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THE IDENTIFICATION OF POINT SOURCES IN A RIVER RECEIVING INDUSTRIAL METAL EFFLUENTS AT THE SERDANG INDUSTRIAL AREA, SELANGOR

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Abstract: Surface sediments from three sampling sites, namely Kuyoh River Industrial Area, Kuyoh River Residential Area and Sri Serdang Lake at the Sri Serdang Area were collected and determined for the concentrations of Cu and Zn. The mean total Cu concentrations in the sediment of the three sites were 347.64, 32.04 and 21.71 µg/g dry weight, respectively, while those for Zn were 219.75, 140.64 and 85.10 µg/g dry weight, respectively. The geochemical distributions of the 'non-resistant' (non-lithogenous) and the 'resistant' fractions for Cu in the three sites were 99.6% and 0.4% for the Kuyoh River Industrial Area, 99.19% and 0.81% for the Kuyoh River Residential Area while for the Sri Serdang Lake they were 97.74% and 2.26%, respectively. For Zn, the geochemical distributions of the 'non-resistant' and the 'resistant' fractions in the three sites were 61.2% and 38.3% for the Kuyoh River Industrial Area, 56.2% and 43.8% for the Kuyoh River Residential Area while for the Sri Serdang Lake they were 52.65 % and 47.35%, respectively. These results showed that the site at the Kuyoh River Industrial Area had the highest concentrations of Cu and Zn. These levels greatly exceeded the natural background levels and so this was considered to be seriously polluted. The topography of the Kuyoh River shows that the sampling site at the Kuyoh River Residential Area is located after the Sri Serdang Lake while the sampling site at the Kuyoh River Industrial Area is located on another branch of Kuyoh River but it is located right after a metal factory which later joins the branch running through the Kuyoh River Residential Area at the downstream. The exact location of the point source and the river flow are two major factors contributing to the elevated levels of Cu and Zn at a particular sampling site. The elevation of the Cu and Zn levels suggest that the regulations on untreated effluents should be strictly implemented by the local authorities in order to remedy the situation.

KEYWORDS: Geochemical distributions, resistant and non-resistant fractions, Cu and Zn, surface sediments.

Introduction

Rivers are potentially degraded due to man-induced addition of pollutants from various types of point and non-point (diffuse) sources in the catchment area. Increased urbanisation and industrial activities are potential anthropogenic factors that could pollute river ecosystems in Malaysia (Idris et al., 2005). Regardless of the control measures taken by the government and other relevant authorities, pollution loading from point and diffuse sources are factors that could affect the health of rivers in various ways (Idris et al., 2005). In Malaysia, Azrina et al. (2006) showed the impacts of anthropogenic land-based activities such as urban runoff on the distribution and species diversity of macrobenthic invertebrates in the downstream of the Langat River. Their work exemplified the effects of anthropogenic sources on the health of the river ecosystem.

Fractionation of heavy metals between carrier phases has been reported for river and intertidal sediments in Malaysia (Yap et al., 2003). Based on the work of Yap et al. (2004b), there are advantages in the use of sediment samples to assess human impacts on the aquatic environment. Firstly, sediment plays a major role in the transport of metals. Secondly, it is frequently used to identify sources of pollution spatially and temporally. Thirdly, sediment can be used to locate the major sink for heavy metals and these elements are persistent in the marine environment.

The Kuyoh River Industrial Area is subjected to the discharge of effluents from various major point sources including industrial metal effluent while the Kuyoh River Residential Area receives mostly the domestic effluents. The Sri Serdang Lake is known as a closed freshwater ecosystem that it is surrounded by a residential area. Waste water and effluents from residential and industrial areas in Sri Kembangan are channelled into the Kuyoh River which links to the Klang River. Water flow from Serdang Jaya, UPM and Sri Serdang also goes into the Kuyoh River. The water flowing from the Lekah River also heads in the direction of the Kuyoh River, which always cause flooding at sections 5 and 9 in Sri Kembangan (Idris et al., 2005). Recently, Yap et al. (2006) found elevated concentrations of heavy metals in the drainage sediment collected from the Sri Serdang Industrial Area. Therefore, this study is a follow-up work in order to determine their possible sources based on locations of sampling sites and river flow.

Materials and Methods

Three locations were selected for this study, namely: the Kuyoh River Industrial Area, Kuyoh River Residential area and Sri Serdang Lake (Figure 1). The sampling trips were conducted in March 2007. The type and colour of the sediment collected from the Kuyoh River Industrial Area is black sandy while the those from Sri Serdang Lake and the Kuyoh River Residential Area are brown and dark brown muddy, respectively.

