut river control site (M1), exceeded the limit established for Cu, Ni, and Pb. On the contrary, Zn concentrations were reported well below the guidelines limit (ICSQG and GSQG). Mineralogical analysis indicated that the Mamut river sediments were primarily composed of quartz and accessory minerals such as chalcopyrite, pyrite, edenite, kaolinite, mica, and muscovite, reflected by the geological character of the study area. Enrichment factor (EF) and geoaccumulation index (I_{geo}) were calculated to evaluate the heavy metal pollution in river sediments. I_{geo} values indicated that all the sites were strongly polluted with the studied metals in most sampling stations, specifically those located along the Mamut main stream. The enrichment factor with value greater than 1.5 suggested that the source of heavy metals was mainly derived from anthropogenic activity such as mining. The degree of metal changes (δ_{fold}) revealed that Cu concentration in the river sediments has increased as much as 20 to 38 folds since the preliminary investigation conducted in year 2004.

Keywords Geoaccumulation index · Enrichment factor · River · Pollution · Heavy metal · Mineralogy

Introduction

Mining is considered as a significant anthropogenic source for heavy metals pollution in the environment (Galan et al. 2003; Canovas et al. 2007; Gandy et al. 2007). Elevated concentrations of heavy metals are often found in the vicinity of disused metalliferous mines due to the dispersion of dissolved and particulate mine wastes. These wastes are capable of contaminating adjacent agricultural soils, food crops, and aquatic

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systems even at several kilometers downstream. Prolonged exposure to heavy metals may cause adverse effects on the health status of the residents living nearby. In tropical region such as the Mamut Copper Mine (MCM) of Malaysia, the distribution of heavy metals into the surrounding environment was further exacerbated by intense precipitation and rapid weathering rate associated with the dynamic fluvial processes. As a consequence, heavy metals such as Cu, Ni, Pb, and Zn are likely to be bioaccumulated in the aquatic primary producers, which eventually enter the food web and transfer to a higher trophic level (Cui et al. 2011). Exposure to heavy metals has been linked to several human diseases via food chain such as kidney damage, cancer, abortion, effect on intelligence/behavior, and even death (Jiries 2003). For instance, Pb is classified as being exceptionally hazardous and toxic to most forms of life and found to be responsible for several numbers of ailments in human such as chronic neurological disorders especially in children (Awofulu et al. 2005). On the other hand, although Zn has been found to have low toxicity to man but prolonged consumption can result fatigue, dizziness, and neutropenia while high content of Co can contribute to dermatitis and carcinogenic (Basketter et al. 2003).

Sediments have been widely used as environmental indicators owing to their ability to trace contamination sources and monitor multifarious of pollutants (Jung 2001; Yu et al. 2011; Mashiatullah et al. 2012). Despite the usefulness, sediments also serve as reservoir of inorganic contaminants, liberating pollutants such as heavy metals back into aqueous phase when the physico-chemical condition is favorable. With the MCM located upstream, prolific toxic materials and heavy metals are likely to be distributed downstream via clastic movement, wind, and water (Jung 2001), which ultimately deteriorates the quality of water and sediments in the vicinity. To date, there has been limited published information and monitoring data on Mamut river sediment except a preliminary investigation reported by Ali et al. (2004). We believed that the level of heavy metals in the Mamut river has been greatly increased in the recent years due to constant supply of the acid mine water from the MCM. In view of the lacking of monitoring studies, this study has been undertaken to assess the degree of selected heavy metals contamination (Co, Cu, Ni, Pb, and Zn) in the superficial sediments along Mamut river using various sediment quality guidelines and geochemical indices. The present study is of utmost importance in determining the current status of sediment pollution in the Mamut river. In addition, this paper also examines the metals distribution and mineral compositions in the solid phase samples as well as the environmental significance of the disused copper mine in the environment.

Materials and methods

Study area

The MCM is located at the Ranau district of Sabah, Eastern Malaysia. Previously, MCM was the largest open pit mine (1943 ha) in South East Asia during its operation from 1975 to 1999. The open pit is located at the southeastern flank of Mount Kinabalu, at an altitude of 1300–1600 m above sea level (Ali et al. 2004). Geologically, the MCM is occupied by ultrabasic rocks, adamellite porphyry, sandstone, and siltstone. Large masses of Tertiary–Cretaceous serpentinite and intrusive quartz monzonite were uplifted during the Late Miocene–Pliocene due to severe tectonic activity. The intrusive introduced magmatic hydrothermal fluids, which subsequently led to quartz–biotite alteration and copper–gold mineralization. Copper–gold mineralization is observed in fractured zones, which are related to the extending ophiolite sequences (Akiyama 1987). Annual precipitation at the mine area varies greatly from years to years, with dry season usually extends from March to August and wet season from December to February. The annual rainfall recorded generally ranged from 2500 to 3500 mm and daily temperature varies from 15 to 28 °C (Mohd. Azizli et al. 1995).

