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Assessment of Physical-Chemical Water Quality Characteristics and Heavy Metals Content of Lower Johor River, Malaysia

Y.Q. Liang¹, K.V. Annammala^{1, 2*}, P. Martin³, E.L. Yong¹, L.S. Mazilamani¹, M.Z.M. Najib¹

¹Department of Water and Environmental Engineering, School of Civil Engineering, Universiti Teknologi Malaysia, Johor Bahru, Malaysia

²Centre of Environmental Sustainability & Water Security (IPASA), Universiti Teknologi Malaysia, Johor Bahru, Malaysia

³Asian School of the Environment, Nanyang Technological University, Singapore

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Abstract

Surface freshwater quality has received more attention in recent years, which is since fresh water is regarded as a limited resource and many threats can negatively affect the water quality. The expansion of urban pollution in the Johor River in Johor State, Malaysia, has been induced by different anthropogenic activities being carried out, which bring potential risks to freshwater quality. The aim of this study was to quantify the physical-chemical properties of water and heavy metal concentrations at 11 sampling sites (S 01-S 11) selected along the Johor River. Eight water quality parameters were determined, and nine heavy metals were determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). Findings revealed that total suspended solid concentration and pH of the water samples satisfied the Class II outlined in the National Water Quality Standards for Malaysia (NWQSM). Most of the ammonia concentrations satisfied the Class II except at stations S 01 to S 03. The nutrient concentration (nitrate, nitrite, and phosphate) were found quite low. On the other hand, the range of certain elements such as Fe (1.75 to 6.90 ppm), Cu (0.06 to 1.34 ppm), and As (0.01 to 0.29 ppm) was found to exceed the Class II standard at all stations. A strong relationship between TSS, As, and Cu concentrations was found, which may be due to Cu and As carried along the river by suspended sediments, coming from the anthropogenic sources into the catchment areas. The results indicated that the river water quality is extremely sensitive to the local land use and practices. Further detailed research into the concentration of the elements in storm water could be the next research focus.

Keywords: Water Quality, Heavy Metal, National Water Quality Standard in Malaysia, River Water

1 Introduction

Rivers ecosystems have received more attention in recent years due to their high economic value as food sources and their wide use for recreational purposes, nature tourism, etc. [1,2]. Freshwater is regarded as a limited resource whose retention is becoming a significant challenge due to the input of pollutant to its resources [3, 35]. The natural processes such as weathering, precipitation, soil erosion, etc. and anthropogenic processes such as agricultural, urban, and industrial activities are recognised as parameters affecting the water quality [3, 34]. Therefore, river water quality is recognised as one of the main issues, especially in developing countries due to the industrialization and economic growth [4, 1, 5]. Such countries, including Malaysia, where the rivers water is recognised as the main water resource, are supporting daily subsistence and multipurpose uses of water resources for local communities [6, 34, 35]. Rapid development causes the expansion of developing areas within river basins, which may increase the pollution loading into rivers [6, 7, 8]. Based on the river analysis in Malaysia, 150 out of 646 rivers in Peninsular Malaysia have been classified as slightly polluted and 39 rivers as polluted. Therefore, identification of the pollutants provenance and providing plans to manage the constantly polluted rivers are important measures [6].

Water quality degradation is often resulted from non-point source pollution; thus, it is hard to control [9]. The water quality in rivers is often influenced by sediment runoff, nutrient inputs, and other harmful chemical pollutants, which originate from land use activities around the catchment area [1]. Different kinds of pollutants enter rivers, which are resulted from different anthropogenic activities [1, 10]. Based on previous studies, the ammoniacal and nutrient input indicates untreated municipal sewage and fertiliser [6, 11]. The higher erosion rate, the higher total suspended solid (TSS) concentration is found in agriculture and urban areas [11]. The spatial variation of physiochemical parameters can be used to determine the pollution status of a river [1, 7, 35]. Physicochemical parameters include the physical parameters (e.g., TSS and temperature) and chemical parameters (e.g., dissolve oxygen (DO), pH, ammoniacal nitrogen (AN),

Corresponding author: K.V. Annammala, (a) Department of Water and Environmental Engineering, School of Civil Engineering, Universiti Teknologi Malaysia, Johor Bahru, Malaysia, and (b) Centre of Environmental Sustainability & Water Security (IPASA), Universiti Teknologi Malaysia, Johor Bahru, Malaysia. Email: kogila@utm.my.

nitrate, nitrite, and phosphate). Therefore, a reliable water quality evaluation is important as the scientific proof for the water resource management to control the pollution and develop better management and planning [12, 35].

