Seasonal Variation And Preliminary Risk Assessment Of Trace Element Pollution In Surface Water From Langat River, Malaysia

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Abstract

Heavy metals are widely used in various industries and became a great concern all over the world due to environmental contamination. This study provides an assessment of seasonal variability and risks to human health associated with the exposure to heavy metals concentrated in Langat river water of Malaysia. The Department of Environment (DOE) Malaysia kindly provided the heavy metal concentration data in water for this study. Several multivariate estimation such as an independent t test, box-and-whisker plot and Principal component analysis were carried out to evaluate the seasonal variation of metals concentration in water.

The average value of ten analyzed metals was 250.81 µg/l and followed in order of abundance by August > Jun > February > October > April > December > March > May > September > January > July > November. The calculated HPI was 123.42, which is far above the critical index value of 100, indicating pollution with respect to heavy metals. Estimates of health risks associated with river water were summarized according to non-carcinogenic and carcinogenic health effects. No potential threat was detected for non-carcinogenic risk as the HI values calculated were <1. Potential carcinogenic risks associated with the ingestion and dermal absorption of heavy metals in water were evaluated probabilistically by performing 10,000 trails for Monte Carlo simulation where potential carcinogenic risk exists in case of Cd and As.

It is necessary to take proper steps to reduce the pollution of heavy metals in Langat River.

Keywords: Heavy metal, Langat, Health risk, HPI.

Background

In recent years, heavy metal toxicity has increased as a serious concern all over the world, as these metals are indestructible and most of them have toxic effects on living organisms, when they exceed a certain concentration [1-3]; [4, 5]; [6]. Heavy metals are ubiquitous in the environment [7-9]. Additionally, man-made pollution sources such as mining, metal smelting and processing, industrial wastewater, fossil fuels burning, application of fertilizer, pesticides, and household garbage can play a significant role towards a high level of heavy metal in water body [6]. Furthermore, in recent years, increased population and the progress in agriculture and industry have complicated this situation [10].

There are many studies in the literature on heavy metal pollution of water sources [11], [12], [13-15]. Edet & Offiong [16] focused on quantifying the trace metals and their assessments on the aqueous environment because the increase in concentration of trace metals in potable water will increase the threat to human health as well as life. Moreover, it is reported that seasonal variations in agricultural activity, storm water runoff, interflow and atmospheric deposition have strong effects on river water quality [17-19]. Therefore, characterization of seasonal variability in surface water heavy metal concentration is necessary for assessing temporal variations of river pollution from natural or anthropogenic contributions [20]. Simultaneously, it is reported that the intake of water with significant amounts of metals particularly arsenic might result in varying cancers and as a result numerous studies were conducted on human health risk assessment concerning metals [21-24].

Health risk assessment is considered to be an important tool for evaluating the consequences of human activities and weighs the adverse effects to public health against the contributions to economic development. Health risk assessment has been developed widely since the 1980s; it establishes the correlation of environmental pollution and human health risk as well as indicates and estimates qualitatively the potential hazardous probability that environmental pollution imposes on human health [25, 26].

Langat River Basin is one of the most important basins in Malaysia, draining a densely populated and developed area of Selangor and supplying water to two thirds of the state. It is chosen as one of the major areas for economic growth especially in developing manufacturing zones in Selangor. Apart from the rise of export intensive industrial zones in the Basin, the Kuala Lumpur International Airport, West Port in Klang, the Multimedia Super Corridor (MSC) and Putrajaya, all of which are situated in the Basin also generate diversified development activities that in turn attract the widespread building of infrastructures and utilities [27]. However, rapid urbanization within the Langat River Basin has caused changes in water quality. According to [28], 42 tributaries in Peninsular Malaysia have been categorized as very polluted,

including the Langat River. Until 1999, there were 13 polluted tributaries all over Malaysia with 36 polluted rivers due to human activities such as industry, construction, and agriculture at the tributaries [29].

In Malaysia, publications covering different aspects of Langat river are numerous [27, 30-33], but to our best knowledge, there is no report on risk assessment on trace metals and their temporal characterizations. Therefore, this study aims to evaluate the seasonal variations of trace metals in Langat River and predict potential health consequences that can serve as a scientific basis for decision-making and policy development.

Materials and Methods

The data for this study was kindly provided by the Department of Environment, Malaysia, observed monthly from 10 sampling points of Langat River, between February 2001 and October 2010.

