Sains Malaysiana 49(4)(2020): 729-742
http://dx.doi.org/10.17576/jsm-2020-4904-02

Baseline Study of Heavy Metal Pollution in a Tropical River in a Developing Country

(Kajian Peringkat Dasar Pencemaran Logam Berat di Sungai Tropika di Negara Membangun)

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ABSTRACT

Massive load of toxic heavy metals is discharged by human activities, as well as by natural actions, give rise to metal contamination in water body. Sg. Sembilang is one of the rivers that is receiving effluent from various sources such as landfill, industrial, residential, and agricultural runoff. In this study, the concentration of heavy metals in nine stations along the Sg. Sembilang was collected for one year period to evaluate their levels of pollution. Ten heavy metals were analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES). The mean concentrations of Fe, Mn, Zn, Al, and Cu were 3.01, 0.68, 0.29, 0.007, and 0.027 mg/L respectively, were below the National Water Quality Standards of Malaysia (NWQS), with the exception of Cd, Cr, Pb, Mg, and Ni. Calculated HPI based on the mean concentration of heavy metals, was found to be 6.05, that is below the critical pollution index value of 100. With respect to sampling locations, station J03 registered the highest value of 7.989. This is probably due to the location of J03 which is very near to the effluent discharge point. The analysis indicates the present scenario of water quality of Sg. Sembilang due to the effect of effluent from the landfill material, and waste water from industry, agricultural runoff and residential area. Required steps should be taken to conserve this river from pollution, and also to lessen the environmental risk.

Keywords: Heavy metals; Heavy Metal Pollution Index (HPI); river water quality; water quality

ABSTRAK

Jumlah logam berat toksik yang dilepaskan hasil daripada aktiviti manusia, serta proses semula jadi telah menyebabkan pencemaran logam dalam badan air. Dalam kajian ini, kepekatan logam berat di sembilan stesen pensampelan di sepanjang Sg. Sembilang telah dikumpulkan selama satu tahun untuk menilai tahap pencemaran di setiap stesen. Sepuluh logam berat dianalisis menggunakan spektroskopi pelepasan optik plasma (ICP-OES) yang digabungkan secara induktif. Hasil menunjukkan kadar kepekatan Fe, Mn, Zn, Al dan Cu masing-masing ialah 3.01, 0.68, 0.29, 0.007 dan 0.027 mg/L di bawah Piawaian Kualiti Air Negara Malaysia (NWQS), kecuali Cd, Cr, Pb, Mg dan Ni. Berdasarkan kepekatan logam berat, nilai HPI didapati berada pada tahap 6.05 iaitu di bawah nilai indeks pencemaran kritikal, 100. Manakala berdasarkan dengan lokasi persampelan, stesen J03 mencatatkan nilai tertinggi 7.989. Ini disebabkan lokasi J03 yang sangat dekat dengan titik pelepasan efluen. Analisis ini menunjukkan senario kualiti air Sg. Sembilang kesan daripada efluen daripada bahan pelupusan sampah dan air sisa daripada industri, larian pertanian dan kawasan kediaman. Pelbagai langkah perlu diambil untuk memulihara sungai ini daripada pencemaran dan juga untuk mengurangkan risiko alam sekitar.

Kata kunci: Indeks Pencemaran Logam Berat (HPI); kualiti air; kualiti air sungai; logam berat

Introduction

River pollution is a crucial and emerging issue in most developing countries today. The amount of waste disposed of in surface water systems has increased due to massive industrial development (Naji et al. 2010). One of the main sources of environmental toxicity is the industrial waste and sewage entering the rivers and streams, putting Aquaculture and Water Quality at risk (Wu et al. 2016). Water quality is vital to mankind as it is directly related to human well - being. The main pollutants in water include the volatile organic compounds, biodegradable and recalcitrants, heavy metals, plant nutrients, suspended solids, microbial pathogens, and parasites (Ayandiran et al. 2018; Panfili et al. 2017; Wang et al. 2013). Heavy metals among the pollutants are seriously affected by the fact that they build up through the food chain and create environmental issues. Higher heavy metal concentrations can lead to damaging complex compounds that critical impact various biological processes (Ali et al. 2016; Bhuyan et al. 2017; Irzon et al. 2018). The existence of heavy metals in industrial wastewater is a significant risk to aquatic ecosystems, animals and humans. Higher concentrations of heavy metals often pose a significant threat to biota and the environment of any ecosystem (Tang et al. 2016; Xu et al. 2017). Heavy metal pollution can be a much more serious issue because they cannot be degraded by natural processes and continue to exist in soil and sediment from where they are rapidly released as sinks into watercourses (Paul et al. 2017; Xu et al. 2017). Heavy metals are generated mostly from natural and human activity sources and can accumulate in sediments, with serious environmental consequences both for local communities and for the quality of the river. The term 'heavy metals' refers to the group of metals and metalloids with a fairly high atomic weight and a specific gravity of ≤5cm3 (Aghoghovwia et al. 2018; Paul et al. 2017; Rosli et al. 201; Wu et al. 2017; Xu et al. 20178). Due to their persistence, bioaccumulation and high toxicity, heavy metal pollutants of all different kinds have gotten a lot of attention in recent years (Bukar et al. 2016). Some heavy metals including chromium, nickel, iron, zinc, copper, and manganese are vital for biological systems in the human body that acts as both structural and catalytic components of proteins and enzymes; while others including cadmium, mercury, lead, and arsenic are widely known to be extremely toxic and contain carcinogenic metalloids which can lead to cancer in the skin, lungs and urinary tract (Rajeshkumar et al. 2018; Shaari et al. 2016). Essential heavy metals, but again, become harmful when their concentration exceeds acceptable limits and toxic metals are extremely toxic though at low doses (Aghoghovwia et al. 2018; Chen et al. 2018; Gafur et al. 2018).

Heavy metal contamination is not a modern phenomenon that arises from industrial development that started whenever people began to process ores. Since then, the use of metals and their environmental effects have sped up, with a significant increase (Gao 2018). Most heavy metals exist in different sources into the river, which can be either natural by degradation and corrosion or anthropogenic (Nguyen et al. 2016; Paul et al. 2017). Metal concentrations differ in the natural environment, both within and between different types of rock. In the surrounding environment, weathering and erosion processes release metals. Human resources relate primarily to agriculture, transportation and industrial activities (Irzon et al. 2018; Meng et al. 2016; Wang et al. 2017). Industries that ascribe heavy metals to river water typically include metal industries, paints, pigments, varnishes, pulp and paper, tannery, distillery, rayon, cotton textiles, rubber, thermal power plants, steel plants, galvanization of iron products and mining industries and also the unsystematic use of pesticides and fertilizers in agricultural fields (Paul et al. 2017). Due to its toxicity, persistence and bioaccumulative nature, the prevalent contamination of the river by heavy metal ions is of great concern. This type of heavy metal pollution can result in major risks to public health through the food chain, particularly from drinking water, which can damage the entire biological environment (Fawaz et al. 2016; Singh & Kumar 2017; Zhang et al. 2016). In recent years, heavy metal pollution has occurred in several countries. Heavy metal concentrations in many other famous rivers' water is higher than the regulations. Additionally, pollution is so much more severe in many small rivers (Kandler et al. 2017).