The anthropogenic activities also cause the entrance of large amount of heavy metals into water system, which has been widespread and stated in many previous studies [13]. The heavy metal pollution, in comparison to other pollutions, is more alarming due to the non-biodegradable characteristic of heavy metal with bio-accumulative behaviour in the system [14, 34]. The excessive heavy metal forms through various processes and pathways, which include natural and anthropogenic sources [15]. Heavy metals are mainly released from anthropogenic sources, especially industrial activities, and mining [13, 16, 17, 34]. Therefore, the physicochemical parameter and heavy metals concentrations are measured to evaluate the water quality.

Many previous studies stated that inappropriate land use induces the deterioration of water quality [9]. Water quality evaluation is important to have effective management control and improve the water quality [3,6]. The Johor River is the main river in Johor State, Malaysia, which is the main freshwater resource in Johor State and for the neighbouring country, Singapore [18]. Based on previously conducted studies, the water quality index of the Johor River is ranged from 47 to 52 and fall into Class IV, which is only suitable for irrigation purposes. There are various anthropogenic activities, including industrial and sand mining activities, along the Johor River, and the end of the estuarine is close to Singapore. Thus, the water quality of the Johor River is of regional concerning interest to control the water pollution and to secure the water supply and quality control to be safe for both countries [19, 40].

The main purpose of this study was to quantify the physical-chemical water quality characteristics and heavy metals concentrations at 11 sampling sites (Figure 1) along the Johor River and to determine the current quality of the river system. Therefore, the objectives of this study are: 1) To compare the water quality status and concentration of heavy metals in the Johor River based on Class II outlined in the National Water Quality Standards for Malaysia (NWQSM), and 2) To study the relationship between the water quality and heavy metals concentration in the Johor River in relation to major land uses within the catchment area. The selection of the Class II outline in NWQSM for comparison purposes was because there are villages confined within the system, such as kampong Berangan where the river is used for recreational purposes.

2 Materials and Methods

2.1 Study Area

The study area selected for the present research is the Johor River basin located in Johor, Peninsular Malaysia (Figure 1). The catchment area is around $2636~\mathrm{km^2}$ and the mainstream length is around $122.7~\mathrm{km}$ [20]. The tributaries of the Johor River include the Seluyut River, Sengi River, Redan River, Temon River, and Tiram River. The mean discharge rate of the Johor River is $37.5~\mathrm{m^3/s}$. The annual mean rainfall intensity in this region is about $2360~\mathrm{mm}$, with mean temperature is around $27~\mathrm{^{\circ}C}$.

2.2 Sampling Collection and Analysis

As mentioned earlier, 11 water sampling stations were selected along the Johor River (Figure 1). 6 out of 11 sampling stations were at the mainstream of the Johor River and the other

5 stations were at the selected tributaries of the river. There were different types of land uses along the river. The site description and the coordinate of the sampling points are summarized in Table 1.

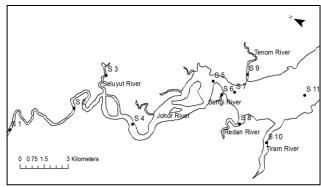


Figure 1: Study area and the water sampling stations of the Johor River

Table 1: The coordinates and the descriptions of the sampling stations

Sampling Coordinate of the Sampline Station										
Station		Coordinate of the	e Sampling Station							
	Name of the river	Latitude	Longitude	Site Description						
S 01	Johor River	1° 38' 4.4874"N		Kota Tinggi Town, located in the upstream, mainly consisting of industrial areas						
S 02	Johor River		103° 53′ 58.5954″E	Plantation						
S 03	Seluyut River	11 0 017 20 1 11	103° 55' 32.0874"E	Sand mining, Oil Palm Plantation						
S 11/1	Johor River	1° 41' 23.1354"N	103° 56' 55.968"E	Oil Palm Plantation						
	Johor River	1° 39' 55.4394"N	103° 55' 53.8674"E	Pulau Dendang, Oil Palm Plantation, Surrounded with mangrove and nipah trees						
S 06	Sengi River	1° 35' 3.9114"N	103° 59' 14.1714"E	Oil Palm Plantation						
S 07	Johor River	1° 35' 34.4034"N	103° 57' 17.5314"E	Downstream, Village						
S 08	Redan River	1° 37' 15.132"N	103° 58' 17.4"E	Oil Palm Plantation						
N 119	Temon River	1° 37' 6.24"N	103° 59' 1.032"E	Village, Urban area, Oil palm plantation						
N 10	Tiram River	1° 36' 58.32"N		Sand mining, Small restaurants close to the riverbank, Oil Palm Plantation						
IS 11	Johor River	1° 37' 37.1994"N	103° 58' 2.1"E	Village, Oil Palm Plantation						