Statistical Analysis

In statistical analysis, a box plot is a graph that can be a valuable source of easy-to-interpret information about a sample of study. Therefore, in the present study, the box-and-whisker plot analysis has been carried out to evaluate the seasonal variation of chemical contaminants in Langat river water. Furthermore, for comparing concentration of metals in dry and wet seasons, t-test analysis was assigned.

Principal component analysis (PCA) is the most common multivariate statistical method used to explore associations and origins of trace elements [34, 35]. It is designed to transform the original variables into new, uncorrelated variables (axes), called the principal components, which are linear combinations of the original variables. The new axes lie along the directions of maximum variance [36]. It reduces the dimensionality of the data set by explaining the correlation amongst a large number of variables in terms of a smaller number of underlying factors (principal components or PCs), without losing much information [37-39]. The principal component (PC) can be expressed as:

$$z_{ij} = pc_{i1}x_{1j} + pc_{i2}x_{2j} + \dots + pc_{im}x_{mj} \quad (1)$$

Where z is the component score, pc is the component loading, x is the measured value of the variable, i is the component number, j is the sample number and m is the total number of variables.

However, in the present study, PCA was used to identify significant variables contributing to water quality variation during both seasons. In this study, all the statistical analysis was conducted using SPSS, Version 14 for Windows XP.

Analysis of HPI

Heavy metal pollution index (HPI) is a technique of rating that provides the composite influence of individual heavy metal on the overall quality of water. The

rating is a value between zero and one, reflecting the relative importance of individual quality considerations and inversely proportional to the recommended standard (S_i) for each parameter [40-42]. In computing the HPI, Prasad & Bose [43] considered unit weightage (W_i) as a value inversely proportional to the recommended standard (S_i) of the corresponding parameter as proposed by [16]. The HPI model [42] is given by:

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i} \quad (2)$$

Where Q_i is the sub-index of the i^{th} parameter. W_i is the unit weightage of the i^{th} parameter and n is the number of parameters considered. The sub-index (Q_i) of the parameter is calculated by:

$$Q_i = \sum_{i=1}^n \frac{\{Mi(-)Ii\}}{(S_i - I_i)} \times 100 \quad (3)$$

Where M_i is the monitored value of heavy metal of i^{th} parameter, I_i is the ideal value of the i^{th} parameter and S_i is the standard value of the i^{th} parameter. The sign (-) indicates numerical difference of the two values, ignoring the algebraic sign. The critical pollution index of HPI value for drinking water as given by Prasad & Bose [43] is 100.

Human Health Risk Assessment

Calculation of Chronic Daily Intake

In this study, the exposed dose is calculated using the following equations adapted from (Rodriguez-Proteau and Grant, 2005):

$$CDI (\mu g/kg/day) = \frac{C_w * IR * EF * ED}{BW * AT} \quad (4)$$

$$DAD (\mu g/kg/day) = \frac{DA_{event} * EV * EF * SA}{BW * AT} \quad (5)$$

Where, CDI is the average daily dose by ingestion and DAD is dismally absorbed dose. DA_{event} is the absorbed dose per event ($\mu g/cm^2$ -event) which is calculated using the equation below:

$$DA_{event} = K_p * C_v * t_{event} \quad (6)$$

Table 1. Input parameter of human health risk assessment

Parameter	Description	Value
CW	Chemical concentration in water	(mg/L)
IR	Ingestion rate	2 L/day
EF	Exposure frequency	365 days/year
ED (Dermal)	Exposure duration (years)	9 years for adult, 6 years for child
ED (Ingestion)	Exposure duration (years)	30 years for adult, 6 years for child
BW	Body weight (kg)	70 kg for adult, 15 kg for child
AT (carcinogenic)	Averaging time in years	Body weight (70kg) x 365
AT (non-carcinogenic)	Averaging time in years	Body weight x 365
Sa	Skin surface area available for contact (cm ²)	18000 (adult) and 6600 (child)
EV	Event frequency (events/day)	1
Kp	Dermal permeability coefficient	Chemical-specific values
t _{event}	Event duration (h/event)	0.25 (adult) and 0.33 (child)

Table 1 shows the input parameters used in the health risk estimation.

