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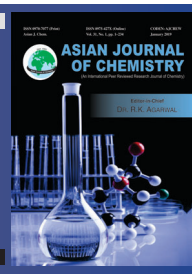

Study of Relationship between Water Quality Parameters, Selective Heavy Metals and Radioactive Elements Content in Rivers at Gebeng, Kuantan, Pahang, Malaysia

SITI UMI KALTHUM AB WAHAB, KAMARUZZAMAN YUNUS*, MOHD ARMI ABU SAMAH*, MOHD SHUKRI MOHD ARIS and ASNOR AZRIN SABUTI

Kulliyyah of Science, International Islamic University Malaysia, 25200 Kuantan, Pahang, Malaysia

*Corresponding authors: E-mail: kama@iium.edu.my; marmi@iium.edu.my

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This study was focused on the correlation between water quality parameters with the level of radioactive elements and heavy metals at six different sampling points of rivers. For achieving these objectives, collected data was done for Balok river and Tunggak river in dry seasons. Both of the rivers selected were located in Gebeng industrial area, Pahang, Malaysia. The physical parameters such as temperature, specific conductivity, pH, turbidity and dissolved oxygen were measured by using hydrolab. The water samples were then collected for tracing the radioactive elements and heavy metals by using inductively coupled plasma-mass spectrometry (ICP-MS). The readings obtained from both *in situ* and *ex situ* analysis was analyzed by using SPSS to know the correlation between water quality parameter, radioactive elements and heavy metals. There were significant relationships found between all water quality parameters and most heavy metals selected (lead and cadmium), except for arsenic. While, for radioactive elements, in the year 2015, there were significant relationships found between most water quality parameters and thorium, exception for uranium. However, for year 2014, there is no significant relationship observed. The findings of the study showed some of the presence of pollutants such as heavy metals and radioactive elements concentrations were reflected some of the water quality parameters at all the sampling locations.

Keywords: Correlation, Radioactive elements, Heavy metals, Water quality, Industrial area, Balok river, Tunggak river.

INTRODUCTION

Heavy metals have no specific meaning. They have a variety of definitions in term of atomic number, density, atomic weight, and toxicity. However, all heavy metals possess metallic properties such as high density, shiny and ductile. Heavy metals are considered as hazardous pollutants to the environment and ecosystem due to their toxicity, persistence and bioaccumulation problems [1]. They can be divided into essential metals and lethal metals based on their toxicity. Heavy metals that are dangerous can be categorized as lethal metals. This was supported by Zahir *et al*. [2]. They reported that mercury, cadmium and lead are totally poisonous to aquatic organisms in the river even at their trace concentrations, so can be categorized as lethal metals.

Heavy metals are arguably considered as dangerous and most severe groups of pollutants due to its high toxicity, profusion as well as ease of accumulation [3]. Meanwhile, for radioactive elements, they are naturally present in the environment. They can be defined as elements that have an unstable nucleus. Some essential metals such as zinc, copper, manganese, nickel and cobalt are classified as micronutrients that played a vital role in aquatic ecosystems. It means that heavy metals are needed and played their own role in human life, too. However, they also can give worst impacts towards the health of consumers if they are taken in quantities that are more than the limit. Heavy metals and radioactive elements, introducing through food chain can cause serious hazards for health of human being [4].

The increase needs and demands of the petrochemical industries and mining industries gave rise to the concentration of radioactive elements in the water besides heavy metal pollution, which is another source of pollution [5]. The rapid development of country and the intensive works of industry very often lead to serious problems such as canal bottom pollution [6]. The condition of the presence of heavy metals and radioactive elements at higher limit can cause poisoning, damage or death

in humans, animals and plants. For instance leads are toxic to the liver and its presence even in low concentrations is hazardous for aqueous and human ecosystems [7]. The higher accumulation of heavy metal concentration in the aquatic environment is catastrophic to aquatic ecosystem, human and has been progressing in Malaysia [8].

Due to bad impact of heavy metals and radioactive elements, their concentration in surface water in Malaysia should be periodically monitored and examined. There is the need for water quality assessment of river in order to understand the importance of water quality towards the health of public and aquatic life [9-11]. The study of water quality aspects of water distribution is important and significant in assuring good quality of water to the consumer [12-15]. Besides, water quality assessment can also be done through evaluation of physical parameters such as temperature, pH, conductivity, dissolved oxygen and turbidity [16,17]. The physical parameters of water such as temperature, pH, conductivity, dissolved oxygen, total dissolved solid and turbidity can be used as an indicator of the pollution level of river [18].