In correlation with government growth policies, Malaysia is currently experiencing a neverending rapid change in land use. Among Malaysia's states, Selangor was the fastest growing and heavily populated state with 3.9 million residents in 2000. The land used for agriculture in Selangor has widened as oil palm plantations have increased. Industrialization policy has led directly to state developments in urbanization, trade, and infrastructure. The increase in land used for both urban and agricultural sectors has led to natural and wetland forest clearing. Modifications in rapid land use have been shown to cause drastic environmental deterioration in various environmental compartments such as forests, wetlands, and aquatic ecosystems. The riverine ecosystem in Malaysia is of particular relevance as the river supplies about 98 percent of the country's water requirements. River water pollution therefore poses a genuine public health risk. The monitoring of river water quality is under the liability of the Department of Environment (DOE), Malaysia (Harguinteguy et al. 2016). Heavy Metal Pollution Index (HPI) has been broadly applied by various researchers for the comparative assessment of metal contamination adjacent current water quality guidelines (Majhi & Biswal 2016). Over the year, there have been numerous studies on heavy metal content in rivers in Malaysia including Sg. Baleh in Sarawak (Chai et al. 2018), Sg. Langat Basin, Selangor (Kadhum et al. 2015), Sg. Kepayang, Perak (Affandi & Ishak 2018), Sg. Linggi, Negeri Sembilan (Khalaf et al. 2018), Sg. Selangor, Selangor (Othman et al. 2018), Sg. Terengganu, Terengganu (Sukri et al. 2018) as well as Sg. Liwagu and Sg. Mansahaban in Sabah (Tair & Eduin 2018). However, until now there is limited information on heavy metal content in Sg. Sembilang, Kuala Selangor, Selangor which received various pollutants from upstream to downstream of the river. The purpose of this study was to analyze the metal concentrations in the Sg. Sembilang from ten different locations along the river. The river water samples were analyzed to investigate the concentrations of ten heavy metals: aluminium (Al), magnesium (Mg), manganese (Mn), copper (Cu), iron (Fe), nickel (Ni), chromium (Cr), cadmium (Cd), lead (Pb) and zinc (Zn).

Materials and Methods

STUDY AREA

The study area is Sg. Sembilang, lies in Sg. Selangor basin, located within Kuala Selangor, Selangor, Malaysia. The catchment area is about 633.79 m3s-1. The river length is approximately 7840 m long and 16 m wide and generally lie in the longitude-latitude quadrangle of 101.37E, 3.19N and 101.30E, 3.19N. There are a number of catchment areas located along the Sg. Sembilang that includes Ladang Bukit Panjong, Ladang Athlone, Ladang Choh, Ladang Jeram and Ladang Bukit Cherakah.

The economy of Sg. Sembilang is based predominantly on agriculture (palm oil plantation) and primary industries. At the upstream of the river lies Jeram Sanitary Landfill which has been built since 1997. Along the river from upstream until before the downstream is covered with palm oil plantation, and there is also a small residential area with a population of around 9500 people. Other than that, there is a small industrial area in downstream of the river which is a factory that process rubber, plastic and timber. At the same time, however, this river is also a major source of income for local people, namely fisheries and aquaculture activities. In addition, Pantai Remis, located in the downstream river, is also a major tourist destination in Kuala Selangor, Selangor. Located south of the river is the tourist attraction and place for seafood enthusiast, Pantai Remis (Figure 1).

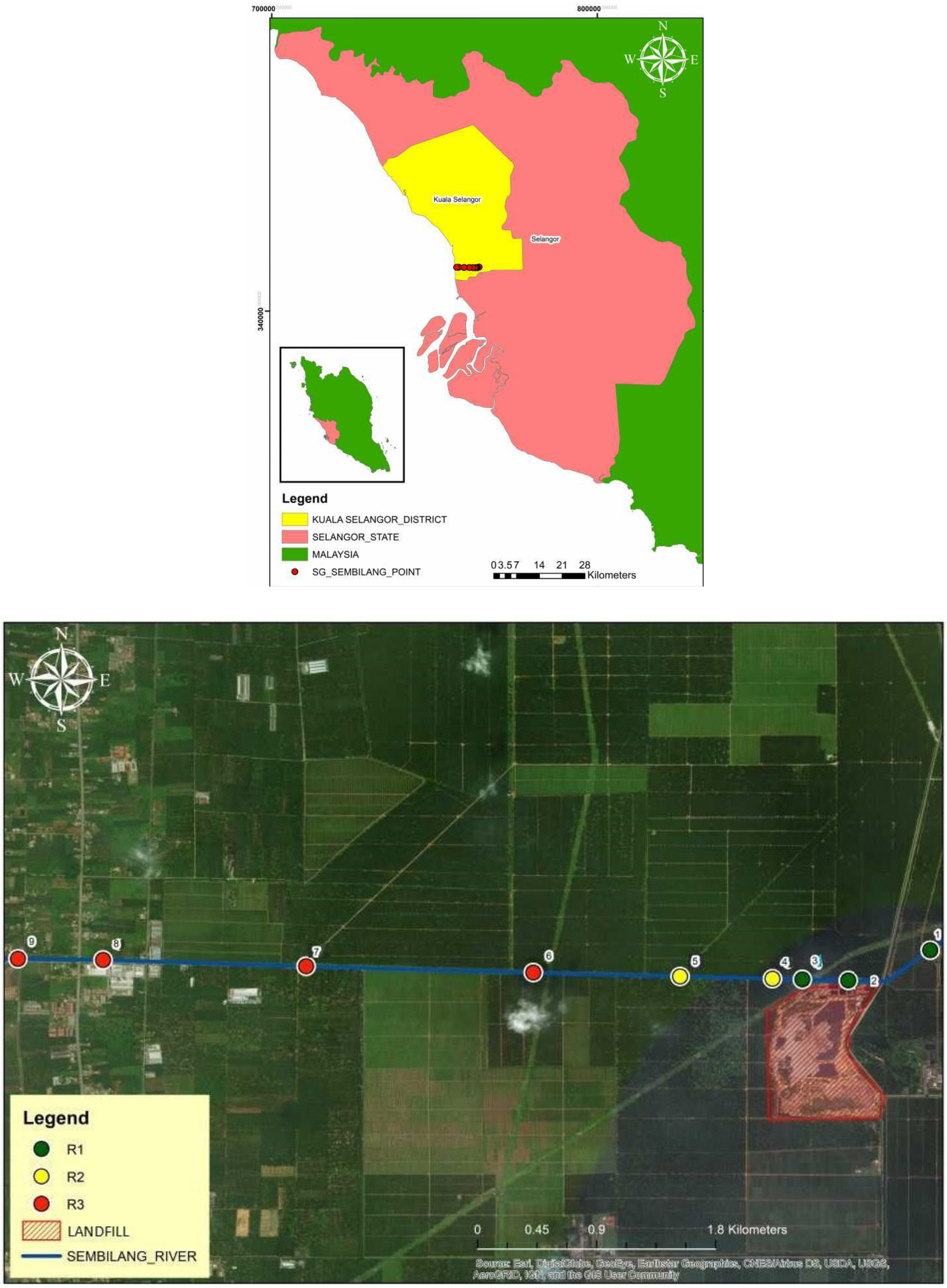


FIGURE 1. Study area and motoring stations locations

DATA COLLECTION

Water quality sampling was conducted to know the present water quality of Sg. Sembilang. Water samples were collected from 9 sampling stations every two months from September 2015 to September 2016. The distance of Sg. Sembilang is approximately 7 km. The samples were analyzed and the results were recorded. To reach each of the sampling stations, it was necessary to drive using vehicles that were capable of traversing muddy terrain and broken tracks. Locations of the sampling stations are presented in Table 1.