Hazard Quotient (HQ) and Hazard Index (HI)

The HQ (ingestion and dermal contact) and HI for non-carcinogenic risk of some trace metals in drinking water have been calculated using equations (7), (8), and (9). If the HQ exceeds 1, there might be a concern for non-carcinogenic effects. To evaluate the total potential non-carcinogenic risks posed by more than one pathway, the hazard index HI was introduced, which was the sum of the HQs from all applicable pathways. $HI > 1$ indicates a potential for an adverse effect on human health or the necessity for further study [44, 45].

$$HQ_{\text{Ingestion}} = \frac{CDI}{RfD_{\text{Ingestion}}} \quad (7)$$

$$HQ_{\text{Dermal}} = \frac{DAD}{RfD_{\text{dermal}}} \quad (8)$$

$$HI = HQ_{\text{Ingestion}} + HQ_{\text{Dermal}} \quad (9)$$

RfD is the reference dose for different elements which is based on USEPA risk based concentration table [46]. The $RfD_{\text{Ingestion}}$ was multiplied by a gastrointestinal absorption factor (ABS_g) to yield the corresponding dermal absorption reference dose (RfD_{Dermal}) [44].

Carcinogenic Risk (CR) Indices

Carcinogenic risks through ingestion and dermal absorption of element with waters were typically predicted by the following equation:

$$\text{Cancer Risk}_{\text{ingestion}} = \text{CDI} \times \text{SFo} \quad (10)$$

$$\text{Cancer Risk}_{\text{dermal}} = \text{DAD} \times \text{SF}_{\text{ABS}} \quad (11)$$

SFo and SF_{ABS} are the oral and absorbed carcinogenic slope factors respectively expressed in $(\mu\text{g/kg/day})^{-1}$ which is based on USEPA risk based concentration table [44]. Absorbed slope factors were calculated using the following equation:

$$\text{SF}_{\text{ABS}} = \frac{\text{SFo}}{\text{GIABS}} \quad (12)$$

Where GIABS is the fraction of contaminant absorbed in gastrointestinal tract in critical toxicity study [44]. Under most regulatory programs, a CR value over 1.00E-05 indicates potential carcinogenic risk.

Results and Discussion

Seasonal variations of trace metals Table 2 shows the summary of the basic statistics of the analyzed parameters in surface water of Langat River from 2001 to 2010. The concentrations of elements displayed a great variation according to different months. Figure 1 demonstrated the monthly variation of some of the variables analyzed as box-and-whisker plot, which is a way of summarizing a set of data measured on an interval scale, and useful for showing the shape of the distribution, central value and variability. In a box and whisker plot, the ends of the box are the upper and lower quartiles, the median is marked by a vertical line inside the box and the whiskers are the two lines outside the box that extend to the highest and lowest observations. The box itself contains the middle 50% of the data. The upper edge of the box indicates the 75th percentile of the data set, and the lower hinge indicates the 25th percentile. The range of the middle two quartiles is known as the inter-quartile range. The outliers are present in which case the whiskers extend to a maximum of 1.5 times the inter-quartile range.

In this study, As, Ca, K, Na and Mg displayed a similar pattern, with comparatively higher values during August, February, June and October, lower in January, May, July and November. Fe also exhibited the similar behavior but the concentration in November was higher. On the other hand, slightly different concentration pattern was observed for Cr and Zn. The Cd and Pb are not presented in the figure as they exhibited a similar pattern because there exist very few data due to being frequently below the detection limits.

The total concentrations of ten metals in surface water of different locations of Langat river had an average value of 250.81 $\mu\text{g/l}$, followed in order of abundance by August (665.95 $\mu\text{g/l}$) > Jun (527.19 $\mu\text{g/l}$) > February (505.59 $\mu\text{g/l}$) > October (424.99

$\mu\text{g/l}$) > April (270.42 $\mu\text{g/l}$) > December (246.81 $\mu\text{g/l}$) > March (187.57 $\mu\text{g/l}$) > May (56.69 $\mu\text{g/l}$) > September (50.99 $\mu\text{g/l}$) > January (27.46 $\mu\text{g/l}$) > July (27.23 $\mu\text{g/l}$) > November (18.82 $\mu\text{g/l}$).