Besides, it is a rapid assessment compared to other monitoring or biomonitor which involves complicated steps and analysis [19]. If not managed well, heavy metals and radioactive elements can pollute water supplies such as rivers and sea, thus at the end, it can decrease the quality of water in those rivers and sea. Since they have a tendency to dilute in the rivers and sea, their prescribed average safety levels in water are often misleadingly high [16,17]. This study was conducted in order to correlate water quality parameters with the level of radioactive elements and heavy metals in the rivers within an industrial area. The relationships between those three focus points which are water quality, heavy metals, and also radioactive elements were discussed. The study was performed in Gebeng, one of the busiest industrial areas in Pahang, Malaysia.

EXPERIMENTAL

Fig. 1 showed the flow chart of research methodology. This research was divided into two parts of analysis which are *in situ* and ex situ analyses.

Study area: The samples were collected at Tunggak river and Balok river, Pahang. Three transect lines (TL1, TL2, TL3) were set up with six sampling points fixed along each transect line for both rivers. The transect lines were classified as upstream (TL1), middle stream (TL2) and downstream (TL3). SB1, SB2, and SB3 were located in Sungai Balok area while ST1, ST2, and ST3 were located in Sungai Tunggak area. Station SB1 and ST1 were situated in the upstream area while station SB2 and ST2 were located in the middle stream area. Station SB3 and ST3 were located in the downstream zone. In short, the total sampling points for both rivers is six. Fig. 2 showed the map of sampling locations in Gebeng.

Sampling methodology: Prior to the sampling process, all sampling gears were well prepared a few days earlier. The apparatus that was used for sampling such as falcon tube were dipped in 5 % nitric acid overnight. After that, all the apparatus was rinsed with distilled water and left to dry. The method for the *in situ* parameter was adapted from the reported method [16,17,19] with some adjustment. Sampling activity was carried

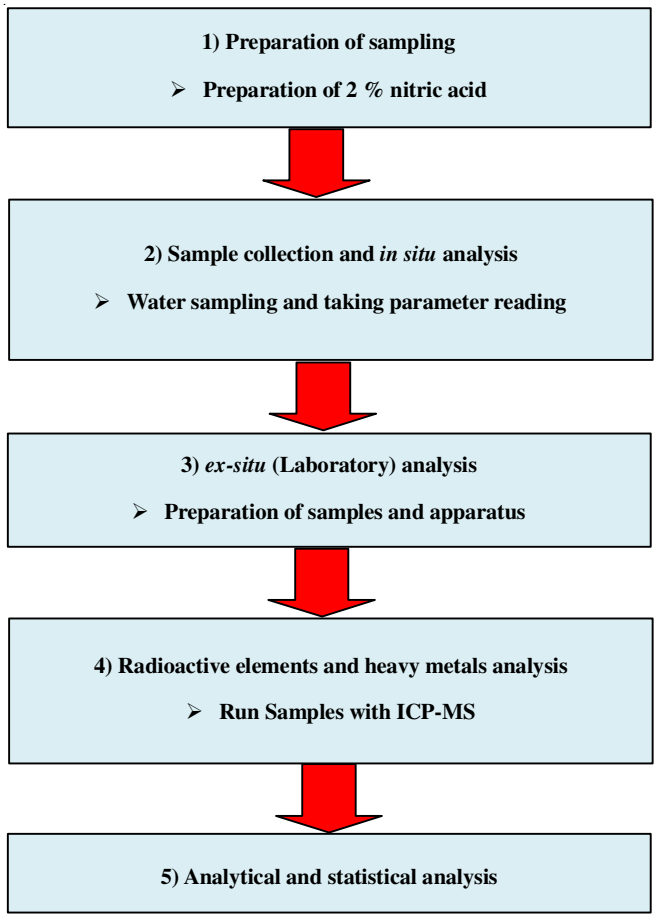

Fig. 1. Flow chart of research methodology

out for up stream, middle stream and down stream in the similar time of sampling at the selected rivers. The sample from each sampling points was taken duplicated to get more accurate result. The sampling collection was done for 2 times in each month for three months to get an average of the results. Physical parameters that were measured involved water temperature, specific conductivity, pH, turbidity and dissolved oxygen (DO). Physical parameter readings were measured by using Hydrolab, while water samples were collected by using a horizontal water sampler. Then, the samples were kept in 1 L PTFE bottle for each sampling point for laboratory analysis. The PTFE bottles were labeled according to the sampling point taken and placed in an ice box in order to preserve the nature and content of the water. Preservation of samples was done by adding 2 mL of 2 % nitric acid in PTFE bottles.

