



Seasonal Influences on The Levels of Particulate Matter, Cd, Cr and Pb in Kuantan River, Pahang

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ABSTRACT

Temporal and spatial variations of selected toxic elements distributions were studied along the Kuantan River. Surface and bottom waters from 9 sampling stations were taken from the estuary towards the upstream of Kuantan River using Van-Dorn water sampler during the rainy and dry season. Water samples were filtered and the filter papers were dried under the laminar flow and weighed until constant weight obtained. Filter papers were analyzed using Teflon Bomb digestion processes. The concentration of particulate Pb, Cd and Cr were in the range of 0.646 to 174.859 mg L⁻¹, 6.047 to 271.497 mg L⁻¹ and ND to 14.480 mg L⁻¹, respectively. Particulate Pb, Cd and Cr obtained mostly higher in May 2012 during the dry season. Particulate Cd and Cr were found above the limits authorize by International Commission for the Protection of the Rhine river against Pollution (ICPR). Apart from the anthropogenic activities, rainy and dry season also become the important factors affecting the particulate metals concentrations and distributions in the waters.


Keywords: Suspended particulate, Matter, Toxic metals, River water, Cadmium, Chromium, Lead.

INTRODUCTION

Riverine environments often have considerably higher concentrations of trace components such as nutrients and many transition metals and metalloids compared to marine

environments. At present, there are increasing number of river water that neither can be used nor treated and were classified as highly polluted. Department of Environment⁴ reports shows that amongst the 143 river basins that being examined, 64% (91) are categorized as clean, 31% (45) are



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slightly polluted and 5% are polluted. Environmental Quality Act (1974) of pollution according to Interim National Water Quality Standards (INWQS) was established in order to monitor the water quality management in Malaysia. All pollutants discharge from industries is controlled by EQA Regulation under INWQS and monitored by authority. Metals ions known as to be toxic as their tissue may degraded which are dangerous and detrimental to nature compared to other various inorganic and organic water pollutants. Lead, chromium and cadmium contamination are quite well known⁵. Therefore, toxic metals demand close monitoring since they are relatively unstable, carcinogenic and bioaccumulative²¹.

Moreover, toxic elements may dissolved in wastewaters and discharged into surface waters and later will be concerted as they enter the food chain¹⁰. Metals that leach into ground waters will contaminate drinking water wells and harm the adjacent community. Information on the level of toxic elements in Malaysia aquatic environment is inadequate, which constituted of a few studies. Development along the east coast of Malaysia rapidly increasing with factories and industrial activities apart from oil and gas-related industries that knowingly founded in the states of Pahang and

Terengganu¹⁴. Kuantan has a humid tropical climate with seasonal monsoon rain where two monsoon periods prevail that is northeast monsoon (October to March) and south-west monsoon (May to September)⁴. Hence, the aim of this study was to determine the spatial and temporal variations of particulate elements during the monsoon (wet) and non-monsoon (dry) season.

MATERIALS AND METHODS

Kuantan River Basin covers an area of 1,586 km² and is approximately 80 km long. Kuantan River flows through two areas that is Ulu Kuantan and Kuala Kuantan and flowing out to the South China Sea⁴. Major settlements in the basin include Kuantan town, Lembing River and Gambang. All apparatus including glasswares and plastic wares that were used in the laboratory and during the sampling were immersed in 10% nitric acid for at least 72 h, rinsed with deionized water and were dried in the oven for 24 hours. Nylon membrane filters paper (47 mm diameter, Whatmann) with pore size of 0.45 μm were immersed in 10 % HNO_3 , washed with deionized water and were dried in class 100 laminar flow hood². The nylon membrane filters were weighed for several times until a constant weight obtained.