The mining ores in the MCM were primarily composed of copper and gold, together with a few minor minerals such as chalcopyrite, magnetite, and pyrrhotite. Approximately 250 Mt of overburden and waste rocks and over 100 Mt of tailing were generated during its operation period (Jopony and Tongkul 2009). Upon closure of the MCM, all mine waste materials including the tailings were left without proper environmental remediation. A visual investigation of the dumpsite has confirmed the occurrence of a passive dispersal mechanism where appreciable amounts of tailing materials were eroded and transported with natural bedload to the river system, threatening the rainforest ecosystem, aquatic life, and indigenous people living downstream. A study carried out by Ali et al. (2004) has found considerable heavy metals contamination in the river water as a result of inadequate post-remedial plan.

Field and laboratory analysis

Sample collection was conducted at six sampling stations, covered from the upstream (M1) to downstream (M2, M3, and M4) of Mamut river and two other tributaries, namely Langanan (T1) and Mantukungan rivers (T2). Sampling station M1 was regarded as a "control" for the Mamut river owing to its upstream location. The sampling locations were determined using global positioning system (GPS) (see Table 1). Fig. 1 shows the locations of the sampling sites. The selection of sampling station primarily depends on sites with good accessibility.

Superficial river sediment (top 5 cm) were collected using a polypropylene spatula and kept in labeled plastic bags until analysis. In the laboratory, the sediments were air dried, passed through a 2-mm mesh screen, and stored in polyethylene bags after homogenization using pestle and mortar. All reagents used were of analytical grade. Stock standard solutions were prepared by using Perkin Elmer Certificate Standards. Cleaning of plastics and glasswares were conducted by soaking into 14 % (*v*/*v*) HNO_3 for 24 h and then rinsed with distilled water (Galan et al. 2003). The sediment samples (1.0-g dry weight) were digested using 18-ml aqua regia at 110 °C for 120 min. The samples were filtered through a Whatman filter paper (pore size 0.45 μm), diluted with 0.1 M of HNO_3 to a volume of 50 ml prior to analyzed using an atomic absorption spectroscopy (Perkin Elmer AAS 4100) to quantify the heavy metals (Co, Cu, Ni, Pb, and Zn) concentrations. Mineral analysis was determined using X-ray diffraction (XRD) analysis Bruker AXS D8 advance diffractometer. Approximately 1 g of sediment was pulverized with pestle and mortar and passed through a pore size <31 μm sieve. The pulverized samples were subsequently scanned by a Cu anode with 60 and 90^{o} 2_{θ}, operating at a velocity of 0.01 (^{o}/s), 40 kV, and 25 mA electric current (Lin et al. 2013). The quality of analytical data was assessed through the implementation of laboratory quality assurance and quality control methods, including the use of standard operating procedures, calibration with standards and analysis of reagent blank. All analyses were conducted in triplicates and the results were expressed as mean values.

Pollution guidelines and indices

The Interim Canadian Sediment Quality Guidelines (ICSQG) and Germany Sediment Quality Guidelines (GSQG) were adapted to assess the sediment quality in a biotoxicity framework. To assess the accumulation of various toxic metals in the river sediments, enrichment factor (EF) and geoaccumulation index (I_{geo}) were calculated.

EF was calculated to determine whether the levels of sediments in the study area were natural or anthropogenic origins. EF is considered as relative abundance of a chemical element in sediment compared to the background concentration or bedrock (Harikumar et al. 2010). Comparisons were made with the background concentrations in the Earth's crust using Al as a reference element, assuming that the content in the earth crust has not been disturbed by anthropogenic activities

Table 1 Location of sampling stations and GPS coordinates

Samples identification	Sampling location	Distance from source	GPS Position	
			Latitude	Longitude
M1	Mamut river	Control	N 06^0 02. 049′	E 116^0 39.120′
M2	Mamut river	5.5 km	N 06^0 02. 869′	E 116^0 42.061′
T1	Langanan river	5.6 km	N 06^0 03. 385′	E 116^0 42.139′
M3	Mamut river	5.7 km	N 06^0 02. 841′	E 116^0 42.819′
T2	Mantukungan river	5.7 km	N 06^0 02. 676′	E 116^0 42.761′
M4	Mamut river	9.8 km	N 06^0 02. 907′	E 116^0 44.439′