Surface water samples were collected in pre-cleaned bottles from the eleven sampling stations. Three physicochemical properties of water (temperature, salinity, and pH) were determined on site by in-situ water quality checker (Horiba U-50 multi-parameter checker). Water samples for dissolved inorganic nutrient concentrations (nitrate, nitrite, phosphate, and ammonia) were syringe-filtered (0.2 µm pore-size Acrodisc filters) into polypropylene centrifuge tubes, frozen in a liquid nitrogen dry shipper in the field, and stored at -20 °C until analysis on a SEAL AA3 segmented-flow auto-analyser system using SEAL methods for seawater analysis. Concentrations for all nutrients were measured in µmol/L and converted into mg/L. For total suspended solid (TSS) measurements, 1 L of surface river water was

collected from each station and filtered through a pre-weighed 25-mm diameter Whatman GF/F filter and stored at -20 °C until sent to the laboratory. Samples were dried for 24 h at 75 °C and re-weighed on a Mettler-Toledo microbalance, and were expressed in mg/L. A total of 11 surface water samples were collected and preserved from the sampling stations to measure and analyse the heavy metals concentration. The water samples were digested by following the standard methods APHA 3030K Microwave-Assisted Digested and were analysed by ICP-MS following the standard methods of APHA 3120B. Nine most-commonly reported heavy metal elements, namely iron (Fe), copper (Cu), arsenic (As), manganese (Mn), silver (Ag), zinc (Zn), nickel (Ni), lead (Pb), and chromium (Cr) were selected, analysed, and presented in this paper (Wuana & Okieimen, 2011).

Correlation coefficient (r) is a statistical analysis of the interdependence of two or more random variables [14]. The correlation coefficients for all the water parameters were calculated to determine the relationship between the physiochemical water quality parameter and heavy metals concentrations.

3 Results and Discussion

The results of the physicochemical parameter of water samples were presented in Figure 2. The physicochemical water parameters considered in this study included temperature, salinity, pH, TSS, phosphate, nitrite, nitrate, and ammonia concentration. Figure 2 (a) shows the temperature of the river water samples. The temperature range of the water samples was between 28.3 to 30.2 °C, which satisfied the Class II outlined in the NWQSM (normal +2 °C). Figure 2 (b) presents the salinity of the river water increased down the river from 0.5 mg/L to 26.8 mg/L. The river flows in a roughly north-south direction end out with the sea water. The saltwater intrusion might cause the salinity of the downstream water to be higher than the upstream. The pH range of the water samples was between 6.8 and 7.5 within the range for the Class II (6 to 9). The TSS concentrations were still acceptable for the Class II. The ammonia concentration guidelines for the Class II is 0.3 mg/L, where stations S 01 to S 03 exceeded the threshold level whereas the other stations were still within the acceptable limit, ranged from below the detection limit (BDL) to 0.3 mg/L. The highest ammonia concentration was found in station S 01 (3.93 mg/L). The level observed herein was slightly higher compared to the average concentration obtained by Yusop et al. (2017) who sampled the water in Kota Tinggi town (2.86 mg/L) [8]. It is tentatively hypothesised that it originates from Kota Tinggi town because the high ammonia concentration was found in Kota Tinggi town [8]. The present study showed a lower nitrate concentration (less than 7 mg/L), which satisfied the Class II. The nitrite concentrations ranged from 0.11 to 1.19 mg/L exceeded the acceptable threshold of 0.04 mg/L. This might be since nitrite is in an unstable state in the oxidation of ammonia to nitrate [21]: therefore, the nitrite concentration increased as the ammonia concentration decreased in Figure 2 (f) and (h). However, the nitrate and nitrite concentrations were still considered quite low. The phosphate concentrations satisfied the Class II with the acceptable threshold of 0.2 mg/L. The nutrient concentrations (nitrate, nitrite, and phosphate) in the Johor River were considered quite low and no significant nutrient pollution was found in this study.