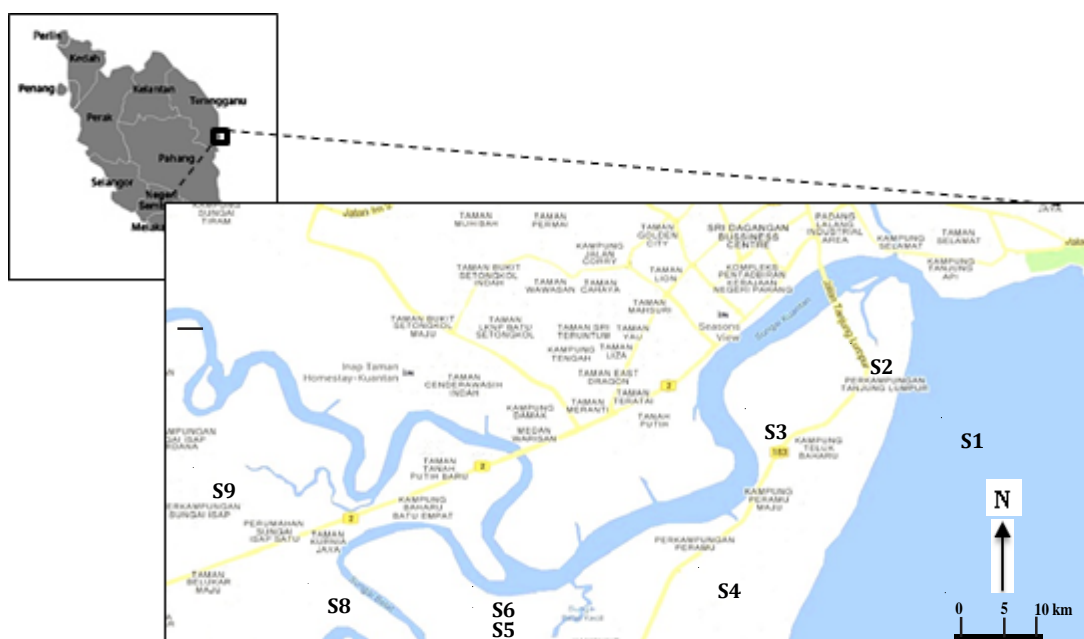


Fig. 1. Map of the sampling stations in Kuantan River basin, Kuantan, Pahang

Surface and bottom water samples were collected in May 2012 and October 2012 from 9 stations using Van-Dorn Water Sampler. Hydrological general physicochemical parameters such as salinity, dissolved oxygen (DO), pH and temperature of the river waters were measured *in-situ* using YSI Hydrolab multisensory probe. Water samples were stored in acid-washed polyethylene bottles (1L) and were kept in ice during the transportation to the laboratory. At the laboratory, within 24 h, water samples were filtered past nylon millipore filters (0.45 μm pore size) that were pre-weighed by using a low-pressure vacuum pump. The membrane filter that contains wet suspended particulate samples were dried under laminar flow for several days, weight and re-weighed until constant weight obtained and labeled as the particulate sample.

Samples were transferred into Teflon bomb for digestion^{8, 16}. Samples were added together with 1.5 mL of mixed acid with the ratio of 3.5 HNO_3 : 3.5 Hydrochloric acid: 3 Hydrofluoric acid in a Teflon vessel and heated for 5 to 7 hours at 150 °C. After cooling session, digested sample were added with 3 mL of mixed of boric acid and EDTA and were heated again for 5 to 7 hours at 150 °C in the oven. Then sample were cooled down before transferred into 10 mL test tube and added for dilution up to 10 mL with Milli-Q water. The same digestion procedures were done for filters without particles and labelled as procedural blanks. Samples digestion was performed in duplicate to certify the reliability of the method. Blanks and quality control samples that were prepared from standard solutions were analyzed for every ten samples so as to check the sample accuracy. Recovery test for particulate metals was conducted using SRM 1646a Estuarine Sediment. The percentage of recovery obtained were ranged 98.230% for Cd, 100.830% for Cr and 104.920% for Pb. Concentration of particulate metal concentration was calculated using the formula:

$$\text{Metal Contents in } \mu\text{g g}^{-1} \text{ dry weights} = \frac{\text{ICP-MS Reading} \times \text{Sample Weight} \times \text{Dilution Factor}}{\text{Sample Dry Weight (g)}}$$

Remarks:

Dilution factor: 10 times

RESULTS AND DISCUSSION

Mean values for physicochemical parameters are listed in Table 1. Water salinity in Kuantan River decreased from estuary to the upper streams stations. Higher salinity was recorded in May 2012 than October 2012 with the mean value of 21.450 ± 9.900 ‰ and 20.080 ± 10.600 ‰, respectively. Mean for water temperature was found higher in May 2012 with value of 29.790 ± 0.630 °C while heavy rainfall was recorded in October 2012. This indicates that May 2012 was the dry season and October 2012 was the wet season. Water pH also showed higher mean value in May 2012 than October 2012 with 7.110 ± 0.580 and 6.550 ± 0.500 , respectively. Meanwhile, dissolved oxygen concentrations varied between 4.460 and 7.670 mg L^{-1} that is indicative of adequate oxygenated river waters.