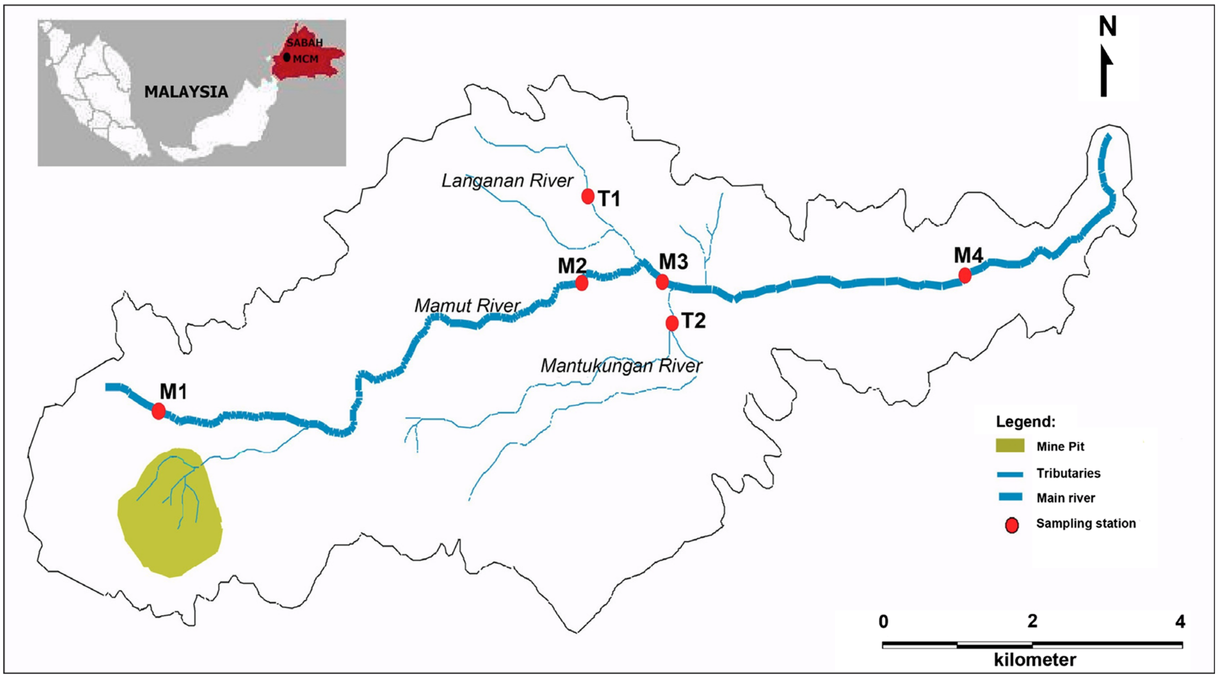

Fig 1 Sampling stations along Mamut river and its tributaries

(Rafiei et al. 2010). According to Rubio et al. (2000), the EF can be calculated as follows:

$$\mathrm{EF} = \left(M/\mathrm{Al}\right)_{\mathrm{sample}} / \left(M/\mathrm{Al}\right)_{\mathrm{background}} \qquad (1)$$

where $[\mathrm{M/Al}]_{\mathrm{sample}}$ is the ratio of concentration of metals in the samples to the natural concentration of Al while $[\mathrm{M/Al}]_{\mathrm{background}}$ is the ratio of background concentration of metals to the natural concentration of Al in the study area. The background value used was based on the average earth crust's metal concentration reported by Mason and Moore (Mason and Moore 1982a, b).

Whereas the I_{geo} is a quantitative measure of the degree of pollution in the aquatic sediments, which classified into seven classes ranging from unpolluted to very strongly polluted (Rubio et al. 2000; Praveena et al. 2008). The I_{geo} values can be determined using the following equation:

$$I_{geo} = \log_2\left(M/1.5 \times B_n\right) \qquad (2)$$

where M is the concentration of metal in sediment, B_n is the geochemical background concentration of metal collected within the study area (Ali et al. 2004), and 1.5 is the correction factor for variation in background values due to lithogenic effects (Moore et al. 2011).

