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Water Quality and Heavy Metal Concentrations in Sediment of Sungai Kelantan, Kelantan, Malaysia: A Baseline Study

(Kualiti Air dan Kepekatan Logam Berat di dalam Sedimen Sungai Kelantan, Kelantan, Malaysia: Kajian Nilai Dasar)

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ABSTRACT

A study on water quality and heavy metal concentration in sediment at selected sites of Sungai Kelantan was carried out. Ten water samples were collected along the river for physical and chemical analysis and twenty-six water and sediment samples were collected for heavy metal analysis. Water was sampled at three different dates throughout the study period whereas sediments were collected once. In addition to heavy metal analysis, sediment samples were also analysed for texture, pH and organic content. The physical and chemical water quality analyses were carried out according to the APHA procedures. Result of water quality analysis (physico-chemical) indicated that Sungai Kelantan is characterised by excellent water quality and comparable to pristine ecosystems such as the National Park and Kenyir Lake. This river was classified into class I – class III based on Malaysian interim water quality standard criteria (INWQS). Heavy metals Pb, Zn, Cu and Cd was detected at low concentration in sediment samples, except for Fe and Mn. The presence of Fe and Mn in sediment samples was though to be of natural origin from the soil. Anthropogenic metal concentrations in sediment were low indicating that Sungai Kelantan has not experienced extreme pollution.

Keywords: Heavy metal; pollution; river; sediment; water

ABSTRAK

Satu kajian kepekatan logam berat di beberapa kawasan terpilih di Sungai Kelantan telah dilakukan. Sebanyak 10 sampel air telah diambil untuk ujian fizikal dan kimia air dan 26 sampel air dan sedimen telah diambil untuk ujian kepekatan logam berat. Sampel air telah diambil sebanyak tiga kali sepanjang tempoh kajian. Sampel sedimen turut dianalisis untuk parameter tekstur, pH and kandungan organik. Analisis fizikal dan kimia air telah dilakukan dengan merujuk kepada prosedur APHA. Hasil ujian kualiti air menunjukkan Sungai Kelantan mempunyai kualiti air yang baik dan secara perbandingan umumnya setara dengan kawasan yang bersih seperti Taman Negara dan Tasik Kenyir. Sungai Kelantan boleh dikelaskan di antara kelas I – III berdasarkan kepada nilai interim piawaian kualiti air Malaysia (INWQS). Kepekatan logam berat Pb, Zn, Cu dan Cd dikesan pada kepekatan yang rendah di dalam sampel sedimen kecuali logam Fe dan Mn. Walau bagaimanapun, kepekatan Fe dan Mn yang diperolehi masih di dalam julat kepekatan semulajadi di dalam sedimen. Kepekatan logam antropogenik di dalam sedimen adalah rendah dan menggambarkan bahawa Sungai Kelantan tidak mengalami pencemaran yang serius.

Kata kunci: Air; logam berat; pencemaran; sedimen; sungai

INTRODUCTION

There is an increasing concern about heavy metal contamination in river systems. Rivers play major roles to the community especially in the fishing industry and a source of water supply for people residing within the vicinity of the area. River contamination either directly or indirectly will affect humans as a final consumer. Although some of heavy metals are required as micronutrients, it can be toxic when present higher than the minimum requirements. Rivers in Malaysia have sometimes been as dumping sites for heavy metal waste legally or illegally. Heavy metals have been introduced into rivers through land surface runoff, rainfall precipitation and factory waste outlet point discharge. Anthropogenic metals may consistently retain within the water bodies or may be taken up by organisms such as plankton, benthos or fish and finally transferred to humans. It is therefore important that a baseline study is conducted to determine the background of heavy metal concentrations in the area before any records of pollution might be accounted for. This is necessary to understand the source of heavy metal pollution for future environmental planning strategies.

A study was conducted to determine the concentration of selected heavy metals in Sungai Kelantan, which was known to be in the category of a clean river. The river water quality was measured together with the metal concentrations in sediments in order to confirm to quality of the river.