Particulate cadmium concentrations ranged from below 0.478 to 11.594 mg L^{-1} . Highest concentrations were encountered at the upstream station of Kuantan River. Mean concentration of particulate, Cd was found relatively higher with value of 4.058 ± 2.432 mg L^{-1} in May 2012 compared to October 2012 (2.184 ± 1.678 mg L^{-1}). Concentrations of particulate, Cd throughout the sampling periods exhibited minor fluctuation with mostly increased concentration from the downstream estuary to the upstream station along the flow path (Fig. 2). Sudden increased was observed at the surface layer of Station 7 and 8 in May which located at the city center, though the concentration observed was slightly dropped at Station 9. Concentrations at the surface layers were higher than the bottom layers. Particulate Cd in Kuantan River waters were found above the limit of 1 mg L^{-1} that approved by International Commission for the Protection of the Rhine against Pollution⁶.

Particulate, chromium showed distinct distributional characteristics and ranged widely, from 6.047 to 168.190 mg L^{-1} as shown in Table 1. Throughout the sampling periods, particulate Cr recorded the highest concentration compared to Cd and Pb. The mean concentration of particulate Cr found in May 2012 was higher than October 2012 with a value of 92.183 ± 30.840 mg L^{-1} and 58.867 ± 25.349 mg L^{-1} , respectively (Fig. 3). The

average Cr concentration in Kuantan River water was measured to be lower than the ICPR limit of 100 mg L^{-1} of Cr^{6+} . Likewise Cd and Cr, maximum values of particulate Pb encountered at the upstream stations, and occasionally in the vicinity of the Kuantan city center. Multifold increasing was observed with distance from river mouth to the upstream along the flow path. The highest mean

concentration of particulate Pb with mean value of $76.642 \pm 36.542 \text{ mg L}^{-1}$ was relatively found in May 2012, while mean concentration in October 2012 was $38.325 \pm 18.883 \text{ mg L}^{-1}$. Throughout the sampling periods, particulate Pb exhibited higher concentrations on the surface layers than bottom layers as shown in Fig. 4. Mean concentrations of particulate Pb are lower than ICPR limit of 100 mg L^{-1} .

Table 1: Summary statistic of element concentration, water quality parameters and rainfall data of Kuantan River basin during sampling period

Month	Element	Average	SD	Min.	Max.
May 2012	Cd (mg/L)	4.058	2.432	0.849	11.594
	Cr (mg/L)	92.183	30.840	36.895	168.190
	Pb (mg/L)	76.642	36.542	21.057	147.430
	pH	7.110	0.580	6.660	7.820
	Salinity (ppt)	21.450	9.900	0.330	34.300
	DO (mg/L)	5.400	0.640	4.460	6.610
	Temperature ($^{\circ}\text{C}$)	29.790	0.630	28.150	30.780
	Rainfall mm (inches)	169 (7.24)	-	-	-
October 2012	Cd (mg/L)	2.184	1.678	0.478	8.182
	Cr (mg/L)	58.867	25.349	6.047	111.576
	Pb (mg/L)	38.325	18.883	7.770	82.320
	pH	6.550	0.500	6.020	7.430
	Salinity (ppt)	20.080	10.600	0.090	33.570
	DO (mg/L)	6.250	0.800	4.710	7.670
	Temperature ($^{\circ}\text{C}$)	28.920	1.010	27.242	30.050
	Rainfall mm (inches)	283.9 (10.996)	-	-	-