Results and discussion

Characterization of minerals in the sediments

Table 2 summarizes the major minerals found in the river sediments. Based on the XRD analysis, the sediment sample of Mamut river and its tributaries were mainly comprised of quartz (SiO_2), together with minor minerals such as chalcopyrite ($CuFeS_2$), pyrite (FeS_2), edenite [$NaCa_2Mg_5Si_7AlO_{22}(OH)_2$], kaolinite [$Al_2Si_2O_5(OH)_4$], mica and muscovite [$KAl_2(AlSi_3O_{10})(F,OH)_2$, or $(KF)_2(Al_2O_3)_3(SiO_2)_6(H_2O)$], reflecting the geological characteristics of the study area. In the upstream (M1), the sediments were primarily composed of quartz. Significant amount of edenite, pyrite, and minor chrysotile were found at the Poring Hot Spring area (M2), suggesting the occurrence of mineralogical reduction during the river transport processes. However, the presence of chrysotile in the upper reach implies that oxidative weathering of serpentine group rocks is favored. The relative proportions of different crystalline phases are closely related to grain-size distribution. As a result, quartz was mainly associated in sand-grained sediments, whereas phyllosilicates appear to predominate the finer fractions. Clay minerals found in the Mamut river often appear as mica, muscovite, and kaolinite.

Concentration of heavy metals (Co, Cu, Ni, Pb, and Zn) in sediments

The maximum, minimum, and mean values of heavy metals in sediments of different stations are presented in Table 3.

The concentration of Co, Cu, Ni, Pb, and Zn (mg kg^{-1}) in river sediment were found in the range of 9.09 to 37.32 for Co, 40.79 to 1347.54 for Cu, 15.11 to 308.10 for Ni, Pb from <0.10 to 49.68, and Zn from 43.87 to 66.98, respectively. This indicates that the heavy metals in the river sediment basically followed the trend of Cu>Ni>Zn>Co>Pb. Station M2 recorded the highest concentration of Cu, Ni, and Pb in the sediments, suggesting analogous geochemical behavior of these metals in the study area. Coprecipitation, sorption onto Al/Fe hydroxides, and origin from common provenance are the plausible reasons that explained the significant correlation coefficient ($p<0.05$) between Cu–Ni ($r=0.90$), Ni–Pb ($r=0.90$), and Pb–Cu ($r=0.90$) (Table 4). On the contrary, elevated concentration of Co and Zn was detected at M4 and T2. The negative correlation found between Pb and Zn ($r=-0.40$) clearly indicates the distinct geochemical character of these metals.

High concentrations of Cu detected in the sediment at M2, M3, and M4 may be explained by the presence of Cu-bearing ore minerals, notably chalcopyrite ($CuFeS_2$) which primarily derived from upstream. Intense rainfall in the study domain also serves as an important agent in dispersing and distributing Cu from its source. Almost all heavy metals concentration except Co and Zn gradually decreases toward the lower reach of Mamut river. Such a drop in concentration is primarily attributed to the incremental flow or both distance and dilution factor from the surrounding terrain (Nieto et al. 2007). It should be noted that the concentration of Co and Zn demonstrate rather erratic trend as compared to Cu, Ni, and Pb. Such irregular behavior is probably attributed to the fact that Co and Zn do not fix permanently to sediments. Instead, these metals are highly susceptible to recycling and remobilization processes via biological and chemical agents, which occur within the sediments and water column (Kronvang 2002; Gadd 2010). In fact, most of the heavy metals can be easily released from the sediment in response to the changing environmental and redox condition.

It was observed that the pebbles and cobbles deposit along sampling station M2 were coated with a thin layer of white precipitate due to the formation of Fe and Al colloids ($Al(OH)_3$) from the opalescence water. Schemel et al. (2000) mentioned that approximately 10 % of the Al dissolved in Cement Creek in Colorado, USA formed particles at pH 4.6, while nearly all of the Al formed particles at about pH 6.5. Analogous observation was also noticed in the Mamut area. Zinc appears to sorb preferentially to Fe hydroxide, but the presence of Al hydroxide enhances removal of Cu, Pb, and Zn over systems with Fe hydroxide alone (Schemel et al. 2000). Thus, it can be suggested that the formation of colloids, transport of metals, and the deposition of colloids are the processes that greatly affect the water and streambed chemistry in the Mamut area. Heavy metals concentration in the sediments of Mamut river were compared with river sediments around the world polluted by copper mining activities. Generally, Cu and Ni concentration in the sediments of Mamut river exhibit greater pollution level compared to other studies except the Upper Tigris river and Salza river. Heavy metals such as Co, Pb, and Zn were found to have comparable concentration with sediment samples from the Great Smoky Mountain river of the United States and Adak Stream of Sweden as presented in Table 3.