Laboratory work and analysis of radioactive elements and heavy metals: The samples were analyzed in accordance with the APHA standard method [20,21] with some adjustment. The samples were filtered by using 0.45 µm nylon filter syringe. The filtered solutions were stored in the refrigerator (-20 ºC) until analysis. Filter solution then was injected and ran in the inductively coupled plasma-mass spectrometer (ICP-MS) to determine the content of heavy metal and radioactive elements. The concentration was recorded in ppb units.

Statistical analysis methodology: After all *in situ* and *ex situ* analyses, the collected data for water quality parameters, heavy metals and radioactive elements were compiled using Microsoft Excel (version 2010) and their relationship was

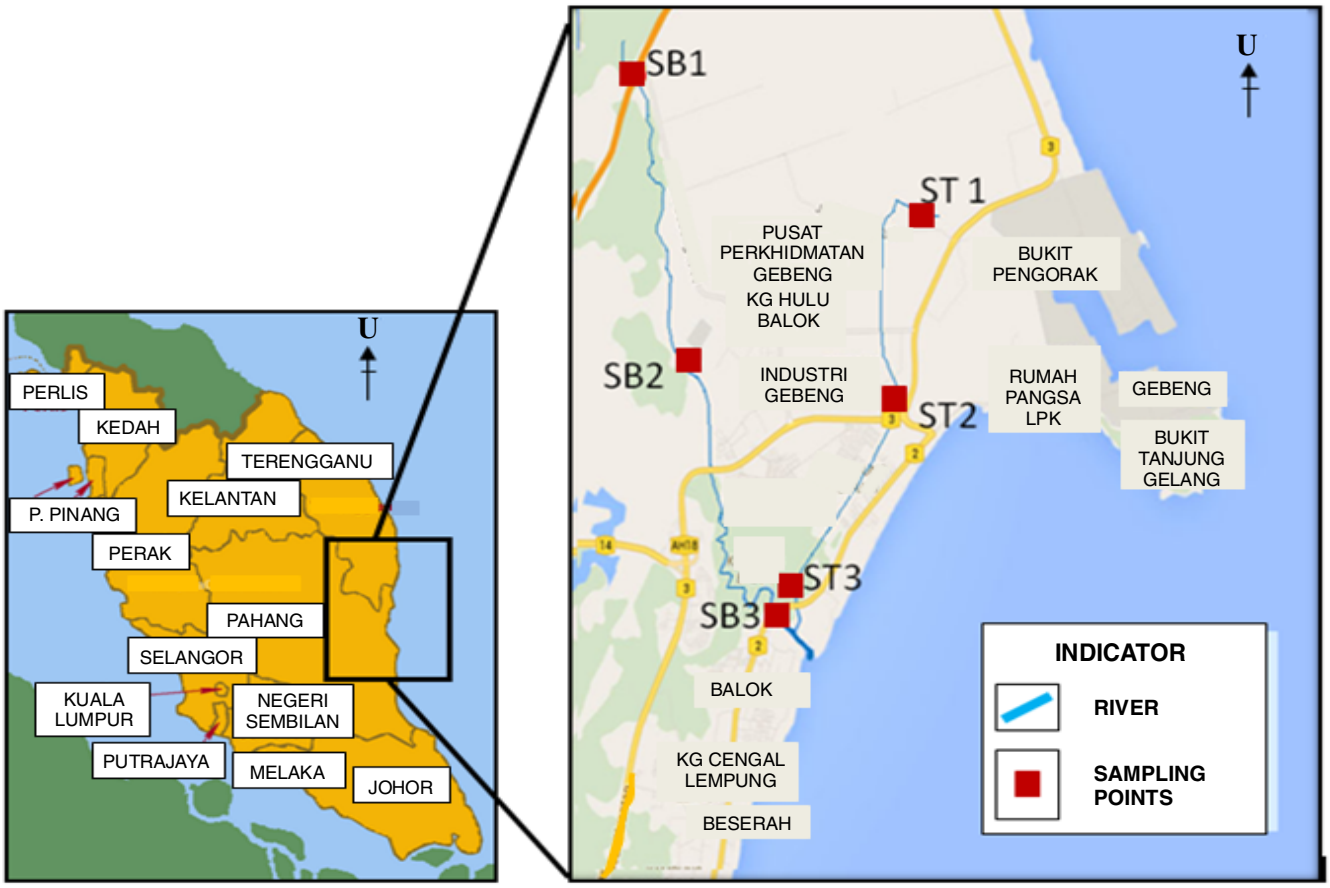

Fig. 2. Map of sampling locations in Gebeng

analyzed by using Statistical Package for Social Science (SPSS) software version 22. The relationships between the concentrations of elements detected in water samples at each sampling points were evaluated by the determination of Pearson correlation coefficients. All errors were calculated at 95 % confidence level.