STUDY AREA AND METHOD

Sungai Kelantan is the second largest river in Peninsular Malaysia and located in Kelantan state of Peninsular Malaysia (Figure 1). The river originates from north-east of Peninsular Malaysia and its tributaries rise in the forested mountains, which comprise of limestone outcrops and caves. The Sungai Kelantan drains the province of Kelantan and supports a catchment of about 12,000 km^2. The river drains through several districts such as Gua Musang, Pasir Putih, Kuala Krai and Kota Bahru and creates a large floodplain area. With the variations of the local monsoon climate, Sungai Kelantan receives variable level of rainfall, which is from 0 to 1750 mm in dry and wet months respectively. The river produces average run off approximately 500m^3/s. During the monsoon season (November to January), Kelantan state receives huge amount of rain water and the river overspills its bank to create the annual flood event. Local people heavily use the river for many purposes such as drinking water supply, agriculture and plantation irrigation, daily uses, fishing and silk 'batik' (a local patterned material produced by waxing and dyeing cloth) production.

A study was conducted from 25th to 30th January 1993. Sampling was undertaken along Sungai Kelantan, which represents from the river mouth up to middle of the river length. A number of 10 sampling stations were identified for water quality analysis and 26 sampling stations (approximately 70 km along Sungai Kelantan) for sediment sampling for metal analysis (Figure 1).

WATER QUALITY

From 10 sampling stations chosen within the study area, two were located near the estuarine zone and affected by the saline water. Physical water quality was measured *in situ* using multisensor probe YSI model 449D for dissolved oxygen, pH, conductivity, temperature, salinity and TDS concentrations.

Concurrently, water was sampled using a Van Dorn water sampler and preserved in polyethylene bottle for analysis of fluoride, nitrite, nitrate, ammoniacal-nitrogen and phosphorus. Duplicate water samples were collected from each sampling station and HACH spectrophotometer DR 2000 ver.3 was used for the chemical water quality

FIGURE 1. Sungai Kelantan's riverine system and sampling points within downstream area

analysis. All measurements and analysis procedures were undertaken according to the APHA, AWWA and EPA guidelines.

SEDIMENT

A number of 26 sampling stations were chosen for sediment sampling along the study area. Sediments were collected using a Petersen sediment sampler, and three replicates were taken from each station. The top 15 mm sediment layer was collected using anti rust scoop and sediments were naturally dried in the laboratory prior to analysis.

SEDIMENT pH

Sediment pH was measured following Duddridge & Wainwright (1981). 20 g of dried sediment was added to 40 ml of distilled water and mixed. pH was measured using a W-500 Witeg Digital pH meter.

SEDIMENT GRAIN SIZE

Sediment grain size was measured according to Badri (1983). 10 gram of dried sediment was sieved through using anti rust laboratory test sieve model BS 410 (63 μm mesh size). Sediment that retained in the sieve were dried repeatedly in oven and final weight was used to calculate the percentage of sediment (< 63 μm) using formula as below:

$$\% < 63\mu = \frac{\text{initial weight} - \text{final weight} \times 100}{\text{initial weight}}.$$

ORGANIC CONTENT

The organic content in sediment was determined following Walkley and Black (1934). 0.25g of dried sediment was added into flask containing 0.17 M potassium dichromate followed by 20 ml of sulfuric acid. The mixture was then heated on the hot plate for 30 minutes. 200 ml of deionised water was then added into the mixture followed by 10 ml of concentrated phosphoric acid. Diphenylamine was used as indicator and titration was done using ferrous ammonium sulphate 0.4N (FAS). All titration including the blank was carried out and the percentage of organic content was calculated as below;

$$\% \text{ organic content} = \frac{Y \times 100}{0.25},$$

where $Y = 3.96(10-(N_{FAS}))$

HEAVY METALS IN SEDIMENT

A sequential extraction method was used to extract heavy metal from the sediment samples. The method that was introduced by Badri & Aston (1983) was used in this study. Sediment samples were extracted at four different fractions by using different reagents. The first fraction of extraction was call easily leachable and freely exchangeable fraction (ELFE), which used ammonium acetate (pH 7) as an extraction reagent. The second fraction is acid reduction fraction (AR), which used hydroxylamine chloride (pH 2) as an extraction reagent. The third fraction of extraction called the organic oxidation fraction (OO) was carried out using the combination of hydrogen peroxide (30%) and ammonium acetate (pH 3.5). The last fraction called the resistant fraction (RF) used concentrated nitrate acid and perchlorid acid at ratio 5:2. The first three extraction fractions (EFLE, AR and OO) were used to extract anthropogenic metals from sediment, which known from the pollution sources. The final fraction of extraction (RF) was used to extracted natural metals that are strongly bounded between particles. The mixture was shaken and centrifuged during each extraction fraction and the solution was filtered prior to the metals analysis. The heavy metals concentration was analysed using atomic absorption spectrophotometry AAS 1100B model Perkin Elmer.