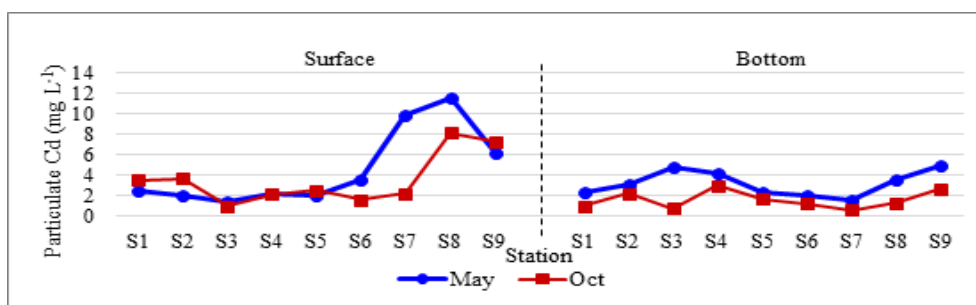


Fig. 2. Concentrations of particulate Cd (mg L^{-1}) at different sampling periods

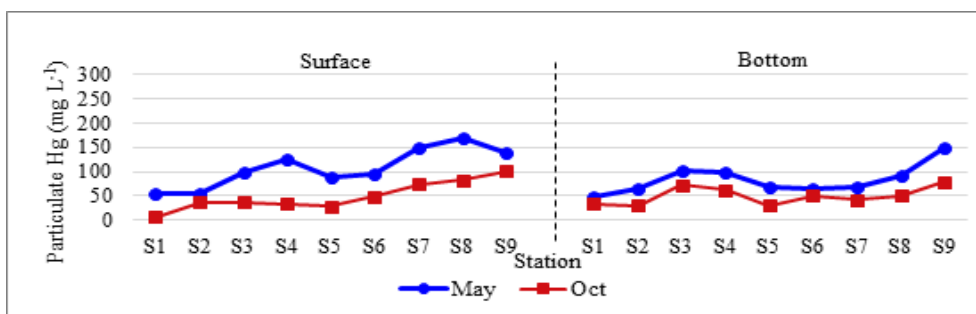


Fig. 3. Concentrations of particulate Cr (mg L^{-1}) at different sampling periods

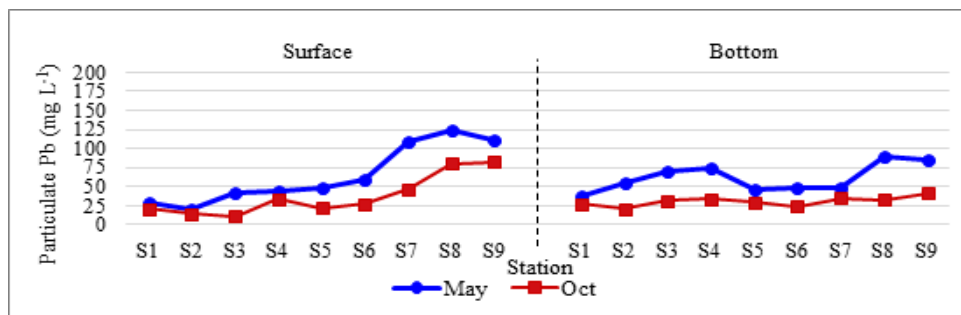


Fig. 4. Concentrations of particulate Pb (mg L^{-1}) at different sampling periods

A positive and significant correlation was found in pH and Cr while less significant was found between temperature and Cr ($p > 0.05$) as shown in Table 2. Inversely, salinity was negative and significantly correlated with Cd and Pb though less significant with Cr and Dissolved oxygen observed was less significant and negatively correlated with Cr and lead. Pearson correlation matrixes of suspended particulate metals are given in Table 3. Overall, correlation analysis showed that most of the particulate elements had a strong and positive relationship with each other. A good positive correlation that was found between almost all heavy metals shows that there were a common source or at least one major source for all of them and may reflect similar behavior. Zhou *et al.*,²⁰ whom also found significant inter-element relationships in SPM claimed that some trace metals have similar reactivity towards biological and non-biological particle and, therefore, possible for some of them will have their particulate-bound concentrations closely related to each other.