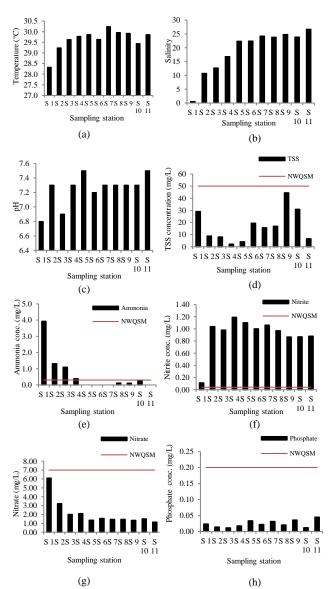


Figure 2: The physicochemical parameters of water samples collected from the Johor River: (a) temperature, (b) salinity, (c) pH, (d) TSS, (e) ammonia, (f) nitrite, (g) nitrate, and (h) phosphate

Heavy metals reviewed in this paper included some significant metals such as Fe, Cu, As, Mn, Ag, Zn, Ni, Pb, and Cr. The selected heavy metal concentrations of the sampling stations were determined and showed in Figure 3. The heavy metal concentrations of iron (Fe) and copper (Cu) of all sampling stations were found to be exceeding the Class II, like arsenic (As) concentration at all sampling stations except S 02. The detected Fe concentrations ranged from 1.75 to 6.9 ppm, which is more than the allowable limit of 1 ppm. The Cu concentrations ranged from 0.06 to 1.34 ppm, also exceeding the acceptable threshold of 0.02 ppm. As concentrations were found ranging from 0.01 to 0.29 ppm, which is more than the limit allowed in the guidelines (0.05 mg/L).

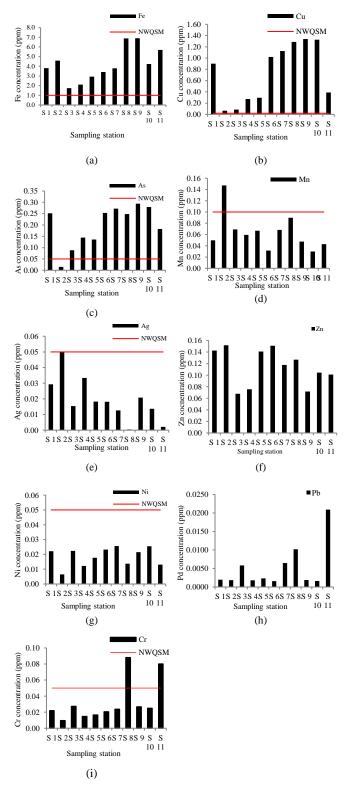


Figure 3: The heavy metal elements concentration in surface water of the sampling stations: (a) Fe, (b) Cu, (c) As, (d) Mn, (e) Ag, (f) Zn, (g) Ni, (h) Pb, and (i) Cr

Based on Figure 3, the highest Fe, Cu, and As concentrations

were detected at S 09 with 6.9, 1.34, and 0.29 ppm, respectively. Fe has been reported to be present in significant amount in both soil and rock [22]. High Cu concentration might be due to fertilizing activities because Cu is one of the micronutrients for oil palm cultivation and also it is the main composition of chemical fertilizers [23, 24]. Based on previous studies, the input of arsenical herbicides and insecticide could contribute to As traces in receiving river system [25, 26]. There are about 172 common herbicides brands in Malaysia, which are glyphosphate-based herbicides, containing Arsenic [27, 28, 29]. Therefore, Fe, Cu, and As were hypothesized to originate from oil palm plantation area adjacent to S 09.

Manganese (Mn) and silver (Ag) concentrations from most of the stations were less than the Class II (0.1 and 0.05, respectively) except at S 02 where the concentrations were 0.15 and 0.05 ppm, respectively. Mn is commonly found in rocks and sediments, which is transported into water through surface runoff [30]. Tesi et al. (2019) and Ako et al. (2014) stated that the Mn and Ag concentrations could be influenced by the sand mining as observed to be present at this sampling site [31, 32]. This could be concluded that the large amount of Mg and Ag are highly possible to be related to the sand mining activities around S 02.