TABLE 1. Location point of study area

Location Point	Status	Coordinate		Remarks
		Latitude (Deg.)	Longitude (Deg.)	
J01	Upstream	3.196	101.373	Sg Sembilang Upstream
J02		3.194	101.370	500 m from landfill area
J03	Downstream	3.194	101.360	Downstream of Sembilang River
J04		3.194	101.353	Palm oil plantation site
J05		3.195	101.330	School/small residential area
J06		3.195	101.326	Factories
J07		3.195	101.320	Industrial zone
J08		3.195	101.315	Highway culvert
J09		3.195	101.311	1 km to the sea

HEAVY METAL ANALYSIS

Water The preparation of the samples was completed after USEPA-2007. 20 mL of each sample was placed in a 50 mL centrifuge tube before adding 0.4 mL of nitric acid (1 + 1) to the samples. The centrifuge tubes are then placed for 2 h in a water bath at 85 °C. In order to cool down the solution until it reached room temperature, the centrifuge tubes were then removed from the water bath. Water samples are then filtered using a syringe filtration unit using a 0.45 µm cellulose acetate membrane filter. This was done to obtain dissolved metal while preventing the spectrometry instrument from being blocked during analysis. A sample of quality control (QC) was also prepared to monitor recovery according to the guidelines of USEPA-2010. The reproducibility and recovery of metal analysis in water samples increased with adequate quantities of metals.

Digested samples were examined by an ICP - optical atomic emission spectrometry to most metal concentrations. For this evaluation of water quality, total dissolved elements and main ions concentrations which were analyzed, includes: aluminium (Al), magnesium (Mg), manganese (Mn), copper (Cu), iron (Fe), nickel (Ni), chromium (Cr), cadmium (Cd), lead (Pb), and zinc (Zn). ICP multi-element standard solution was used as the standard solution. To float the calibration curves, five standards were examined. The wavelengths and the corresponding detection limit (LOD) of each component, including the quantitative limit. The statistical variances between the sampling stations were conducted at a significant $p<0.05$ level using the Kruskal - Wallis test. The Tukey's test was used to compare the mean values. Environmental risk assessment was performed by equating the index of heavy metal pollution (HPI) in the area of study. The HPI has been obtained using (1)

$$HPI = \sum QiWi \qquad (1)$$

where Wi is the score weight for each parameter preferred for heavy metal assessment and is directly related to the suggested standard, i.e. the highest allowable amount for heavy metals' drinking water (Si). The rating is a value between zero and one. Qi, is the Subindex of the i^{th} parameter and was calculated using (2).

$$Qi = \frac{(Mi - Ii) \times 100}{(Si - Ii)} \qquad (2)$$

where Mi is the measured value of the i^{th} parameter; Ii is the desired maximum value (ideal) of the i^{th} parameter; and Si is the suggested i^{th} parameter standard. The crucial index of pollution is 100. The Si and Ii values have been taken from the Malaysian national water quality standard for the current study.

RESULTS AND DISCUSSION

The heavy metal of river water samples was collected and analyzed based on their concentration. Prior to the data analysis, data were first checking for normality and analysis shows that all data is not distributed normally among the sampling point. Hence, this analysis adopts Kruskal-Wallies test, that is a non-parametric test. From the Kruskal-Wallies test, only Mg showed significant difference among the stations with p value of 0.007. This indicates a fairly strong relationship between concentration of Mg and sampling point along the river. Follow up tests were run to calculate pairwise differences among sampling stations. The outcome of these tests indicates a significant difference between sampling stations.

Large quantities of heavy metals deteriorate the aquatic environment causing a momentous challenge and exposure to human health and environment. The concentrations of Aluminum (Al), Magnesium (Mg), Manganese (Mn), Copper (Cu), Iron (Fe), Zinc (Zn), Cadmium (Cd), Nickel (Ni), Chromium (Cr), and Lead (Pb) were analyzed. The results of heavy metal concentrations in surface waters of Sg. Sembilang are shown in Table 2 and Figure 2. The average concentration of studied metals in water followed a decreasing order of Mg> Al> Fe> Mn> Zn> Cu> Ni> Cr> Pb> Cd. Only the higher value of heavy metal from standard level are further elaborated.

Al concentration in water samples from Sg. Sembilang ranged from 0.0736 to 23.16 mg/L with a mean of 5.862 ± 2.111 mg/L (Table 2). Mean Al levels in study area were above National Water Quality Standard (NWQS) permissible limit of 0.06 mg/L for raw water. Earlier study conducted at Sg. Sembilang reported Al concentrations that ranged from 0.48 to 1.5 mg/L (Bhuyan et al. 2017). The existence of aluminum ions in river water due to the landfill waste. As the effluent from the landfill is disposed near to J03, the value increases to the max value at station J03 with average value of 8.9338 mg/L that was exceeded the permissible limit (0.06 mg/L) of NWQS. After that, the average value decreases up to the station J09 with Al concentration 2.9584 mg/l.

Leaching of Al to rivers can be reduced by modern, controlled farmland drainage techniques (Sutela & Vehanen 2017). Al concentration in surface water differ with pH of the water. High levels of Al in natural water only occur when the pH is below 5. The concentration in most surface water is very low because the pH of approximately 95% of natural water ranges from 6 to 9 (Zuziak & Jakubowska 2017). This is the same as Al concentration in Sg. Sembilang where at pH in the range of 6.573 - 3.832, Al concentration increases from J01 to J05 and it decreases to J09 where the pH of the river in this area is increasing. Study also found that Al concentrations in coastal area typically range from 0.5 to 2 µg/L and 0.008 to 0.68 µg/L in the open ocean. This is impressive given that many coastal sites are signatory to point source or diffuse Al inputs including urban runoff and general industrial inputs and also atmospheric aluminum deposition into surface water discharges associated with Al and Al production activities (Angel et al. 2015). This can be illustrated by the concentration of Al at J09 with 2.983 mg/L where the station is located a few meters from the coastal area of Pantai Remis. The Al concentration at this station is the lowest compared to the other nine stations.

In most forms of life, copper (Cu) is an essential component. However, Cu may become harmful at high bioavailable concentrations. With its use in industry and agriculture (e.g. Cu consist of fungicides and herbicides), Cu leaked into the environment from these sources is substantial (Bui et al. 2016). In the environment, Cu's fate depends on changes in physical and chemical speciation properties (pH, redox, ionic strength) and relationships with environmental components (mineral or organic particles) (Guinoiseau et al. 2018). The concentration of Cu was greater than 0.02 mg/L, indicating Class-V in National Water Quality Standards of Malaysia. Cu can occur in all three possible forms, i.e. dissolved, colloidal and particulate, in freshwater systems (Borah et al. 2018). In the present study, Cu content ranged from 0.0198 - 0.131 mg/L (Table 2). At J01, that is located at the upstream of the river, Cu content was high and may be due to the soil, agriculture and geological formations. The high content of Cu might be due to the increase in temperature, which increases the release of Cu ions from the sediments and thus rises the total content of Cu in the water column (Zhang et al. 2018). Cu was lowest at J09 with a value of 0.0198 mg/L. The result shows that the concentration of dispersion varies due to several factor affected on upstream, landfill and downstream stations. The upstream station may be affected by soil, agricultural and geological formation, while the landfill and downstream stations may be affected by effluent and industrial factors.