RESULTS AND DISCUSSION

WATER QUALITY

Generally, Sungai Kelantan is characterised by good water quality. Water quality data for Sungai Kelantan is tabulated in Table 1. Dissolved oxygen (DO) concentrations in Sungai Kelantan was much higher than minimum requirement for aquatic organisms that is 4 mg/L (Baker 1980). The DO mean concentration was 7.2mg/L ± 0.40, and as regards with Malaysian interim water quality standard, Sungai Kelantan was classified into class I. Physically, Sungai Kelantan is second largest river in Malaysia. The consistence velocity creates homogenous condition that was indicated by low standard deviation value. The pH value also classified Sungai Kelantan in class I. The pH values were slightly acidic, which is normal for tropical rivers. Turbidity of Sungai Kelantan was slightly high but this can considered normal for Malaysian rivers. Only rivers with orders 1 and 2 are

TABLE 1. The physical and chemical water quality of Sungai Kelantan (the mean is average of 3 replicates ± SD)

Parameter	Unit	Mean values
Dissolved oxygen	mg/L	7.2 ± 0.40
pH		6.4 ± 0.41
Carbon dioxide	mg/L	2.1 ± 1.00
Water hardness	mg/L ($CaCO_3$)	16.1 ± 0.25
Turbidity	FTU	44.0 ± 17.0
Total dissolved solids	mg/L	36.6 ± 13.52
Conductivity	μS/cm	587 ± 33
Fluoride	mg/L	0.59 ± 0.36
Nitrite	mg/L	0.06 ± 0.01
Nitrate	mg/L	0.62 ± 0.24
Ammonium-N	mg/L	0.08 ± 0.02
Orthophosphate	mg/L	0.31 ± 0.11

characterised by low turbidity and are normally located within the dense forest (untouch ecosystem). Sampling stations in this study are located within order 4 to order 5, which is normally affected by human activities and the water has changed to a brownish colour. In addition, sampling was undertaken just after the monsoon season (between October to December) and most rivers are normally more turbid within this period.

Most of chemical parameters were detected at low concentrations except for phosphate (orthophosphate) which was found slightly high. The quality of river is determined by land activities. It has been reported that 60% of water quality is determined by inland activities. Sungai Kelantan is being used by the local community for many purposes such as bathing, cleaning, agriculture, plantation and small-scale mining. The continual and improper use of soaps and fertilisation could contribute to the phosphate input into the river. However, the comprehensive sampling and monitoring is necessary to confirm this matter. With regards to Malaysian interim water quality standard, the physical and chemical water quality classify Sungai Kelantan between classes I to III, which indicates that Sungai Kelantan still has good water quality (Table 2).

TABLE 2. Malaysian interim national water quality standard (INWQS)