The top 3-5 cm of the surface sediments were collected at each sampling site. A cleaned plastic spatula was used to collect the surface sediments. Each sediment sample was placed in an acid-washed polyethylene bag and frozen (-10°C) prior to analysis. Sediment samples were dried at 105°C for at least 16 hours until constant dry weight. The samples were sieved through a 63 µm stainless steel sieve and shaken vigorously to produce homogeneity (Yap et al., 2002a,b).

For the analysis of total heavy metal concentrations in the sediment samples, the direct aqua-regia method was used. About 1 g of each dried sediment was digested in a combination of concentrated nitric acid (Anala R grade, BDH 69%) and perchloric acid (Anala R grade, BDH 60%) in the ratio of 4:1, first at low temperature (40°C) for 1 hour and then the temperature was increased to 140°C for at least 3 hours (Yap et al., 2006).

The geochemical fractions employed in this study are the easily, freely, leachable or exchangeable (EFLE), acid-reducible, oxidisable-organic and resistant fractions(Badri and Aston, 1983; Yap et al., 2002a,b). This sequential extraction technique (SET) followed the method by Badri and Aston (1983) as slightly modified by Yap et al. (2002a,b). The four fractions considered, the extraction solutions and the conditions employed were as followed. (1) EFLE: About 10g of sample was continuously shaken for 3 hours with 50 ml of 1.0 M ammonium acetate (NH_4CH_3COO), pH 7.0, at room temperature. (2)'Acid-reducible': The residue was continuously shaken for 3 hours with 50 ml of 0.25 M hydroxylammonium chloride ($NH_2OH.HCL$) acidified to pH 2 with HCL, at room temperature. (3) 'Oxidisable-organic': The residue was first oxidised with 30% H_20_2 in a water bath at 90-95˚C. After cooling, the metal released from the organic complexes was continuously shaken for 3 hours with 1.0 ammonium acetate (NH_4CH_3COO) acidified to pH 2.0 with HCL, at room temperature. (4) Resistant: The residue from (3) was digested in a combination of concentrated nitric acid (69%) and perchloric acid (60%) as in the direct aqua-regia method. The residue used for each fraction was weighed before the next fractionation was carried out. The residue was washed with 20 ml of DDW. It was then filtered through Whatman No.1 filter paper and the filtrate was stored until metal determination. For each fraction of the sequential extraction procedure, a blank was employed using the same procedure to ensure that the samples were free from contaminants.

The prepared samples were determined for Cu and Zn by using an air – acetylene flame Atomic Absorption Spectrophotometer (AAS) (Perkin-Elmer AAnalyst 800). The sediment data were presented in µg/g dry weight. Multiple – level calibration standards were analysed to generate calibration curves against which sample concentrations were calculated. Standard solutions were prepared from 1000 mg/L stock solutions of each metal (Mer–CK Titrisol). A quality-control sample was routinely run through during the period of metal analysis. To avoid possible contamination, all the glassware and equipment used were acid – washed (Yap et al., 2006). Certified Reference Materials for Soil (International Atomic Anergy Agency, Soil-5, Vienno, Austria) were also ran and the recoveries for Cu and Zn were satisfactory (90 - 105%).

Results and Discussion

Based on Table 1, the mean total Cu concentrations based on the aqua-regia method in the sediment of the Kuyoh River Industrial Area, Kuyoh River Residential Area and Sri Serdang Lake were 347.64 > 32.04 > 21.71 µg/g dry weight, respectively. A statistical analysis (One-way ANOVA) showed that there was a statistically-significant difference ($P < 0.05$) among the three sites for Cu. From Table 1, it is clear that samples from the Kuyoh River Industrial Area recorded the highest level of Cu when compared to the other sites.

Based on Table 2, the mean total Zn concentration based on the aqua-regia method in the sediment of the Kuyoh River Industrial Area, Kuyoh River Residential Area and Sri Serdang Lake were 219.75 > 140.64 > 85.10 µg/g dry weight, respectively. Statistical analysis showed that a significant variation ($P < 0.05$) was found among the three sites for Zn (One-way ANOVA) in which the most significant difference was found between the Kuyoh River Industrial Area and the Sri Serdang Lake ($P< 0.05$) (Table 2).

Since there is no reported sediment-quality guideline for heavy metal concentrations in Malaysia, the present data are compared to the reported sediment-quality guidelines for Cu (>55 µg/g dry weight) and Zn (>150 µg/g dry weight) polluted sediment set by the Hong Kong Environmental Protection Department (Liang and Wong 2003). Based on the comparison, the results from the Kuyoh River Residential Area and the Sri Serdang Lake were considered as uncontaminated sediments while the Kuyoh River Industrial Area was considered as seriously contaminated sediment for Cu and Zn.