The sediment quality of Mamut river was likewise compared with the limits of ICSQG and GSQG (Fig. 2). The concentration of Cu, Ni, and Pb exceeded both assigned limits of ICSQG and GSQG at M2, M3, and M4. The concentration of Pb was found to exceed the quality guidelines at M2 and M3, whereas Ni exceeded the guidelines for all sampling stations except M1. On the other hand, the concentrations of Zn basically comply with both guidelines limits and no standard (both ICSQG and GSQG) was assigned for Co.

Enrichment factors (EF)

Table 5 presents the EF values of metals in the study area. Note that we employed Fe as the reference elements for the EF calculation of sample T1 because we were unable to obtain the Al concentration from the sample. According to Zhang and Liu (2002), EF values greater than 1.5 suggests that the metals pollution are from anthropogenic origin whereas EF values between <0.01 to 1.5 indicate that the metals existence are derived from the crust materials or natural processes. In this study, the EF values in sediments followed the order Ni>Cu>Co>Zn>Pb.

Table 2 Mineral composition of Mamut river sediments samples

Station	M1	M2	T1	M3	T2	M4
Major minerals	Quartz Biotite	Quartz Edenite Pyrite Chrysotile	Quartz Smectite	Quartz Kaolinite Mica Chalcopyrite	Quartz	Quartz Muscovite Chrysotile

The highest EF value was recorded for Ni (1.00 to 26.64). Besides, Co, Cu, Pb, and Zn were ranged from <0.01 to 4.39; <0.01 to 15.22; <0.01 to 0.13, and <0.01 to 0.33, respectively. Enrichment factor of heavy metals

Table 3 Range, mean, and standard deviation of heavy metals in Mamut river sediments samples

Station		Co	Cu	Ni	Pb	Zn
M1 (*n*=6)	Range	9.09–9.36	42.22–42.42	15.11–15.13	11.11–11.13	43.87–44.11
	Mean	9.22	42.31	15.15	11.12	43.96
	SD	0.14	0.10	0.06	0.01	0.13
M2 (*n*=6)	Range	30.24–30.26	1347.45–1347.54	307.92–308.10	49.33–49.68	64.85–64.90
	Mean	30.25	1347.50	308.00	49.50	64.88
	SD	0.01	0.05	0.09	0.18	0.03
T1 (*n*=6)	Range	12.73–12.77	40.79–40.81	119.84–119.86	–	59.99–60.01
	Mean	12.75	40.80	119.85	< 0.02	60.00
	SD	0.02	0.01	0.01	–	0.01
M3 (*n*=6)	Range	31.37–37.32	1193.71–1197.07	251.33–253.83	41.04–43.99	62.79–66.98
	Mean	35.00	1195.00	252.50	42.50	65.00
	SD	3.18	1.81	1.26	1.48	2.10
T2 (*n*=6)	Range	22.89–23.03	47.99–48.49	119.84–119.86	0.49–0.51	67.6–68.41
	Mean	22.95	48.45	119.85	0.51	68.00
	SD	0.08	0.44	0.01	0.01	0.41
M4 (*n*=6)	Range	35.64–35.85	826.19–826.22	128.42–289.88	13.75–13.79	66.28–66.34
	Mean	35.70	826.20	209.10	13.77	66.30
	SD	0.06	0.02	80.73	0.02	0.03
This study	Range	9.09–37.32	40.80–1347.54	15.11–308.10	0.49–49.68	43.87–68.41
	Mean	24.31	583.38	170.74	23.48	61.36
Upper Tigris River, Turkey[a]	Range	245.00–515.60	2081.50–2869.30	122.10–534.60	456.6–660.10	614.20–1061.50
	Mean	359.50	2562.60	418.10	582.90	860.00
Salza River, Germany[b]	Range	6.00–27.00	20.00–12000.00	16.00–100.00	30.00–6900.00	64.00–38600.00
	Mean	12.10	1829.00	34.50	1115.0	5779.00
Great Smoky Mountain River, USA[c]	Range	6.00–27.00	5.00–76.00	4.00–38.00	8.00–45.00	5.00–199.00
	Mean	27.80	37.40	20.40	25.30	117.40
Adak Stream, Sweden[d]	Range	0.30–1.60	1.10–3600.00	0.70–4.10	0.60–300.00	1.60–19.00
	Mean	0.80	250.80	2.10	22.30	1.50