Mn is typical elements in the earth's crust and can be discovered in a length of minerals in rocks and soils (Essington 2015). Mn is extremely responsive to redox environment and somewhat mobile in the aquatic environment and dictate at lower pH (Fremion et al. 2016). The concentrations of Mn vary from station to station along the river. The results show that all stations exhibit more than 0.2 mg/L of Mn concentration that represent Class V of NWQS of Malaysia. The concentrations of Mn ranged between 0.015 and 1.685 mg/L. These concentrations of Mn increased gradually from J01 to J05, then decreased at J07 and J08. After the landfill station, the values increase at downstream stations. The distribution of the concentration is not caused by the landfill effect, it might be from other sources such as soil and agricultural patterns for the upstream stations and industrial effect for the downstream stations of Sg. Sembilang. Mn do not necessarily pose a health risk to humans (Nguyen et al. 2016). Mn can be assimilated by aquatic organisms mainly under its ionic form Mn2+, as an essential nutrient at low concentrations. However, it can be harmful to aquatic biota as a toxic element with LC50 (Lethal Concentrations) in the mg/L order of magnitude. It is important to note that the chronic criteria for the safety of aquatic biota is normally range from 1 to 2 mg/L. However, at high concentration, Mn can also present as a protection facing more toxic substances (Superville et al. 2018).

Natural waters encompass differential quantities of iron confide on different criteria. The main elements of interest in the aquatic environment are ferrous and ferric ions. Fe normally occurs in fresh water bodies in either soluble ferrous ion (Fe2 +) or insoluble ion (Fe3 +) (Sarkar & Shekhar 2018). The analysis for ten river water samples showed Fe concentration in all ten stations beyond the permissible limit of NWQS (1 mg/L). The Fe concentration in these samples ranged from 1.667 to 4.623 mg/L (Table 2). Figure 2 for mean Fe concentration in samples taken obtained from the study area illustrates the fact that most of the study area high Fe concentration in surface water (more than 1 mg/L) with the highest Fe concentration site situated downstream of Sg. Sembilang in J03. This has also been detected for the river water samples with concentration of Fe declining downstream of the river. It first huge fluctuation in Fe concentration in river water was reported in sample from J03, near to the landfill, which is known for effluent discharge into the river. On the other hand, in locations downstream of Sg. Sembilang, low levels of Fe are reported. Here, the sampling stations were much closer to the industrial area and residential area and it could therefore be stated that the leakage of Fe in these locations resulted from localized anthropogenic outlets (industrial and residential waste water).

TABLE 2. Statistical summary of heavy metals in water samples from Sg. Sembilang (in mg.l-[1])

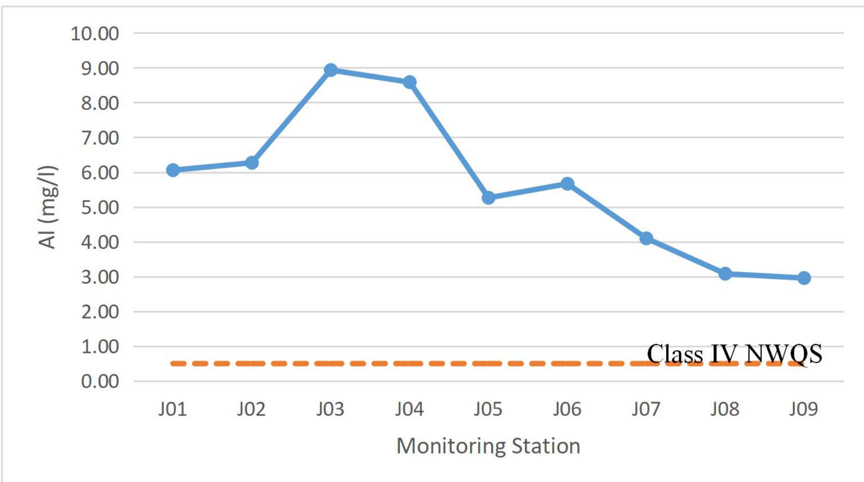
Heavy metal	Statistical parameter	NWQS (Class I-V)	J01	J02	J03	J04	J05	J06	J07	J08	J09
Fe	Mean		1.667	2.736	4.533	3.991	2.822	3.016	2.493	2.289	1.927
	Median	1	1.554	2.736	4.224	3.436	2.025	1.188	1.082	0.950	0.612
	SD		0.703	1.235	2.969	2.618	2.583	3.831	3.158	2.869	2.488
Al	Mean		6.058	6.271	8.934	8.587	5.264	5.667	4.099	3.082	2.958
	Median	0.06-0.5	6.163	5.515	7.780	7.029	4.835	3.360	2.438	1.881	1.166
	SD		4.751	5.245	7.872	5.904	4.691	6.701	4.738	3.309	4.307
Mg	Mean		8.660	10.818	14.900	15.160	21.048	20.299	18.666	21.020	22.857
	Median	150	8.378	8.362	13.012	14.884	17.420	15.181	14.227	18.708	21.060
	SD		4.725	8.207	7.050	4.589	10.356	10.041	8.873	8.071	9.948
Zn	Mean		0.133	0.194	0.173	0.529	0.185	0.229	0.277	0.268	0.260
	Median	2-5	0.113	0.098	0.157	0.241	0.165	0.260	0.262	0.268	0.244
	SD		0.072	0.230	0.107	0.701	0.096	0.086	0.135	0.115	0.280
Cu	Mean		0.032	0.023	0.026	0.041	0.024	0.031	0.022	0.021	0.020
	Median	0.02-0.2	0.002	0.002	0.006	0.037	0.005	0.009	0.0003	0.002	0.002
	SD		0.050	0.034	0.038	0.036	0.037	0.043	0.037	0.033	0.032
Mn	Mean		0.497	0.568	0.792	0.813	0.804	0.793	0.584	0.705	0.560
	Median	0.1-0.2	0.488	0.460	0.821	0.730	0.715	0.738	0.402	0.522	0.554
	SD		0.205	0.366	0.422	0.384	0.374	0.497	0.564	0.552	0.423
Cr	Mean		0.005	0.004	0.008	0.009	0.006	0.008	0.005	0.007	0.006
	Median	0.05-0.1	0.004	0.003	0.009	0.012	0.005	0.005	0.004	0.008	0.006
	SD		0.005	0.004	0.006	0.006	0.005	0.007	0.004	0.007	0.004
Cd	Mean		0.001	0.002	0.002	0.002	0.002	0.001	0.002	0.002	0.001
	Median	0.01	0.800	0.600	0.900	0.900	0.900	0.900	1.500	0.900	1.100
	SD		0.003	0.003	0.002	0.003	0.002	0.002	0.002	0.002	0.002
Pb	Mean		0.004	0.003	0.004	0.011	0.005	0.004	0.003	0.002	0.003
	Median	0.05-5	0.002	0.001	0.001	0.010	0.001	0.002	0.0005	0.000	0.001
	SD		0.006	0.006	0.006	0.011	0.008	0.006	0.006	0.004	0.005
Ni	Mean		0.010	0.010	0.018	0.021	0.016	0.017	0.012	0.014	0.012
	Median	0.05-9	0.008	0.010	0.017	0.019	0.015	0.019	0.010	0.014	0.011
	SD		0.006	0.006	0.009	0.005	0.006	0.010	0.010	0.010	0.008