Table 2: Correlation analyses of physicochemical parameters with particulate elements

	Salinity	Temperature	pH	DO
Cd	-.240**	-.101	-.020	.073
Cr	-.162*	.147*	.201**	-.157*
Pb	-.316**	.002	-.010	-.171*

** . Correlation is significant at the 0.01 level (2-tailed).

* . Correlation is significant at the 0.05 level (2-tailed).

Table 3: Pearson's correlation matrix indicating the overall elements association within particulate metals

	Cd	Cr	Pb
Cd	-	.366**	.677**
Cr	-	-	.656**

** . Correlation is significant at the 0.01 level (2-tailed).

Suspended particulate matter of Cd, Cr and Pb showed multifold increasing trends from the downstream estuary to the upstream stations along the river flow path. Increasing concentration in particulates metals after the monsoon season subsides was due to adsorption onto re-suspended or elevation of natural particles that formerly present. Study of the Neckar River in Germany, showed higher elements that originated from anthropogenic found in suspended fine sediment compared to the coarse particle⁹. Therefore, from the trend observed, two particulate matter sources were discovered that is flocculation processes derived particles from urban and industrial wastes or natural particles instigated by erosion⁹.

Fine particles originated from the run-off of the sewage discharges may be the main source of this metal. During the low current of the river, there are high probabilities the particles were adsorbed. Heavy rainfall during monsoon may result to adsorption of large soluble fraction of Cd onto suspended solids throughout the dry season. Research by Ouseph also discovered higher concentration in particulate metal content during the low rainy season¹¹. Desorption of Cd with an increase in salinity due to the formation of stable chloro-complexes also have been reported³.

Desorption of Cd from particles in the estuarine site may be the cause for the metal-enrichment in May 2012. During the wet season, enormous large particles as well as metal-deficient smaller particles were washed off by the monsoon shower to the river waters. Then, the metals were mixed with metal-rich particles causing a low concentration in the particulate cadmium. Study found that Cd was connected with finer particles for example clay minerals¹³.

The main sources of elevated concentration of particulate Cr possibly came from the riverine input and run-off from terrestrial. Flocculation are higher since Cr has a great microparticulate element while the river water enters the estuary. Study in San Francisco Bay claimed that industrial and municipal discharges and weathering contributed to the enrichments of particulate Cr in suspended matter¹. Moreover, there are more study shown that Cr has greater particulate and microparticulate elements, low solubility whereby during the particulate splitting process, colloidal combination may have followed⁷. Although no clear spatial pattern could be established, maximum values of particulate Cr were always found at the stations situated nearby the city centers (S3, S4 and S5) as well as upstream stations (S8 and S9) corresponding to low salinity values. The potential source of Cr in the Kuantan River is possibly from the boats paints that consist higher amounts of Cr in the form of zinc chromate instigating the leaching of substantial quantities of the metal to the water. The nearness of the stations to the city centers, residential areas and the domestic waste discharges into the Kuantan River might have increased the metal content.

Meanwhile, during the heavy rainfall, particulate Pb that entered to the river systems in the soluble form were precipitated onto particles subsequent after the monsoon period ended and resulted in high concentration in May 2012. Higher

particulate component of Pb were probably because of the low propensity to create allied with particles by scavenging⁷. Furthermore, experimental study carried out by Shulkin and Bogdanova¹⁵ and field studies by Westerlund *et al.*,¹⁸ confirmed that Pb has high affinity to the solid phase. Another mechanism, dissolved Pb that released from sediments were re-adsorbed onto the suspended particles also may affects the particulate Pb concentration. Other aspects that may involves in higher concentration of particulate Pb includes shipping wastes, discharges from petroleum industries, land run-off sources, and natural sources such as biological activities and effects of wind. In the Kuantan River, one of the major source of Pb were the emanations from recurrent boating activities. Further monitoring need to be done in Kuantan River as the rapid development from adjacent city centers may increase the pollution of river water.

CONCLUSION

The concentration of the particulate elements was found higher in May and also showed increasing trend from downstream estuary to the upstream stations. Agricultural, boating and recreational activities, effluents and domestic wastes from surface run-off and drains may contributed to the significant amounts of particulate metals in the Kuantan River. Further monitoring need to be done in the river as the rapid development from adjacent city centers may increase the pollution of river water.

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