The Ag, Zn, Ni, and Pb concentrations from all sampling stations were below the Class II. Based on NWQSM, these concentrations are not significant pollution source for water resources. Chromium concentrations from most of the stations were less than the Class II outlined in the NWOSM except at stations S 08 and S 11 (which were recorded as 0.09 and 0.08 ppm, respectively). According to literature, the chromium concentrations commonly come from anthropogenic sources, especially industrial waste produced by the production of corrosion inhibitors and pigments [21, 33]. Stations S 08 and S 11 are surrounded with oil palm plantation, but there is not any previously conducted study showing a relationship between the oil palm plantation and the chromium concentration. Thus, further studies are needed to determine the source of chromium concentration.

The correlation between the physicochemical parameter and the heavy metal concentration was calculated and presented in Table 2. A significant correlation was observed in the change of several heavy metal concentration with TSS concentration.

Table 2: The correlation coefficient between physicochemical parameters and heavy metal concentrations.

	Temp	Salinity	pН	TSS	Nitrite	Phosphate	Ammonia	Nitr
Cr	0.30	0.42	0.26	-0.06	-0.04	0.36	-0.25	-0.
Mn	-0.04	-0.31	0.06	-0.38	0.25	-0.29	0.13	0.
Fe	0.17	0.40	0.35	*0.52	-0.16	0.43	-0.19	-0.
Ni	0.00	0.12	-0.37	*0.54	-0.28	0.00	0.02	-0.
Cu	0.11	0.37	-0.01	**0.80	-0.27	0.12	-0.14	-0.
Zn	-0.36	-0.22	0.05	-0.10	-0.22	-0.01	0.25	0.
As	0.11	0.38	-0.02	**0.73	-0.34	0.30	-0.12	-0.
Ag	** -0.51	*-0.65	-0.24	-0.07	-0.06	-0.40	0.47	*0.
Pb	0.34	0.39	0.33	-0.31	0.04	*0.55	-0.26	-0.
Pb	0.34		0.33					

^{**} very strong correlation

* strong correlation

The correlations between Ag concentration with temperature

and salinity were -0.51 and -0.65, respectively, which indicates a negative significant relationship. The correlation between the Ag concentration and nitrate concentration was 0.55, which indicates a positive significant relationship. Both Pb and phosphate concentrations were 0.55, which indicates a positive significant relationship.

A very strong relationship was found between TSS concentration and Cu and As (with correlation coefficient of 0.8 and 0.73, respectively). The correlation between Fe and Ni concentrations and TSS concentration were 0.52 and 0.54, respectively, which is considered a strong correlation. The heavy metals are carried along with organic load and/or sediment [14]. Therefore, this is probably due to the suspended sediment brought along the Cu, As, Fe, and Ni into the channel through surface runoff. The highest concentrations of TSS, Cu, and As were found in SC 9; this can support the predictive statement that the surface sediment carries heavy metals from anthropogenic sources into the river water.

4 Conclusion

The present study conducted the physicochemical water quality evaluation and heavy metal analysis on the selected tributaries and main rivers in the Johor River flowing through the Johor State in Malaysia. Findings revealed that temperature, TSS concentration, and pH of the water samples satisfied the Class II outlined in the NWQSM. Most of ammonia concentrations were within the acceptable limit except at stations S01 to S 03. The phosphate, nitrate, and nitrite concentrations were considered quite low with no significant pollution to the river.

The range of certain elements such as Fe (1.75 to 6.90 ppm), Cu (0.06 to 1.34 ppm), and As (0.01 to 0.29 ppm) were found to be exceeding the Class II standard at all stations. The highest Fe, Cu, and As concentrations were found from S 09 (Tenom River), which is mainly dominated by oil palm plantation areas. Most of the heavy metal's concentrations showed that the most possible sources of heavy metals are non-point source run-off from anthropogenic sources. A strong positive relationship between Fe, Ni, As, and Cu with TSS concentration was detected, which can be due to the heavy metals being carried by suspended sediments into adjacent water body. To conclude with, proper execution of erosion and sediment control plans could protect the river health from further deteriorating impacts. Further detailed research into the concentration of the elements induced by storm water could be the next research focus.

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Ethical issue

Authors are aware of, and comply with, best practice in publication ethics specifically with regard to authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that there is no conflict of interest that would prejudice the impartiality of this scientific work.

Authors' contribution

K.V. Annammala, P.Martin and M.Z.M. Najib collected the samples and carried out the experiment. Y.Q. Liang wrote the manuscript with support from K.V. Annammala, E.L. Yong and L.S. Mazilamani. All the authors provided critical feedback to improve the manuscript.

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