[a] Varol and Sen (2012)

[b] Wennrich et al. (2004)

[c] Hammarstrom et al. (2003)

[d] Bhattacharya et al. (2006)

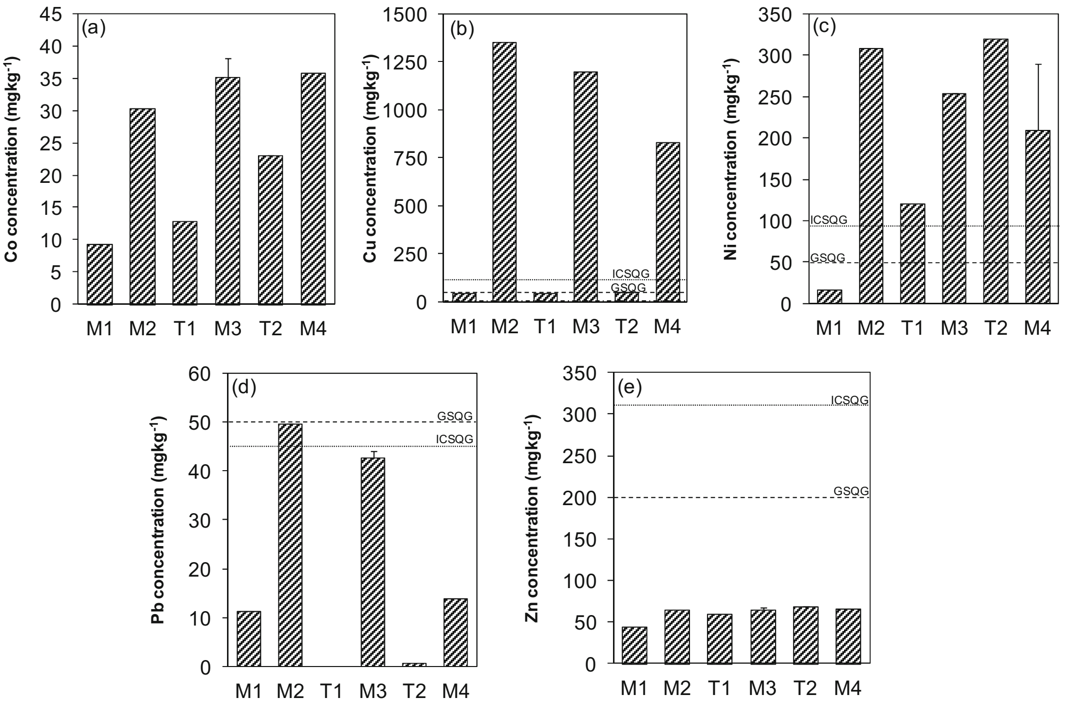

Fig 2 Metals concentration in sediments **a** Co, **b** Cu, **c** Ni, **d** Pb, and **e** Zn. The limit of metals in ICSQG—Cu: 197.0; Ni: 36.0; Pb: 91.3; Zn: 315.0 (in mg kg^{-1}) and in GSQG–Cu: 60.0; Ni: 50.0; Pb: 100.0; Zn: 200.0 (in mg kg^{-1})

(except Ni) in sediments at the tributaries (T2) were lower than 1.5, suggesting natural source of Ni. However, the degree of enrichment that exhibits great spatial distribution basically corresponds to the difference in metals removal rate from the sediments or the variations in the magnitude of metals sorption. The composition of minerals in the sediments often influences the distribution of metals in the river system. Thus, low EF values of Zn in the study area could be explained by the relatively depleted amount of Zn in the ore materials and its weak sorption affinity toward solid phase samples.