Zinc (Zn) plays an important role in many biological processes and is an vital trace element for passable plant growth and procreation and for the health of animals and humans. (Guinoiseau et al. 2018). Zn is discovered in surface and groundwater and reaches the natural environment from various sources including mine drainage, industrial and municipal waste, urban runoff and, in particular, soil particle degradation featuring Zn. As per the Food and Agricultural Organization (FAO) and to World Health Organization (WHO) drinking water containing Zn > 3 mg/L appears to be opalescent, evolves a greasy film when cooked and has an unwanted astringent taste (Noulas et al. 2018).

Average Zn concentrations in water samples collected at ten stations in Sg. Sembilang over the study period are presented in Figure 2 and Table 2. No significant difference are observed between sampling stations. Zn concentration in water samples from Sg. Sembilang ranged from 0.133 to 0.640 mg/Lin stations J01 and J03, respectively, with a mean of 0.2884 ± 0.1645 mg/L. Mean Zn levels in study area were below National Water Quality Standard (NWQS) permissible limit of 0.4 mg/L for raw water except for station J03 and J05. The higher concentration of Zn at J03 can be attributed to the landfill effluent. It can also be derived from Table 2 that the concentrations of this metal measured in the water sample of J04 were generally higher than the levels issued by NWQS (0.4 mg/L) as well as at station J05 where the concentration were also exceeding the permissible level with 0.529 mg/L. The slightly high Zn values for J05 can be attributed to the presence of palm oil plantation along the river which is the fertilizers and pesticides used for the plantation.

Zn occurs naturally in water, but the concentrations of Zn increase abnormally due to the addition of Zn by human activities. This is showed by Zn concentrations at J01 which is the lowest concentrations of Zn among ten other sampling stations. Studies have shown that some soils are highly polluted with Zn and are discovered in locations where Zn has to be extracted or polished or where wastewater sludge from industrial areas is used as a plant food (Ismail et al. 2013). Sg. Sembilang that passing palm oil plantation could carry with it the Zn. During the treatment process, the metal can enter the water and also some corrosion and joint dissolution can be the possible source of Zn leeching into the water (Rahmanian et al. 2015). This can be seen in Figure 2 where Zn concentration increased from J01 to J03 and J05 where recorded the highest value and decreased to J09 which is located downstream of the river.

2a)



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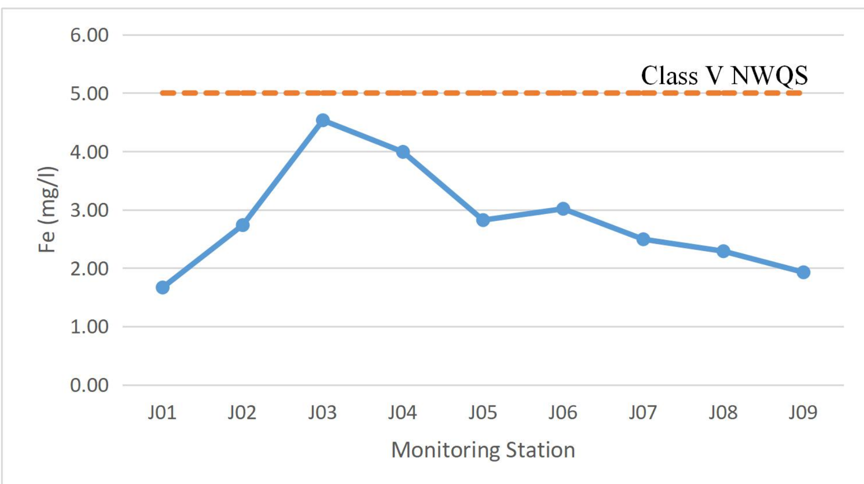

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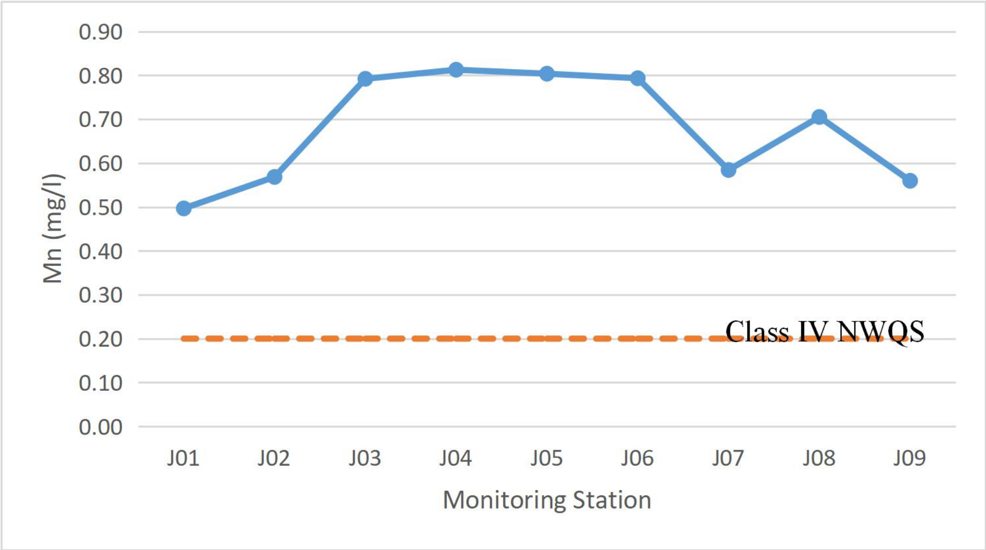
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Mn (mg/l)
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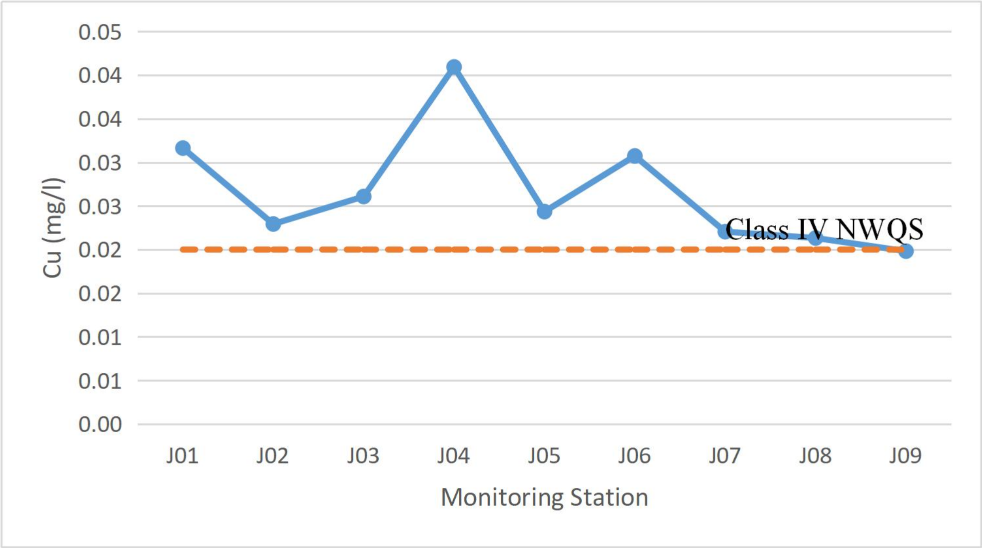
Monitoring Station