Table 2. Descriptive Statistics of the variables analysed during the period from 2001 to 2010

Trace Element	Minimum ($\mu\text{g/l}$)	Maximum ($\mu\text{g/l}$)	Mean ($\mu\text{g/l}$)	Std. Deviation
As	0.001	0.022	0.005	0.003
CD	0.001	0.003	0.001	0.000
Cr	0.001	0.018	0.002	0.002
Pb	0.010	0.011	0.010	0.000
Zn	0.010	0.095	0.033	0.020
Ca	2.772	44.548	15.384	9.746
Fe	0.020	0.856	0.307	0.198
K	1.391	47.022	11.907	11.232
Mg	0.132	114.152	24.180	31.328
Na	3.954	1114.958	205.215	266.810

Figure 1- Box-and-Whisker plots of the monthly evolution of some of the variables concentrated in Langat River, Malaysia.

The weather in Malaysia is characterised by two monsoon regimes, namely, the Southwest Monsoon from late May to September, and the Northeast Monsoon from November to March. The Northeast Monsoon brings heavy rainfall, particularly to the east coast states of Peninsular Malaysia and western Sarawak, whereas the Southwest Monsoon normally signifies relatively drier weather. The transition period in between the monsoons is known as the inter-monsoon period. An independent t test was conducted (Table 3) to compare the concentration of metals in dry and wet seasons where no significant difference was observed in all of the elements and this result is opposite to the result of Han River where significant differences occurred between these two seasons [20]. This study found that the dry season had a highest concentration of As, Cd, Cr, Pb, Ca, Fe, K, Mg and Na compared to the wet season. The higher elements concentrations in dry season was because of high evaporation and intense anthropogenic activities [47] whereas the diluting effect in flood season due to Northeast monsoon climate resulted in the subsequent diminution of the elements concentration [20]. On the other hand, concentration of Zn was slightly higher in wet season which might be the result of precipitation and seasonal anthropogenic activities that play imperative role in governing trace metals in stream water [48]. According to Vega et al. [49], 80% of annual precipitation fell in the rainy season and subsequently diluted the river pollutants. However, there was considerable difference in their total mean concentrations between the wet (197.25 µg/l) and dry (265.61 µg/l) seasons but in the case of Han River, China, the difference between these two season was very little [20].

Table 3. Analytical result of Independent-Samples T Test

	Season	N	Mean	Std. Deviation	Std. Error Mean
As	Wet season	46	.00413	.002760	.000407
	Dry Season	49	.00464	.002966	.000424
CD	Wet season	46	.00103	.000221	.000033
	Dry Season	49	.00104	.000216	.000031
Cr	Wet season	46	.00225	.002140	.000316
	Dry Season	49	.00282	.003007	.000430
Pb	Wet season	46	.01001	.000059	.000009
	Dry Season	49	.01002	.000129	.000018
Zn	Wet season	46	.03374	.019263	.002840
	Dry Season	49	.03271	.020233	.002890
Ca	Wet season	46	13.84060	9.364752	1.380757
	Dry Season	49	15.89302	10.374973	1.482139
Fe	Wet season	46	.31032	.201354	.029688
	Dry Season	49	.31510	.210507	.030072
K	Wet season	46	10.42926	10.978843	1.618742
	Dry Season	49	12.54087	11.712804	1.673258
Mg	Wet season	46	18.90476	28.173721	4.153988
	Dry Season	49	25.94992	34.472603	4.924658
Na	Wet season	46	160.42215	248.011693	36.567329
	Dry Season	49	215.12647	289.316012	41.330859

PCA of the normalized dataset extracted four PCs with eigenvalues > 1 , explaining about 81.41% and 82.56% of the total variance of information contained in the original dataset for dry and wet season respectively (Table 4 and 5). In this study, the factor loadings were classified as strong, moderate and weak corresponding to absolute loading values of >0.75 , $0.75-0.50$ and $0.50-0.30$, respectively [20, 50].