	Classes					
Parameters	I	IIA	IIB	III	IV	V
DO mg/l	7	5-7	5-7	3-5	3	1
BOD mg/l	1	3	3	6	12	12
COD mg/l	10	25	25	50	100	100
TSS mg/l	25	50	50	150	300	300
NH_3-N mg/l	0.1	0.3	0.3	0.9	2.7	2.7
pH 6.5-8.5	5-7	5-7	3-5	3	1	
Colour (TUC)	15	150	150	-	-	-
Elect. Conductivity umhos/cm	1000	1000	1000	-	6000	-
Floatables	NV	NV	-	-	-	-
Odour	NOO	NOO	NOO	-	-	-
Salinity (%)	0.5	1	1	-	-	-
Taste	NOT	NOT	NOT	-	-	-
Total Dissolved Solids (mg/l)	25	50	50	150	300	300
Temperature	normal	normal	normal	-	-	-
Turbidity (NTU)	5	50	-	-	-	-
Faecal Coliform (count/100ml)	10	100	50	5000	5000	>5000
Total Coliform (count/100ml)	100	5000	5000	50000	50000	>50000
Al (mg/l)	-	0.05	-	-	0.1	-
As (mg/l)	-	-	-	0.44	-	-
Sa (mg/l)	-	0.005	-	0.01	0.01	-
Cd (mg/l)	-	-	-	0.011	0.011	-
Cr III (mg/l)	-	-	-	0.01		
Cu (mg/l)	-	-	-	0.012	0.2	-
Hardness (mg/l)	N	100	-	-	-	-
Ca (mg/l)	A	0.05	-	-	-	-
Mg (mg/l)	T	-	-	-	-	-
Na (mg/l)	U	-	-	-	-	-
K (mg/l)	R	0.3	-	1	1	-
Fe (mg/l)	A	-	-	-	-	-
Pb (mg/l)	L	0.05	-	-	5	-
Mn (mg/l)		0.001	-	0.004	-	-
Hg (mg/l)	L	-	-	-	-	-
Ni (mg/l)	E	0.05	-	-	0.2	-
Se (mg/l)	V	0.01	-	-	0.02	-
Ag (mg/l)	E	0.05	-	-	-	-
Sn (mg/l)	L	-	-	-	0.05	-
U (mg/l)	S	-	-	-	2	-
Zn (mg/l)		-	-	-	0.35	-
B (mg/l)	-	-	-	3.4	-	-
Cl (mg/l)	-	200	-	-	-	-
CN (mg/l)	-	0.02	-	-	-	-
F (mg/l)	Nl	1	-	-	-	

SEDIMENT

PHYSICAL PARAMETERS

The sediment's pH ranged from 5.8 to 7.8. Sediment samples located close to the estuary were more alkaline, due to infusion of salt water from the sea during high tide. However, most of the sediment samples were slightly acidic and were found to be within the natural range for freshwater ecosystem. Only 34 % of sediment from Sungai Kelantan has grain size less than 63μm diameter, and majority were located close to the estuary. The estuarine area is recognised as a sink for sedimentation, which includes suspended particles (Olausson & Cato 1980). The very fine particles that drifted from upstream finally will precipitate within the estuarine area. The percentage of organic content in river sediments was low (0.1% to 2.8%), which is consequent from large grain size.

HEAVY METAL CONCENTRATIONS

Mean concentrations of lead, zinc, copper, cadmium, ferum and manganese in sediment of Sungai Kelantan are shown in Table 3. Total metal concentrations in sediment were lower as compared to the concentration in earth crust for baseline concentration for heavy metals as described by (Merian 1991). Heavy metal concentrations in the crust has been widely used to compare the natural concentration in sediment. These values could be used to evaluate the load of anthropogenic metals from its surrounding (Merian 1991). In general, this indicates no major anthropogenic metals-load into the river.

NON-RESISTANT FRACTION

The non-resistant fraction includes the first three fractions (EFLE, AR and OO), which represent anthropogenic metals. The concentrations of Pb, Zn, Cu, and Cd were found to be lower than the resistant fraction except for Fe and Mn which were 62% and 89% more than the total concentrations, respectively (Table 3) (Figure 2). As regard to the non-resistant fraction, the study indicates that Sg. Kelantan is free from serious metal pollution. Each studied metal was found at very low concentration and was in line to the EPA guideline (Table 4).

Organic oxidation fraction showed highest composition of heavy metals in the non-resistant fraction followed by the ELFE and AR fraction (Figure1). Solomon & Forstner (1984), Nriagu & Coker, (1980) and Rapin et al. (1983) demonstrated that this fraction accumulated the highest metal concentration as compared to ELFE and AR fraction. pH was found to play a major role in metal absorption in organic oxidation fraction. The presence of humic and fulvic acid in organic materials in reduction condition creates more efficient metal adsorption (Ritchie & Posner 1992). Results from this study indicate that sediment pH was from 5.8 to 7.8, which provides an excellent condition for metal absorption.