Table 4 Correlation coefficient (*r*) matrix of the studied heavy metals in the Mamut river sediment

	Co	Cu	Ni	Pb	Zn
Co	1.000	0.111	0.084	0.391	0.156
Cu	0.714	1.000	0.015	0.037	0.468
Ni	0.754	0.899*	1.000	0.037	0.538
Pb	0.500	0.900*	0.900*	1.000	0.505
Zn	0.657	0.371	0.319	−0.400	1.000

*Significant correlation at 0.05 level (2-tailed)

**Significant correlation at 0.01 level (2-tailed)

Geoaccumulation Index (I_{geo})

Table 6 presents the I_{geo} classification used in this study. The I_{geo} and degree of metal changes or "fold change" (δ_{fold}) in the river sediments following year 2004 was calculated and is presented in Table 7. Fold change was initially introduced by Tusher et al. (2001) to measure change in the expression level of a gene in microarray and RNA-Seq experiment. In this study, we employed this calculation to describe how much changes in concentration of heavy metals from an initial

Table 5 Enrichment factor (EF) of metals in sediments of studied area

EF	M1	M2	T1*	M3	T2	M4
Co	0.59	1.12	< 0.01	2.50	1.41	4.39
Cu	0.40	7.46	< 0.01	12.80	0.45	15.22
Ni	1.00	11.79	< 0.01	18.71	7.62	26.64
Pb	0.05	0.13	–	0.22	< 0.01	0.12
Zn	0.11	0.10	< 0.01	0.19	0.17	0.33

*EF calculation using Fe as reference element

Table 6 Geoaccumulation index classification (Muller 1979)

Sediment accumulation index (I_{geo})	I_{geo} class	Pollution intensity
>5	6	Very strongly polluted
>4–5	5	Strong to very strongly polluted
>3–4	4	Strongly polluted
>2–3	3	Moderately to strongly polluted
>1–2	2	Moderately polluted
>0–1	1	Unpolluted to moderate polluted
<0	0	Practically unpolluted

(background) to a final (present) value. To obtain a clearer insight of the extent of metals contamination since the previous assessment, we compared the river sediments metals content of this study with those determined by Ali et al. (2004). Calculations were made and denoted as δ_{fold} (Eq. 3), where one can directly determine the extent of heavy metals changes since 2004 by referring to the equation as follow:

$$\delta_{\text{fold}} = M_{\text{present}} \Big/ M_{\text{background}} \tag{3}$$

where M_{present} represent the metals concentration obtained from this study, while $M_{\text{background}}$ denotes literature data reported in Ali et al. (2004) (Table 7). A $\delta_{\text{fold}}>1$ indicates accumulation of metals whereas $\delta_{\text{fold}}<1$ corresponds to depletion of metals in the sediments since the first measurement in 2004.

Based on the I_{geo} values (Fig. 3), the sediments at most of the sampling stations were strongly polluted by Co, Cu, Ni, Pb, and Zn. Cobalt at station M1 and T1 fell in class 4 and 5 indicating strong to very strong pollution levels. Normally, background or historical data that best represent the study area should be used. Nevertheless, such data was unavailable in this study and therefore, we chose the widely used average earth crust's metals concentration reported by Mason and Moore (1982a, b). From the results, variation of I_{geo} values within the sampling stations might be due to a manifold of natural and anthropogenic processes (weathering and mining) and also the complex lithology that occurred in the study area. The enriched Cu and Ni concentration in the sediment samples along the Mamut river was demonstrated by high values of EF and I_{geo}. Elevated concentrations of Cu at downstream stations were clearly due to the high metal influx arised from mining discharge. Particularly, the factor that primarily governs the high Cu concentration at downstream sediments could be explained by the dissolution of chalcopyrite—a Cu-bearing mineral that occurs ubiquitously at the mine site.

To further confirm the dissolution and redeposition of Cu along the river, we processed the data by calculating the δ_{fold} value. The sampling stations M1, T1, and T2 showed relatively low δ_{fold} values, ranging from 1.0 to 1.2, indicating no or very little metal accumulation from the mine. Conversely, stations M2, M3, and M4 were found to experience severe contamination of Cu after year 2004, evident by the high δ_{fold} values. The δ_{fold} values suggest that the contamination of Cu at these stations had generally increased 32, 28, and 20 folds,

Table 7 Geoaccumulation index (I_{geo}) and degree of metal changes (δ_{fold}) in the sediment of the study area

Metals	M1		M2		T1		M3		T2		M4	
	I_{geo}	δ_{fold}[a]	I_{geo}	δ_{fold}[a]	I_{geo}	δ_{fold}[a]	I_{geo}	δ_{fold}[a]	I_{geo}	δ_{fold}[a]	I_{geo}	δ_{fold}[a]
Co	4.33	6.4	6.04	20.9	4.79	8.8	6.25	24.1	5.64	15.8	6.28	24.6
Cu	11.37	1.0	16.37	32.3	11.32	1.0	16.19	28.6	11.57	1.2	15.66	19.8
Ni	9.30	0.03	13.65	11.1	12.29	4.3	13.36	9.1	12.29	4.3	13.09	7.5
Pb	7.62	0.94	9.78	4.2	–	–	9.56	3.6	3.18	0	7.93	1.2
Zn	8.78	6.6	9.35	9.7	9.24	9.0	9.35	9.7	9.42	10.1	9.38	9.9