Table 4. Loadings and eigenvalues of trace metal contents in significant principal components for Langat river water samples in dry weather

Elements	PC1	PC2	PC3	PC4
As	.425	-.248	.537	.459
Cd	.090	.090	.533	-.413
Cr	-.041	-.218	.760	.161
Pb	.121	.408	-.077	.770
Zn	-.016	.759	.489	-.201
Ca	.925	.037	-.028	-.167
Fe	.241	.875	-.112	.029
K	.978	-.037	-.074	-.069
Mg	.983	-.084	-.048	-.016
Na	.982	-.077	-.057	-.017
Eigenvalues	4.006	1.641	1.420	1.075
Comulative %	40.058	56.473	70.671	81.417

Table 5. Loadings and eigenvalues of trace metal contents in significant principal components for Langat river water samples in wet weather

	1	2	3	4
As	.566	.335	-.509	-.020
CD	-.118	.339	.167	-.628
Cr	.292	.236	-.818	.180
Pb	-.132	.299	.247	.775
Zn	.118	.848	-.077	-.160
Ca	.932	-.101	.057	.028
Fe	-.043	.831	.400	.100
K	.948	-.073	.178	-.009
Mg	.968	-.041	.201	-.005
Na	.970	-.041	.195	-.004
Eigenvalues	4.096	1.800	1.296	1.064
Comulative %	40.959	58.961	71.925	82.566

During the dry season, PC1 explained 40.05% of the total variance and demonstrated strong positive loadings on Ca, K, Mg and Na, and weak positive loading on As. PC2 (16.41% variance) had strong positive loadings on Zn and Fe, whereas weak positive loadings on Pb. PC3 (14.19% variance) exhibited strong positive loading on Cr, moderate positive loadings on As and Cd, and weak positive loading on Zn. PC4 exhibiting 10.74% of the total variance, had strong positive loadings on Pb, weak positive loading on As and weak negative loading on Cd. On the other hand, in the case of wet season, PC1 contributed 40.95% of the total variance because of the strong positive loadings of Na, Mg, K and Ca, and moderate positive loadings of As. PC2 explained 18% of the total variance, had strong positive loadings on Zn and Fe; PC3 and PC4 had negative loadings on As and Cd, respectively. However, PC4 demonstrated only positive loading on Pb.

Ca, K, Mg, Na, Zn, Fe and Pb were the significant variables contributing to water quality variation during both seasons while during wet season, negatively correlated trace metal concentration was observed. Similar results were found in the case of Han River where negatively correlated water quality variability was observed during the wet season [20]. This study also supports the findings of the same study where it was reported that there might be a difference in important water quality variables in different seasons.

In order to calculate the Heavy metal pollution index of the water, the mean concentration values of the selected metals (As, Cd, Cr, Pb, Zn, Ca, Fe, Mg and Na) have been taken into account. In Table 6, detailed calculation of HPI with unit weightage (W_i) and standard permissible value (S_i) are presented. The S_i values for As, Cd, Cr, Fe, Pb and Zn have been obtained from the publication of Edet & Offiong [16] and for Ca, Mg and Na obtained from WHO's drinking water standard [51]. The K was not included for the HPI calculation because of no availability of S_i value for this element.

Table 6. HPI Calculation for Langat River water

Heavy metal	Mean value	Standard Permissible value	Highest desirable value	Unit weightage	Sub index
	Mi (ppb)	Si (ppb)	Ii (ppb)	Wi (1/Si)	Qi
As	0.005	50	10	0.020000	24.99
CD	0.001	5	3	0.200000	149.95
Cr	0.002	50		0.020000	0.00
Pb	0.010	100	10	0.010000	11.10
Zn	0.033	5000	3000	0.000200	150.00
Ca	15.384	75000		0.000013	0.02
Fe	0.307	300	200	0.003333	199.69
Mg	24.180	50000		0.000020	0.05
Na	205.215	200000		0.000005	0.10

$$\sum W_i = 0.253571667, \sum W_i Q_i = 31.295, HPI = 123.42$$

The calculated value of heavy metal pollution index (123.42) is far above the critical index value of 100. This indicates that the water is contaminated with respect to the heavy metals. Well below values of HPI have been calculated for Giri and Tons Rivers of India [43] and Lower Cross River basin of Nigeria [16], whereas very high values have been observed in River PovPov which is an iron-ore mining area of Nigeria [52]. However, the higher value of HPI in Langat river is not very surprising because the rapid development and population increase in the Langat Basin has resulted in tremendous stress on the ecosystem health of the Langat River [33]. The sources of the Langat River pollution are identified as industrial discharge (58%), domestic sewage from treatment plants (28%), construction projects (12%) and pig farming (2%) [33, 53]. It is assumed that the heavy metal pollution index model used here is considered to be promising and is proven to be a constructive tool in evaluating the overall pollution level of river water in terms of heavy metals.