TABLE 3. Heavy metal concentrations in sediment (mg/kg dry weight). (Means are values from 3 relplicates ± SD)

Metal fraction	Heavy metal	Mean value
Total concentration from all fraction	Pb	20.82 ± 0.28
	Zn	18.67 ± 0.56
	Cu	6.74 ± 0.02
	Cd	1.82 ± 0.02
	Fe	3860 ± 30
	Mn	394 ± 16
Resistant Fraction		
	Pb	17.32 ± 0.28
	Zn	17.12 ± 0.56
	Cu	5.09 ± 0.02
	Cd	1.45 ± 0.01
	Fe	1490 ± 30
	Mn	45 ± 16
ELFE Fraction		
	Pb	0.05 ± 0.03
	Zn	0.16 ± 0.00
	Cu	0.03 ± 0.01
	Cd	0.01 ± 0.00
	Fe	0.01 ± 0.00
	Mn	74 ± 0.40
AR Fraction		
	Pb	0.28 ± 0.00
	Zn	0.56 ± 0.01
	Cu	0.42 ± 0.01
	Cd	0.01 ± 0.00
	Fe	570 ± 13
	Mn	79 ± 0.40
OO Fraction		
	Pb	3.17 ± 0.04
	Zn	0.83 ± 0.00
	Cu	1.20 ± 0.01
	Cd	0.35 ± 0.01
	Fe	1800 ± 20
	Mn	196 ± 10

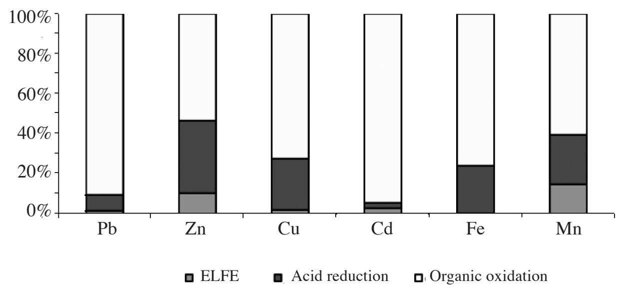

FIGURE 2. The composition of non-resistant fractions

EASILY LEACHABLE AND FREELY EXCHANGEABLE (ELFE) FRACTION

Heavy metals in this fraction are weakly bounded to the sediment surface by the Van De Wall chain and are easily removed from the sediment particle (Arakel & Hongjun 1992). This fraction can be considered as a temporary

TABLE 4. Sediment criteria proposed by EPA Region V [a]

Heavy metal	Not Polluted	Slightly Polluted	Severely Polluted	Average conc. in earth crust. [b]
Pb	< 40	40 – 60	> 60	16
Zn	< 90	90 – 200	> 200	80
Fe	< 17000	17000 – 25000	> 25000.	50000
Ni	< 20	20 – 50	> 50	100
Mn	< 300		> 500	1000
Cd			>6	0.2
Cr	< 25	25 – 75	> 75	200
Cu	< 25	25 – 50	> 50	70

[a] all conc. in mg/kg dry weight, [b]Goldschmidt,
Source: Engler (1980)

phase before metals are transported to another medium. This study indicates that Mn was accumulated highest in this fraction as compared to other metals. The presence of low concentration of Pb, Zn, Cu Cd and Fe in the sediments indicated no anthropogenic loading to the river.

ACID REDUCTION FRACTION (AR)

This fraction binds metals and forms a more stable stage with the sediment particle in the oxide condition (Tessier et al. 1979). Ferrous and manganese in the oxide and hydroxide forms have high potential to absorb metals into the sediment. Manganese was found accumulated highest in this fraction followed by Fe, Zn and Cu. Colloid of ferrous and manganese act as scavenger in sediment by forming a thin layer on the surface of the sediment particle (Arakel & Hongjun 1993). Zn and Cu were also found high in this fraction, 0.56 ± 0.01 mg/kg and 0.42 ± 0.01 mg/kg respectively. Solomon and Forstner (1984) has gathered similar finding where Zn was detected highest in this fraction, whereas Hare et al. (1991) found that Pb was the highest.

OXIDATION FRACTION (OO)

Heavy metal absorptions in this fraction are determined by the presence of humic and fulvic acid that are stable under reduced condition (Ritchie & Posner 1992). As mentioned earlier, this fraction is considered as the sink for heavy metal accumulations (Lion et al. 1980; Rapin et al. 1983; Salim 1983). Most of anthropogenic metals have accumulations the highest in this fraction especially Pb and Cd, with more than 50% of total non-resistant fractions. Badri (1983) found that organic content in sediment has great influence to the metal absorption. Mohd Noor Ramlan (1989) also obtained similar results from his study at the several estuarine ecosystems in Malaysian rivers.