2d)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Cu (mg/l)
Class IV NWQS
J01
J02
J03
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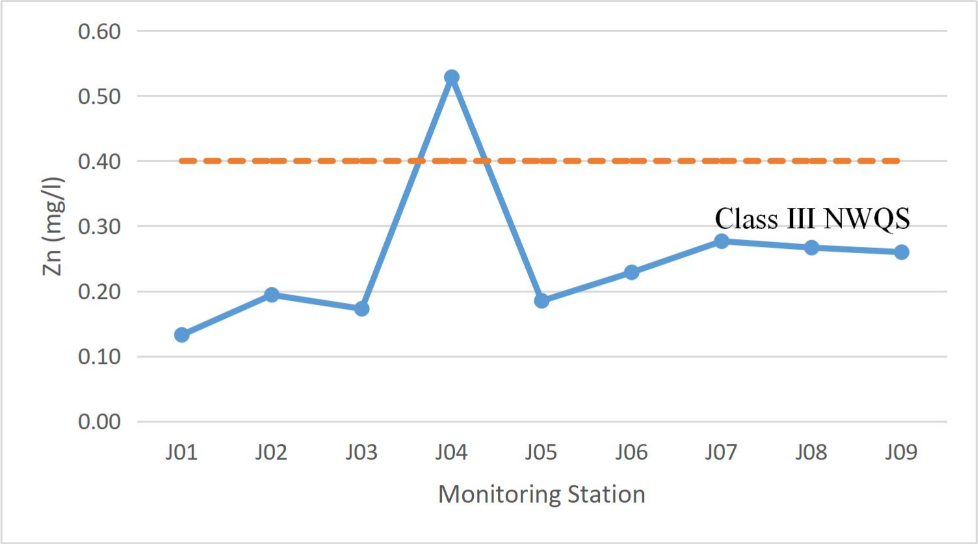
J05
J06
J07
J08
J09
Monitoring Station

2e)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0.50
0.40
0.30
0.20
0.10
0.00
Zn (mg/l)
Class III NWQS
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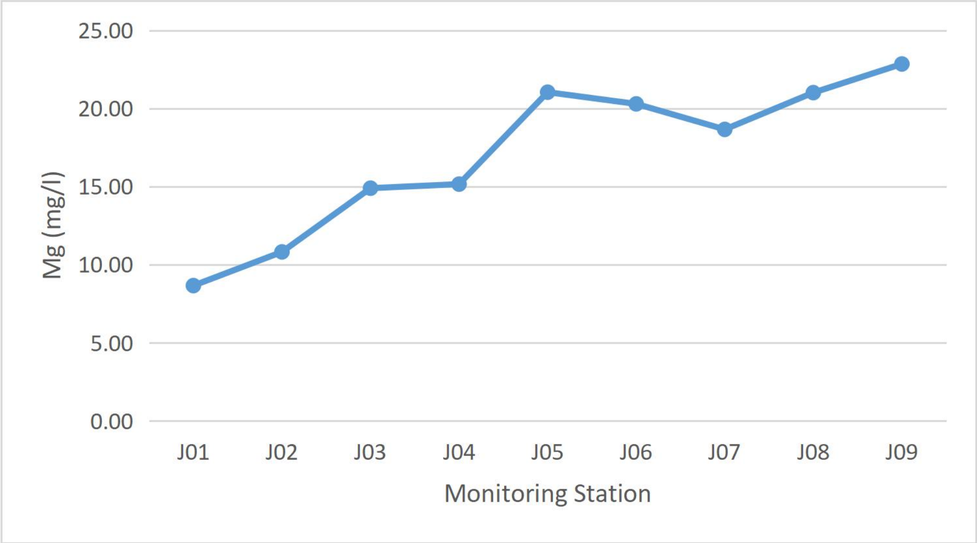
Monitoring Station

2f)


25.00
20.00
15.00
10.00
5.00
0.00
Mg (mg/l)
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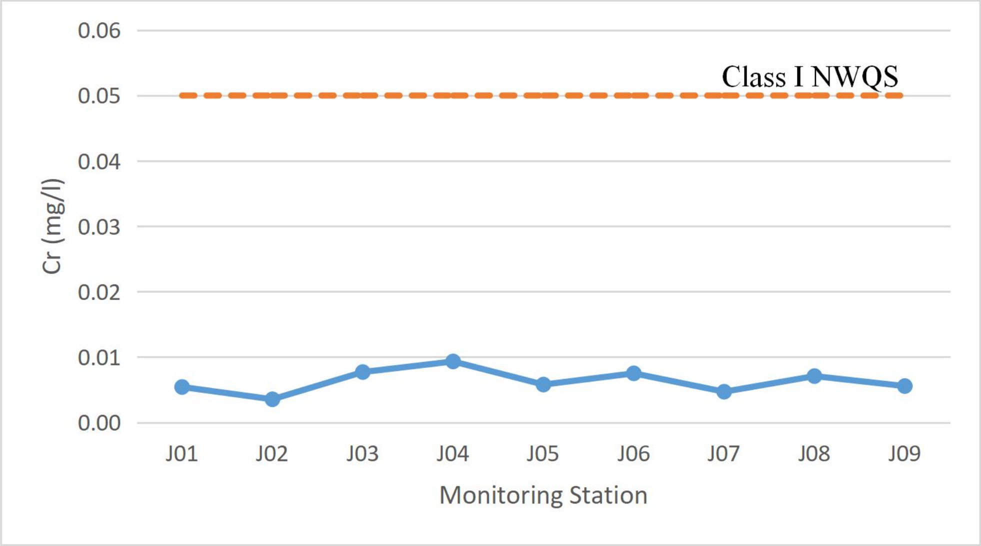
J09
Monitoring Station

2g)


0.06
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Cr (mg/l)
Class I NWQS
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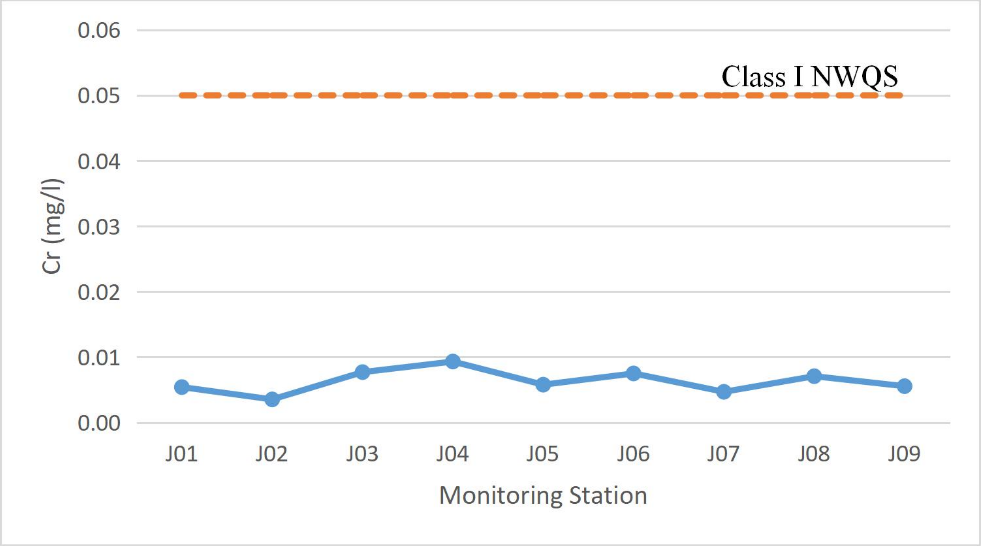
Monitoring Station