Risk Assessment On Human Health

Three main pathways can be responsible for the exposure of trace metals in human beings which are direct ingestion, inhalation and dermal absorption through skin exposure, where ingestion and dermal absorption play a significant role in the case of drinking water [20, 23, 24, 54]. Considering these two pathways, the estimated health risk associated with water from Langat River was summarized according to non-carcinogenic and carcinogenic health effects (Table 7). Potential non-carcinogenic risks was reflected by hazard quotient and estimated by comparing exposure or average intake of contaminants for each exposure route (ingestion, dermal) with corresponding reference dose (RfD). If the HQ exceeds 1, there would possibly be concerns for non-carcinogenic effects. The hazard index (HI) was introduced to evaluate the overall potential non-carcinogenic risks posed by more than one pathway and it is measured by the sum of the HQs from all applicable pathways. The potential

for an adverse impact on human health or the requirement for further studies is indicated by $HI > 1$ [20, 54].

Table 7. Reference dose, Hazard quotient and cancer risk for each element of Langat River, Malaysia

Element	RfD (Ing)	RfD (Der)	Dermal HQ		Ingestion HQ		HI		Cancer Risk		
	($\mu\text{g/kg/day}$)	($\mu\text{g/kg/day}$)	adult	child	adult	Child	(adult)	Child)	Ingestion	Dermal	Σ Risk
As	0.3	0.123	2.38×10^{-03}	5.39×10^{-03}	4.34×10^{-04}	6.49×10^{-04}	2.82×10^{-03}	6.03×10^{-03}	2.51×10^{-05}	5.66×10^{-05}	8.17×10^{-05}
Cd	0.5	0.005	1.34×10^{-02}	3.02×10^{-02}	5.94×10^{-05}	8.87×10^{-05}	1.34×10^{-02}	3.03×10^{-02}	2.29×10^{-06}	1.03×10^{-04}	1.05×10^{-04}
Cr	3	0.015	1.05×10^{-02}	2.36×10^{-02}	2.32×10^{-05}	3.47×10^{-05}	1.05×10^{-02}	2.37×10^{-02}			
Pb	1.4	0.42	1.53×10^{-04}	3.46×10^{-04}	2.04×10^{-04}	3.05×10^{-04}	3.58×10^{-04}	6.51×10^{-04}	3.31×10^{-07}	7.45×10^{-08}	4.05×10^{-07}
Zn	300	60	2.15×10^{-05}	4.84×10^{-05}	3.18×10^{-06}	4.75×10^{-06}	2.46×10^{-05}	5.32×10^{-05}			
Fe	700	45	4.39×10^{-04}	9.92×10^{-04}	1.25×10^{-05}	1.87×10^{-05}	4.52×10^{-04}	1.01×10^{-03}			

The result of the current study shows that the non-carcinogenic risk of As, Cd, Cr, Pb, Zn and Fe are all less than 1, suggesting that these elements posed little hazard. Similar results were found in the case of Yangtze River and Han River of China [20, 24]. The results also demonstrated that the non-carcinogenic risk to children is higher than the adult, in both the case of dermal absorption and ingestion. However, comparatively higher risk is associated with dermal absorption than ingestion in adult and children which indicates that concentration of these metals may pose little or no health threat via ingestion. This finding is dissimilar with the findings of Yangtze River, where the calculated value of HQ_{dermal} was lower than $HQ_{\text{ingestion}}$ [24]. Overall, the non-carcinogenic risk for children is higher than the adults ($HI_{\text{adult}}, 0.02 < HI_{\text{children}}, 0.06$). The HI of analyzed trace metals was found in the following order: Cd (48.7%) > Cr (38.0%) > As (10.2%) > Fe (1.6%) > Pb (1.3%) > Zn (0.08%) where Cd was the largest contributor and the least contributor was Zn. [20] indicated that As was the most important non-carcinogenic pollutant in Han River. Similarly, in the case of Yangtze River of China, all the analyzed metals demonstrated that the HQ (ingestion) value was smaller than unity but As was near unity which suggested that this element might be of serious health concern [24]. Furthermore, in drinking water, the maximum value of As in central Cankiri (1.19) and Kursunlu (3.35) town were higher than one for ingestion and dermal pathways [45]. However, in the present study, the position of As is in the middle suggesting comparatively lower impact on health.