RESULTS AND DISCUSSION

Water quality parameters reading: Five water quality parameters *viz*. dissolved oxygen (DO), pH, specific conductivity, temperature and turbidity were evaluated in this study. Table-1 below showed the water quality parameters average reading for Balok river and Tunggak river. For both rivers, the value of temperature showed that there are slightly different between all sampling points taken for both years 2014 and 2015 which were about the range of 25 to 35 ºC. The similar range of temperature also found in the study done by Hadibarata *et al*. [22]. While for the specific conductivity, in year 2014, SB2 showed the highest specific conductivity reading while for year 2015, SB3 showed the highest data for Sungai Balok. For Sungai Tunggak, the highest value of specific conductivity was taken from ST3. Here, specific conductivity means the capability of water in conducting electricity and it is closely related to dissolved ions content in river water [17].

The third water quality parameter taken in this study was pH. The pH was shown to be the most stable parameter. It is because the readings taken did not show drastic differences between all sampling points. Both Sungai Balok and Sungai Tunggak in this study recorded pH of about 5-9 for both years

TABLE-1
WATER QUALITY PARAMETERS AVERAGE READING FOR BALOK AND TUNGGAK RIVERS

Locations / Parameters	Year	SB 1	SB 2	SB 3	ST 1	ST 2	ST 3
Average temperature	2014	28.53	27.29	28.335	0	0	0
	2015	31.215	28.675	30.1516	27.24	29.746	30.428
Average specific conductivity	2014	0.044	22.66	12.74	0	0	0
	2015	20.339	9.104	46.426	0.0551	0.8930	53.241
Average pH	2014	5.365	7.965	8.16	0	0	0
	2015	7.1175	6.5416	8.0175	5.3675	7.8966	7.99000
Average turbidity	2014	52.5	104.75	42.4	0	0	0
	2015	171.36	34.341	67.0083	54.000	97.791	65.1500
Average dissolved oxygen	2014	5.125	4.81	5.945	0	0	0
	2015	2.9133	2.1391	3.02000	1.8358	2.3725	3.37333

2014 and 2015. This result is similar to the findings of pH reading in Danga river and Pendas river again as reported by Hadibarata *et al*. [22]. For turbidity, which is refers to the concentration of particulate matter suspended in river water, both Sungai Balok and Sungai Tunggak showed in this study recorded high turbidity for both years 2014 and 2015. The upstream area of Sungai Balok, SB1 showed the highest with 171.37 NTU for year 2015.

The concentration of dissolved oxygen in river discloses the total of supply of oxygen in the river water. The average of dissolved oxygen observed at Sungai Balok in year 2014 was very high as compared with the average of dissolved oxygen observed for both Sungai Balok and Sungai Tunggak in year 2015 mainly at sampling point SB3 with reading of 5.945 mg/L. However, this result is dissimilar to the findings of dissolved oxygen reading in Danga and Pendas rivers [22]. The study showed that dissolved oxygen trend was increase as the year increase. From the water quality parameters readings taken for both year 2014 and 2015, then their correlation test was study in order to know their relationship with the selected heavy metals and also the radioactive elements concentration in the river water.

Statistical differences in analysis of water quality parameters and selective heavy metals: Spearman correlation test was used to investigate the association between the water quality parameters and the concentration of selective heavy metals in both of Tunggak river and Balok river. Spearman correlation test was used to evaluate the relationship of monotonic between two ordinal or continuous variables. In a relationship of monotonic, the variables have a tendency to change together, but not necessarily at a constant rate. The heavy metals chosen were lead, cadmium and arsenic. However, for year 2014, only lead was selected to be analyze.

The correlation test was done by using SPSS. Table-2 showed the correlation between the water quality parameters and the concentration of heavy metals for both year 2014 and 2015. The results found that there is a strong, negative and significant relationship between lead and specific conductivity parameter ($p < 0.05$). However, for other water quality parameters tested, the result was found that there was weak and positive relationship ($p > 0.05$). In short, the relationship between dissolved oxygen (DO), pH, temperature and also the turbidity with the selected heavy metal, which is lead, were not significant.

The results shown for year 2015 for heavy metals found that there was a strong, negative and significant relationship between lead and all the water quality parameters, which is dissolved oxygen, pH, specific conductivity, temperature and turbidity ($p < 0.05$). The relationship between cadmium and all water quality parameters, which is dissolved oxygen, pH, specific conductivity, temperature, and turbidity also showed the same relationship too ($p < 0.05$).