2g)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Cr (mg/l)
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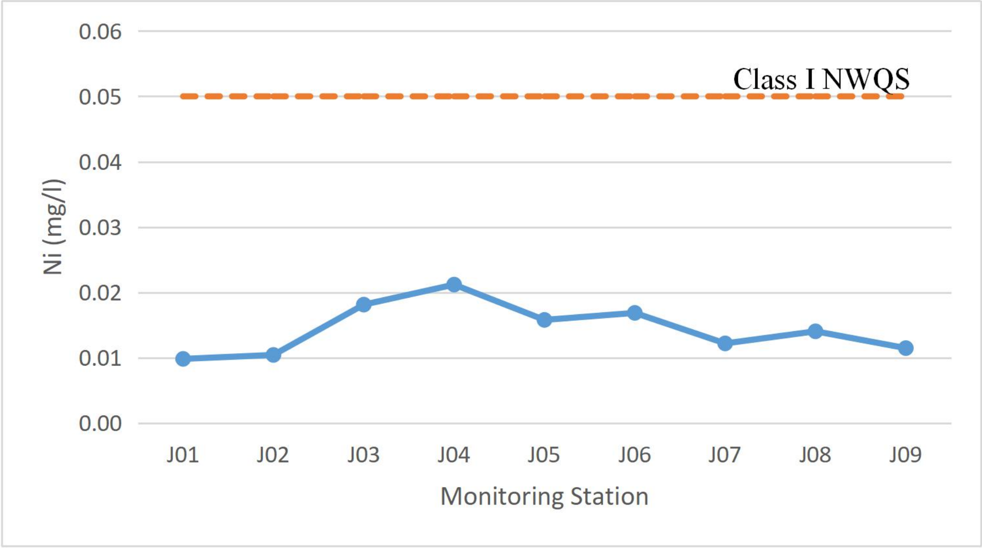
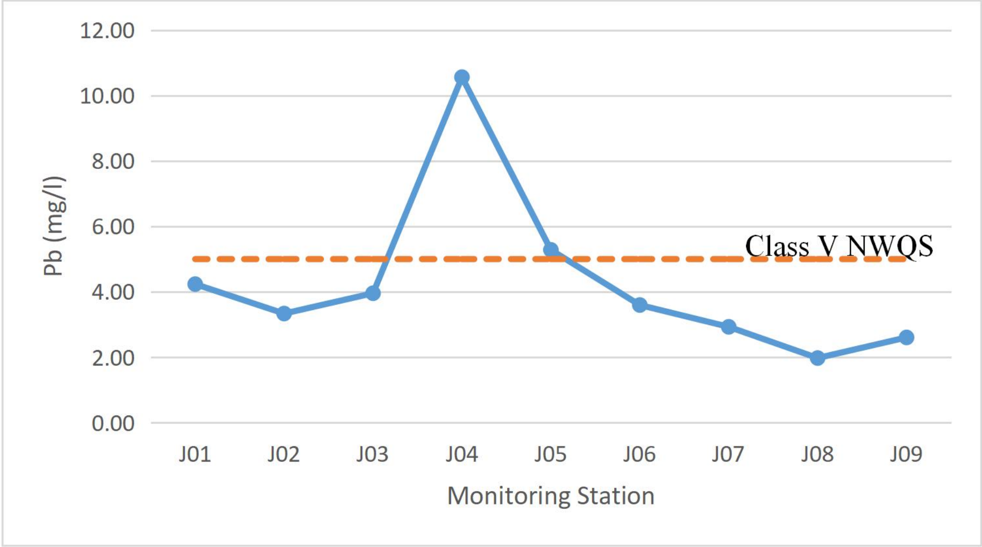
Monitoring Station

2h)



2i)



2j)

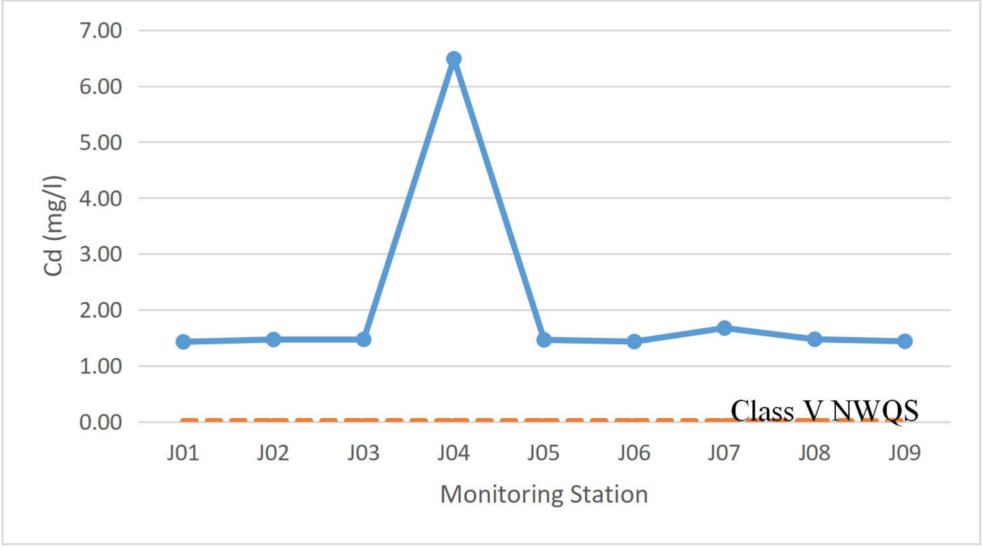


FIGURE 2. Average concentrations of heavy metals with below and higher than NWQS standard

OTHER HEAVY METAL ANALYSIS

Because of their relentless and bioaccumulative nature, heavy metals are of huge concern and may pose possible environmental toxic effects, influx and perseverance (Abraham & Susan 2017; Islam et al. 2017). In aquatic flora and fauna, heavy metals can accrue which can invade the human food chain and lead to health problems (Islam et al. 2017). Some heavy metals are vital for biological processes in the human body and act as both systemic and catalytic components of proteins and enzymes (Chen et al. 2018). A wide variety of natural and anthropogenic sources, including industrial, agricultural and domestic waste, release heavy metals into the environment (Jeelani et al. 2017; Xia et al. 2018).