Cancer risk can be outlined as the upper bound lifetime probability of an individual developing cancer as a result of exposure to a potential carcinogen. The acceptable range of carcinogenic risks by the US EPA was 10^{-6} to 10^{-4} [20, 55]. Of the ten targeted chemicals, carcinogenicity values were only reported for As, Cd, and Pb as no values of carcinogenic potency slope were available for the rest. As shown in Table 7, the carcinogenic risk ranged from 3.31×10^{-7} (Pb) to 2.51×10^{-5} (As) and

7.45×10^{-8} (Pb) to 5.66×10^{-5} (As) in water ingestion and dermal absorption, respectively. For residence of Langat river basin, the carcinogenic risk of As, Cd and water was calculated where the total ingestion risk was lower than the total dermal carcinogenic risk. The total carcinogenic risk of Cd was almost 260 times higher than Pb and 1.2 times higher than As.

This study performed 10,000 trails for Monte Carlo simulation for risk assessment by using Excel 2010 for all area data (Figure 2, 3, 4). The simulation assumed normal distribution of data with mean (AS = 8.17×10^{-5} , Cd = 1.05×10^{-4} , Pb = 4.05×10^{-7}) and standard Deviation (AS = 6.00×10^{-5} , Cd = 2.21×10^{-5} , Pb = 3.71×10^{-9}). The data are tested on both one tailed and two tailed. Except for AS, the data for both one tailed and two tailed is the same for Cd and Pb due to the very small value of standard deviation. It is logical that the risk cannot be negative. Thus, the outcome of one tailed is more preferable than two tailed.

Figure 2- Frequency Distributions of the Simulation (One Tailed) for As.

Figure 3- Frequency Distributions of the Simulation (One Tailed) for Cd.

Figure 4- Frequency Distributions of the Simulation (One Tailed) for Pb.

Based on one tailed analysis, the simulated mean of AS is 0.0000814 that can optimally reach at maximum value of 0.000311939 and minimum value of 0.00000001. However, there is a probability that at the 95% risk level, the value would be 0.0057 and at 99%, the risk level would be 0.0018. In the case of Cd, the simulated mean is 0.00010561 that can optimally reach a maximum value of 0.00019239 and minimum value of 0.00001438. However, there is a probability that at the 95% risk level, the value would be 0.0073 and at 99%, the risk level would be 0.0027. The simulated mean of Pb is 0.00000041 that can optimally reach a maximum value of 0.00000042 and minimum value of 0.00000039. However, there is a probability that at the 95% risk level, the value would be 0.0080 and at 99%, the risk level would be 0.0025. As the carcinogenic risk between $\times 10^{-6}$ and $\times 10^{-4}$ suggests potential risk [56], the calculated values of this study indicate that Cd and As in Langat river pose potential health risk to the residents. Similar results were found in the study of [20, 24]. However, it was reported that the Cd was not a carcinogenic risk source of Haihe river basin of China [9]. The As and Cd have been proven to cause potentially carcinogenic effects in previous studies [20, 24, 57]. Therefore, special concern should be paid to ensure safety of consumer and sustainable aquatic ecosystem of the Langat River.

Conclusion

This study investigated the seasonal variation and health risk of As, Cd, Cr, Pb, Zn, Ca, Fe, K, Mg, and Na in the Langat River, one of the most important rivers in Malaysia. Concentrations of analyzed metals demonstrated great seasonality with highest concentration of As, Cd, Cr, Pb, Ca, Fe, K, Mg and Na in dry season compared to wet season. Box plot analysis revealed a dramatic variation in the concentration of analyzed metals in different months. This study found that the dry season had a highest concentration of As, Cd, Cr, Pb, Ca, Fe, K, Mg and Na compared to the wet season. The principal component analysis identified Ca, K, Mg, Na, Zn, Fe and Pb as the significant variables contributing to water quality variation during dry and wet seasons.

The heavy metal pollution index of Langat river water has been found to be higher than the limit of 100, pointing to the fact that the water is polluted with heavy metals. Human risk assessed in people exposed to trace metals using exposure risk assessment model, indicated that the non-carcinogenic risk was less than 1, suggesting little hazard. Whereas Cd and As indicated potential carcinogenic risk as the calculated risk was higher than $\times 10^{-6}$. Therefore, this study concludes that there is significant health risks associated with the water of Langat River. The findings of this study can be useful for further studies as well as for the policy makers.

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