[a] Data obtained from Ali et al. (2004), where Co=1.45, Cu=41.77, Ni=27.78, Pb=11.83, Zn=6.70

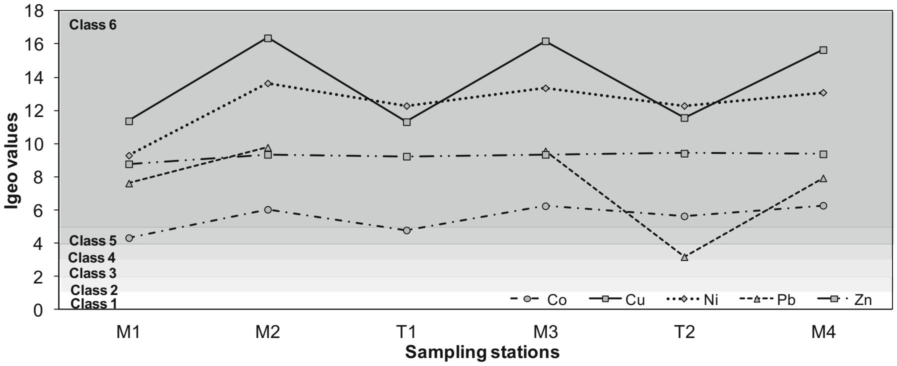

Fig 3 I_{geo} values of metals in the sediments samples of the study area

respectively. Likewise, Co recorded similar trend where the enrichment of the metal in the river sediments were rather apparent. Other metals in the river sediments only reported minor increase in concentration with a magnitude from 0 to 11 fold since year 2004. Fold change values with $\delta_{\text{fold}}<1$ were only observed at station M1 for Ni (0.03) and Pb (0.94), suggesting depletion of these metals through weathering processes. In future investigations, it is recommended that the hydrochemical, biological, and ecological studies should be incorporated to elucidate the influence of various pollution factors to the entire riverine ecosystem (Mashiatullah et al. 2012; Lim et al. 2013).

Conclusion

In conclusion, the Mamut river sediments were severely contaminated by heavy metals especially Cu, Ni, and Co. Toxic heavy metals were found in the range of 9.09 to 37.32 mg kg^{-1} for Co, 40.79 to 1347.54 mg kg^{-1} for Cu, 15.11 to 308.10 mg kg^{-1} for Ni, Pb from <0.10 to 49.68 mg kg^{-1}, and Zn from 43.87 to 66.98 mg kg^{-1}, respectively. The heavy metals abundance in the river sediment basically exhibit the following decreasing order: Cu>Ni>Zn>Co>Pb. Coprecipitation, redox reaction, sorption onto Al/Fe hydroxides and origin from common provenance are the plausible processes that explained the significant positive correlation ($p<0.05$) between Cu, Ni, and Pb. Substantial amount of edenite, pyrite, and minor chrysotile were found precipitated in the sediments at the Poring Hot Spring area (M2), suggesting the occurrence of mineralogical reduction during the fluvial transport. The combined utilization of pollution indices such as I_{geo}, EF, and SQGs were proved to be useful and robust in assessing metals pollution derived from both natural and anthropogenic processes. The calculation of EF and I_{geo} showed that the river sediments were strongly contaminated by heavy metals as a result of anthropogenic activities (mining effluents). Some inconsistencies in EF and I_{geo} suggest the complexity of the study area's geology and the inappropriate adoption of background data in the I_{geo} equation. The calculation of δ_{fold} is particularly essential when one needs to understand the changes of pollutants over a period of time. Copper and Co appear to greatly contaminate the river, indicated by the high δ_{fold} values. After 10 years since the first investigation (year 2004), the Cu concentration in the Mamut river sediments appears to increase from 20 to 38 folds, indicating constant influx of this metal into downstream environment.

It is recommended that effective remediation strategy and environmental management plan are required to control and reduce the input of toxic metals (Cu and Co) from further polluting the environment. The discussion and findings in this study has major ecotoxicological and agronomic importance to policy makers and can be served as useful reference for future reclamation and remediation efforts in the mine area.

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