For the detailed heavy metal analysis of Sg. Sembilang water, Cadmium (Cd), Cromium (Cr), Magnesium (Mg), Nickel (Ni) and Lead (Pb) were analyzed in the laboratory. From the analysis, it shows that these heavy metals were found in less concentration through the time being of the sampling in Sg. Sembilang from upstream to downstream stations. Table 2 shows the percentage of the other heavy metals affected in Sg. Sembilang due to the different sources of pollutions. It was observed that the concentration of metals (Cd, Cr, Pb, Mg and Ni) is below permissible limit of NWQS. The concentrations were characterized by range of Cd (0.0014 - 0.005 mg/L), Cr (0.0035 - 0.012 mg/L), Pb (0.002 - 0.019 mg/L), Mg (0.0076 - 0.0193 mg/L) and Ni (0.0076 - 0.019 mg/L).

Cd concentration in water samples from Sg. Sembilang ranged from 0.001 to 0.002 mg/L in stations J01 and J03, respectively. On average, Cd concentrations in all ten water samples were 0.0018 ± 0.0011 mg/L (Table 2), therefore, the concentration of Cd in water was below the acceptable limit of 0.001 mg/L of NWQS. Common environmental sources of Cd include mining, smelting, fossil fuel burning, municipal waste incineration, Ni - Cd batteries and varied industrial processes (Singh & Kumar 2017). Greater concentration of Cd in J04 may have been demonstrated due to contiguity with dissolved rock and minerals and also sources of agriculture. Furthermore, the use of fertilizers, disposal of sewage sludge and deposition of atmospheric aerosol are key drivers of Cd in this area.

The existence of lead (Pb) in the environment is deemed pollution as compared to anthropogenic activities, Pb from the natural source proves to be small (Singh & Kumar 2017). In the present study, concentration of Pb varied from 0.002 - 0.019 mg/L with mean ± SD value of 0.0045 ± 0.0025 mg/L. All studied samples were found less than the NWQS suggested allowable limit. Pb pollution thru the river can be caused by anthropogenic soil activity enrichment. At J04, the highest mean Pb concentration was observed. The misuses of palm oil plantation pesticides in this area are key contributors to the river's Pb water pollution.

Ni is a water - soluble heavy metal that originates in the water column from hydro - geochemical processes and anthropogenic actions. Neither industrial waste, crude oil plants, color plants, glass and ceramic industries and rejected batteries are important origin of Ni pollution (Sakai et al. 2017; Singh & Kumar 2017). In the present study, Ni varied from 0.0076 - 0.019 mg/L with mean ± SD value of 0.015 ± 0.004 mg/L. As stated by NWQS, all samples were found under the allowable limit (0.9 mg/L). Highest mean concentration of Ni was in downstream at site J02 and J04. Downstream of Sg. Sembilang lies within landfill and palm oil plantation, therefore, this could be the possible reasons of high concentration of Ni in downstream. As a result, the river could have held up as an effective agent for dispersing Ni from its source region (Singh & Kumar 2017). Cr is a highly toxic metal, but the Cr concentration did not exceed the standard limit (2.5 mg/L) as recommended by NWQS in any sample. In the present study, Cr varied from 0.0035 - 0.012 mg/L with mean ± SD value of 0.0069 ± 0.0025 mg/L. Lowest mean concentration of Cr was found at J02.

Heavy metal pollution index is an appropriate tool to identify the surface water pollution as it integrates various parameters to appear at exact amount that can be correlated with the crucial amount to determine the amount of pollution capacity. The mean values of the preferred metals are taken into account in order to determine the HPI of the water. Table 3 details the calculations of HPI with standard permissible value. The HPI value for Sg. Sembilang was below the critical value of 100, 6.05 (Table 3). For each sampling location, HPI was also measured separately to examine the pollution load and evaluate the water quality of the preferred areas. Considering the classes put forward the highest value of HPI was found in location J03 and was 7.989 lower from the critical value of 100.

TABLE 3. HPI calculation for surface water sample

Metals	Mean ($\mu g.l^{-1}$)	Highest Permissible value ($\mu g.l^{-1}$)	HPI
Iron(Fe)	3009.78	1000	0.30
Magnesium(Mg)	16678.30	150000	0.00
Manganese(Mn)	677.77	200	1.69
Zinc(Zn)	288.45	2000	0.01
Aluminium (Al)	5861.88	500	2.34
Cadmium(Cd)	1.53	10	1.53
Chromium(Cr)	6.86	100	0.07
Copper(Cu)	26.74	200	0.07
Lead(Pb)	4.41	5000	0.00
Nickel(Ni)	15.02	200	0.04
Total			6.05

Sampling stations J01 (HPI-5.4148); J02 (HPI- 5.794); J04 (HPI- 7.668); J05 (HPI- 6.020); J06 (HPI-6.182); J07 (HPI-5.173); J08 (HPI-4.862) and J09 (HPI-4.350) water quality with classify to metals, fall in the lower class (HPI<15). The lowest HPI value was found in J09. In regard to the risky metallic pollution of river, the river water quality is considered to have low and moderate heavy metal pollution. Precautions must be taken into consideration where agricultural activities, industrial waste water, as well as landfill effluent discharge into the river are observed. Excessive usage of river water for agriculture, industrial, and recreational purposes are among the most significant reasons that make the river monitoring implantation inevitable.

Conclusion

In this study, the water sample of Sg. Sembilang was analyzed to assess the levels of heavy metals in river water. Concentration of Al, Fe, Mn, Mg, Zn, Cu, Cd, Pb, Ni, and Cr were studied. It was found that Al and Mn were higher than the permissible values in the standard. The data gathered at the stations located within the upstream of the river (J01 and J02) shows low risk potentials while the data from the downstream stations (J03 to J09) proves to hold higher risk potentials. The main sources are landfill effluent, agricultural runoff, as well as industrial wastewater discharge to the river in downstream. However, the results show no statistical correlation among the behavior of different metals in water column alongside the river, which may be attributed to their same entry source. Calculated HPI based on the mean concentration of heavy metals, was found to be 6.05 that is below the critical pollution index value of 100. With respect to sampling locations, station J03 registered the highest value of 7.989. This is probably due to the location of J03 which is very near to the effluent discharge point. The finding shows that the selected water samples from the river are polluted with regard to heavy metals. This analysis indicates the present scenario of water quality of Sg. Sembilang because of effluent from the landfill, material and waste water from industry, agricultural runoff and residential area. It also shows the varying dispersion of heavy metals concentrations among the sampling stations. This study has shown that significant parameters that contribute to the quality of water along the river include natural pollutants and anthropogenic pollutants. In addition, multivariate analysis applications can be used as a potential application for water quality studies of other tropical rivers having the same variation of seasons and pollutant sources as the study area. Thus, the present study reveals that there is an association of water quality studies with environmental management that can be used as a practical relevance for the study of environmental impacts on water ecosystems. This study can be used as a guide to new studies and water quality management studies such as water management for aquafarming, water security, ecological impact assessment, and catchment planning.

Acknowledgements

The authors would like to acknowledge the University of Malaya Research Grant (FL001-13SUS, GPF070A-2018) for the financial support. We would also like to thank the relevant authorities and companies who have contributed and assisted throughout the study period. We are most grateful and would like to thank the reviewers for their valuable suggestions, which have led to substantial improvement of the article.

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Received: 17 March 2019
Accepted: 1 January 2020