In general, a comparison of the Cu concentrations from the three sites to several other sites in Malaysia (Table 3) showed that the Kuyoh River Industrial Area was more polluted than the other rivers except for the Sepang Besar River. The Kuyoh River Residential Area was in the Cu range of some polluted sites while the Sri Serdang Lake was in the range of Cu for the urban Kelana Jaya Lake (Table 3). In comparison to reported regional studies for Cu, the Kuyoh River Industrial Area was in the Cu range of the Kaohsiung River of Taiwan and the Shing Mun River of Hong Kong but was more polluted than the Singapore River of Singapore and the Pearl River of China. The Cu level in the Kuyoh River Residential Area was in the range of the Singapore River of Singapore and the Pearl River in China while the Cu level in the Sri Serdang Lake was in the range of the Taihu Lake of China (Table 3). A comparison of the Zn concentrations from the three sites to several other sites in Malaysia showed that the metal pollution level of the Kuyoh River Industrial Area was elevated like those of other polluted rivers. The Kuyoh River Residential Area was in the range of some other rivers while the Sri Serdang Lake was in the Zn range of the urban Kelana Jaya Lake (Table 3). In comparison to regional reported studies for Zn, the Zn level in the Kuyoh River Industrial Area and the Kuyoh River Residential Area were in the Zn range of rivers from China (Cheung et al., 2003; Wang et al., 2003), Singapore (Sin et al., 1991) and Hong Kong (Sin et al., 2001) except for the Kaohsiung River in Taiwan (Chen and Wu, 1995) while the Sri Serdang Lake was in the Zn range of the Taihu Lake of China (Table 3).

The Cu and Zn geochemical fractions and their percentages for the three sites are also presented in Tables 1 and 2, respectively. In general, the four geochemical fractions for Cu and Zn were significantly higher ($p < 0.05$) in the Kuyoh River Industrial Area followed by the Kuyoh River Residential Area and the Sri Serdang Lake. A high percentage of the 'oxidisable-organic' fractions for Cu and Zn from the three sites indicated that the absorption of Cu mainly involved organic matter. This may be due to the high affinities of these metals to humic substances which are fractions of organic matters and are chemically very active in complexing with elements such as heavy metals (Forstner and Wittmann, 1981).

The 'non-resistant' fractions of Cu and Zn in the sediment are certainly of much concern from the ecotoxicological point of view (Yap et al. 2002b). This fraction could have an impact on living organisms since this 'non-resistant' fraction is most likely due to anthropogenic sources. The levels of the 'non-resistant' fractions of Cu and Zn found in sampling sites could be mostly due to man-induced activities (Yap et al., 2002b). However, the bioavailabilities of the heavy metals in the sediments could be influenced by changes of environmental conditions such as pH, sediment redox potential etc (Yap et al., 2003). In comparison with the reported EFLE fractions of Cu and Zn in polluted sediments from freshwater sites in Malaysia (Yap et al., 2007), the Kuyoh River Industrial Area had higher EFLE fractions of Cu and Zn (Table 4).

The river-water flow passes through the Sri Serdang Lake and ends at the Kuyoh River Industrial Area. At the end of the flow, the Kuyoh River Industrial Area joins with the Kuyoh River Residential Area. The differences in the metal concentrations and loads in the sites of this study were related to the point source of pollution in the vicinity. The Kuyoh River Industrial Area is subjected to the discharge of effluents from various major and minor industries. Therefore, it recorded the highest concentrations for Cu and Zn while the Sri Serdang Lake and the Kuyoh River Residential Area are surrounded mainly by residential areas. They showed lower concentrations of Cu and Zn. Increased concentrations of Pb, Cu, Co, Ni, Mn and Zn were reported by Klavins et al. (2000) only at the lower reaches of the largest rivers and locally around known industrial pollution sources in Latvia. The high concentrations of Cu and Zn in the Kuyoh River Industrial Area could also be due to the direction of the river-water flow. Sin et al., (2001) reported on the extent of heavy-metal cation (Al, Cd, Cr, Cu, Pb and Zn) contaminations in the Shing Mun Rivers, a major river in the northeastern part of Hong Kong. It flows through the heart of the Sha Tin New Town and drains into Tolo Harbour. They showed that the highest concentrations of Al and Cd occured in the Shing Mun Main River Channel. Azrina et al. (2006) studied four pristine stations from the upstream and 4 stations at the downstream receiving anthropogenic impacts along the Langat River. The better water-quality index and the higher biodiversity indices at the clean upstream stations than at the polluted downstream stations indicated the importance of river-water flow and the locations of the sampling sites whether before or after the point sources. Therefore, the present findings indicated that the of river-water flow and the location of a point source for the sampling sites are two major factors that should be taken into consideration when designing a monitoring study along a freshwater ecosystem.