However for arsenic, the different results showed by the correlation test. The reading found that there were weak, positive and not significant relationships with all the water quality parameters tested which are dissolved oxygen, pH, specific conductivity, temperature and turbidity. In short, in year 2015, there were significant relationships ($p < 0.05$) found between all water quality parameters and most heavy metals selected (lead and cadmium), except for arsenic.

Statistical differences in analysis of water quality parameters and selective radioactive elements: As one the objectives of this study is to investigate the association between the water quality parameters and the concentration of radioactive elements, Spearman correlation test by using SPSS was also used. The selective radioactive elements chosen in this study were thorium and uranium. The study regarding water quality parameters and selective radioactive elements were done for two consecutive years.

Table-3 showed the correlation between the water quality parameters and the concentration of selcted radioactive elements *viz*., thorium and uranium. For year 2014, the p-value for all the correlation is more than 0.05, which is a not significant relationship. The analysis showed that there is no association between all the water quality parameters selected and the level of concentration of dissolved oxygen, pH, specific conductivity, temperature and turbidity. It can also be concluded that for year 2015 for the radioactive elements of thorium, there was a strong, negative, significant relationship between thorium and all the water quality parameters, which is dissolved oxygen, pH, specific conductivity, temperature ($p < 0.05$) except with turbidity ($p > 0.05$). This means that any general conclusions drawn from this study needed to be tempered by the knowledge that thorium and all the water quality parameters were not independent except for the turbidity. However, the relationship between uranium and turbidity showed a strong, negative, significant relationship ($p < 0.05$) rather than other water quality parameters which is dissolved oxygen, pH, specific conductivity and temperature ($p > 0.05$).

To sum up, in year 2015, there were significant relationships ($p < 0.05$) found between most water quality parameters and thorium, except for uranium, which showed the contradictory result of analysis. This result was dissimilar to the finding by Lauria *et al.* [23]. They stated that there was a significant relation-

TABLE-2
CORRELATION BETWEEN WATER QUALITY PARAMETERS AND CONCENTRATION OF HEAVY METALS IN YEAR 2014 AND 2015

Physical parameters	Year 2014		Year 2015					
	Lead		Lead		Cadmium		Arsenic	
	r	p value	r	p value	r	p value	r	p value
Dissolved oxygen	0.935**	0.006	-0.829*	0.042	-0.886*	0.019	0.829*	0.042
pH	1.000**	0.000	-0.600	0.208	-0.600	0.208	0.600	0.208
Specific conductivity	-0.935**	0.006	-0.943**	0.005	-0.943**	0.005	0.943**	0.005
Temperature	0.806	0.053	-0.657	0.156	-0.886*	0.019	0.657	0.156
Turbidity	0.806	0.053	-0.029	0.957	-0.314	0.544	0.029	0.957

*Spearman's Correlation, p = 0.05, ($p < 0.05$ = significant)

TABLE-3
CORRELATION BETWEEN THE WATER QUALITY PARAMETERS AND THE CONCENTRATION OF RADIOACTIVE ELEMENTS IN THE YEAR 2014 AND 2015

Physical parameters	Year 2014				Year 2015			
	Thorium		Uranium		Thorium		Uranium	
	r	p value	r	p value	r	p value	r	p value
Dissolved oxygen	-0.564	0.322	0.000	1.000	-0.657	0.156	0.829*	0.042
pH	-0.872	0.054	-0.300	0.624	-0.771	0.072	0.714	0.111
Specific conductivity	-0.359	0.553	0.100	0.873	-0.600	0.208	0.943**	0.005
Temperature	-0.308	0.614	-0.200	0.747	-0.143	0.787	0.543	0.266
Turbidity	0.872	0.054	0.300	0.624	0.143	0.787	-0.086	0.872

*Spearman's Correlation, p = 0.05, (p < 0.05 = significant)

ship or correlation between uranium and specific conductivity of water.

Conclusion

In conclusion, there were significant relationships found between most of the water quality parameters and all radioactive and heavy metals, except for uranium and arsenic for year 2015. The characteristics between thorium and uranium were different and independent towards each other. However, for year 2014, the results of the correlation between radioactive materials and water quality parameters showed no relationship between them. All the significant correlations of elements detected are indicative of a common source of pollution in the rivers. The decreased water quality of rivers is generally due to the increase of diverse pollutants in the rivers. The examples of the pollutants involved were heavy metals and radioactive elements. The results obtained that the rivers water is not suitable for use as drinking water and can harm human health. Therefore, as the recommendation, the clean should be remediated first to get the clean water supply. Besides, periodically monitoring activity should be performed in the rivers. One of the effective ways is by clean and remediates from the point source and enforcement of law.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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