RELATIONSHIP BETWEEN SEDIMENT PROPERTIES AND HEAVY METAL CONCENTRATION

Table 5 shows the relationship between the sediment properties with heavy metal concentration in sediment. The Pearson simple correlation test was undertaken and result indicates that sediment grain with size less than 63μm and organic contents demonstrated great influence to heavy metal accumulation in sediments. pH does not exhibits clear influence in heavy metal accumulation could be due to the homogenous pH values along the sampling stations. The small grain size (<63μm) clearly demonstrates significant influence to the metal absorption in sediments.

Vaithiyanathan et al. (1993) reported that metal absorption rates are various at different sediment grain sizes. Hart (1982) also reported that organic content has a high relationship with heavy metal concentrations in sediment. Results from this study indicate that Sungai Kelantan has received minimum anthropogenic metal load as compared to existing polluted rivers in Malaysia such as Sungai Juru, Sungai Sepang, Sungai Kelang and Sungai Melaka (Table 6). Only Fe and Mn were found to be high in Sungai Kelantan sediments, which could be due to the natural land composition type. Development and expansion of water base activities such as small scale agriculture, plantation and industrialising near the river are possible sources for soil erosion to the Sungai Kelantan. However, these are non toxic metals which are usually found abundance under natural environmental condition.

CONCLUSION

Sungai Kelantan is characterised by good water quality except for some physical characteristics that fluctuate as a result of natural annual season changes. Although the river is used for various water-based activities, it still receives minimum anthropogenic metals and can be considered as free from any heavy metal pollution problem.

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TABLE 5. Correlation coefficient of sediment properties to heavy metal concentration in each fraction.

Fraction	Heavy Metals					
	Pb	Zn	Cu	Cd	Fe	Mn
ELFE Fraction						
pH	0.125	-0.815	0.364	0.445	0.226	-0.444
Grain size (<63μm)	0.108	0.463	-0.314	0.132	0.042	*0.606*
Organic content (%)	0.092	0.435	-0.311	0.203	0.046	0.583
AR Fraction						
pH	-0.530	-0.426	-0.571	0.484	-0.426	-0.509
Grain size (<63μm)	0.209	0.319	0.116	0.040	0.319	*0.623*
Organic content (%)	0.046	0.405	0.127	-0.083	0.404	0.583
OO Fraction						
pH	-0.363	0.083	-0.063	-0.900	0.276	0.506
Grain size (<63μm)	0.475	0.276	0.355	*0.529*	-0.143	0.049
Organic content (%)	0.481	0.276	0.445	0.400	-0.028	0.021
Resistant Fraction						
pH	-0.308	-0.353	0.152	0.026	-0.247	-0.875
Grain size (<63μm)	*0.648*	*0.650*	*0.590*	*0.539*	*0.670*	*0.503*
Organic content (%)	0.669	0.617	0.693	0.437	0.565	0.449
Non-Resistant Fraction						
pH	-0.725	-0.205	0.234	-0.178	0.147	0.256
Grain size (<63μm)	0.241	0.444	0.401	*0.514*	*0.652*	0.288
Organic content (%)	*0.656*	0.484	0.498	0.419	0.163	0.282

Note: Italic indicates a significant coefficient correlation

TABLE 6. Comparison of heavy metal concentrations in sediment in non-resistant fraction from other studies

Location	Heavy Metals (mg/kg dry weight)					
	Pb	Zn	Cu	Cd	Fe	Mn
Sungai Juru[(a)]	33	35	11.7	0.58	2905	213
Sungai Malacca[(a)]	158	125	262	1.21	3910	71
Sungai Sepang[(a)]	7.4	167	105	0.90	3100	38
Kelang Sungai[(b)]	1.16-54.10	6-271	1.07-55.27	0-8.13	380-1180	13-595
This study	3.50	1.50	1.65	0.37	2410	348

[(a)]Mohd Noor Ramlah (1989); [(b)] Khairiah Jusoh (1988)

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