Conclusion

The findings of the present study indicated that a sampling site located close to the factories had the highest concentrations of Cu and Zn. The direction of the river-water flow for the sampling sites was also important for the identification of a point source of metal pollution along a river. These metal concentrations were dominated by the nonresistant fraction based on the geochemical study indicating anthropogenic source. Serious attention should be given to the Sri Serdang Industrial Area since the data of this study indicated untreated effluents directly dumped into the drainage. The result obtained should serve as an early warning to the local authorities to implement the industrial effluent regulations so as to rectify the situation.

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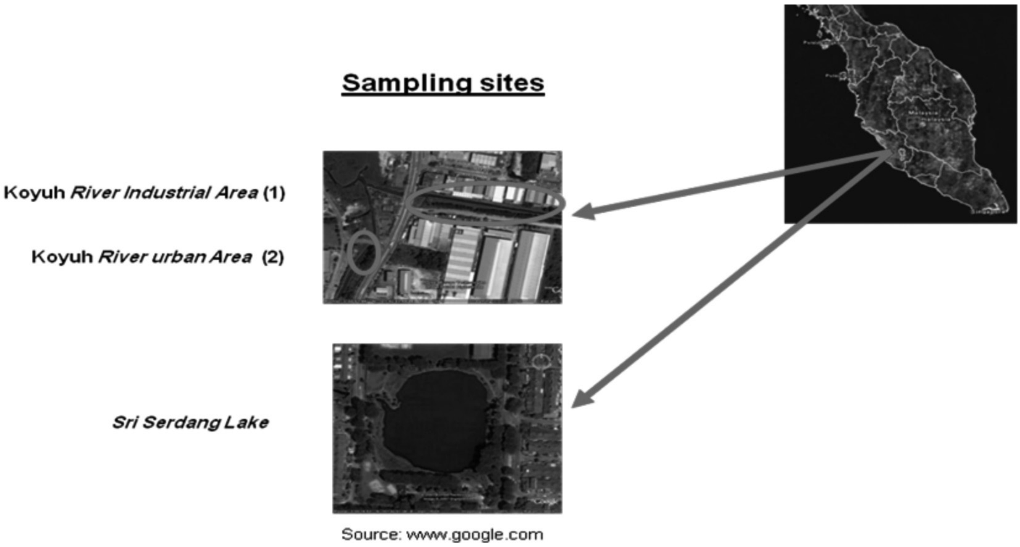

Figure 1: The sampling locations in Kuyoh river and Sri Serdang lake.

Table 1. Mean (µg/g dry weight) ± standard error of Cu geochemical fractions in the surface sediment collected from all the sampling sites.

Site	EFLE		Acid-reducible		Oxidisable-organic		Nonresistant		Resistant		Total (100%)		Aqua-regia	
Kuyoh River Industrial Area	25.89 ± 0.24 (7.5)	A	4.71 ± 0.04 (1.4)	A	315.21 ± 141.64 (90.8)	A	345.81 ± 0.42 (99.6)	A	1.33 ± 0.00 (0.4)	A	347.15 ± 0.21	A	347.64 ± 0.55	A
Kuyoh River Residential Area	1.06 ± 0.02 (3.4)	B	0.47 ± 0.00 (1.5)	B	29.35 ± 13.64 (94.3)	B	30.88 ± 0.02 (99.2)	B	0.24 ± 0.01 (0.8)	B	31.12 ± 0.03	B	32.04 ± 0.29	B
Sri Serdang Lake	0.75 ± 0.02 (3.6)	C	0.38 ± 0.04 (1.8)	B	19.26 ± 8.81 (92.4)	C	20.39 ± 0.17 (97.8)	C	0.47 ± 0.00 (2.3)	C	20.84 ± 0.09	C	21.72 ± 0.32	C

Note: The values in parentheses represent the fraction in percentages; means with different lettters within the column are significantly different, $p < 0.05$.

Table 2. Mean (µg/g dry weight) ± standard error of Zn geochemical fractions in the surface sediment collected from all the sampling sites.

Site	EFLE		Acid-reducible		Oxidisable-organic		Nonresistant		Resistant		Total (100%)		Aqua-regia	
Kuyoh River Industrial Area	65.97 ± 0.01 (30)	A	33.02 ± 0.01 (15)	A	35.26 ± 0.01 (16)	A	134.25 ± 15.03 (61)	A	85.01 ± 0.03 (39)	A	219.27 ± 0.04	A	219.75 ± 0.31	A
Kuyoh River Residential Area	21.32 ± 0.02 (15.3)	B	26.74 ± 0.01 (19.1)	B	30.48 ± 0.03 (21.8)	B	78.54 ± 3.76 (56.2)	B	61.21 ± 0.03 (43.8)	B	139.74 ± 0.05	B	140.64 ± 0.70	B
Sri Serdang Lake	5.28 ± 0.01 (6.2)	C	15.52 ± 0.02 (18.3)	C	23.93 ± 0.03 (28.2)	C	44.73 ± 7.63 (52.7)	C	40.22 ± 0.02 (47.3)	C	84.92 ± 0.00	C	85.10 ± 0.19	C

Note: The values in parentheses represent the fraction in percentages; means with different lettters within the column are significantly different, $p < 0.05$.

Table 3. Total concentrations (µg/g dry weight) of Cu and Zn in sediments from previous regional and Malaysian studies.

Locations	Cu	Zn	References
Regional studies			
Singapore River, Singapore	10.00 – 80.00	100.00 – 550.00	Sin *et al*. (1991)
Kaohsiung River, Taiwan	40.00 – 998.00	NA	Chen and Wu (1995)
Pearl River, China	8.70 – 140.00	46.40 – 533.30	Cheung *et al*. (2003)
Shing Mun River, Hong Kong	207.00 – 1660.00	32.00 – 2200.00	Sin *et al*. (2001)
Taihu Lake, China	12.60 – 5470.00	49.20 – 7390.00	Wang *et al*. (2003)
Malaysian studies			
Langat River	NA	71.00 – 374.00	Sarmani (1989)
Pasir River	2.00 – 23.00	2.00 – 25.00	Lim and Kiu (1995)
Rambai River	31.00 – 144.00	51.00 – 483.00	Lim and Kiu (1995)
Terengganu River	0.21 – 1.70	6.00 – 28.00	Mushrifah *et al.* (1995)
Juru River	14.00 – 72.00	29.00 – 316.00	Lim and Kiu (1995)
Sarawak River	1.00 – 10.20	8.00 – 48.40	Lau *et al*. (1996)
Tengi River	ND – 139.00	74.00 – 300.00	Sahibin *et al.* (2000)
Sepang Besar River	10.60 – 573.40	107.00 – 602.20	Saed (2001)
Sepang Kecil River	51.17 – 57.86	81.53 – 91.96	Saed (2001)
Kg. Pasir Puteh	103.40	149.30	Yap *et al*. (2004a)
Urban Lake of Kelana Jaya	2.62 – 73.70	34.30 – 529.00	Ismail *et al*. (2004)
Sri Serdang Industrial Area	43.0 – 551.2	169.3 – 296.3	Yap *et al*. (2006)
Kuyoh River Industrial Area	347.64	219.75	This study
Kuyoh River Residential Area	32.04	140.64	This study
Sri Serdang Lake	21.71	85.10	This study

Note: NA= not available
ND= not detected

Table 4. Concentrations [mean µg/g dry weight ± standard error] of heavy metal of the surface sediments collected from several drainages of Peninsular Malaysia (Yap *et al.,* 2007**).**

Metal	Item	Johor Petrochemical site		Serdang Metal Industrial site		Kuala Kurau town		Klang town	
		Mean	SE	Mean	SE	Mean	SE	Mean	SE
Cu	F1	3.64	0.05	1.75	0.22	0.30	0.00	0.91	0.00
	F2	1.20	0.07	0.45	0.03	0.17	0.00	0.01	0.00
	F3	91.40	1.07	707.4	0.98	67.01	1.99	65.88	1.07
	F4	47.57	5.20	627.0	15.53	60.43	0.55	41.68	2.14
Zn	F1	56.39	0.03	59.96	0.27	51.93	0.40	49.94	0.14
	F2	48.84	0.09	63.09	0.08	63.35	0.21	57.22	1.26
	F3	23.12	0.20	165.70	0.55	86.58	0.34	154.32	0.04
	F4	62.49	6.05	350.70	5.11	127.36	2.28	223.60	0.06

Note: F1: EFLE, F2: Acid-reducible, F3: Oxidisable-organic, F4: Resistant