Determination of Heavy Metal Concentration of Benut River at Simpang Renggam, Johor

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Abstract. The present study is aimed to determine heavy metal concentration in Benut River, Simpang Renggam, Johor. Heavy metals such as copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), aluminum (Al), nickel (Ni), chromium (Cr) and Arsenic (As) were selected for the water quality assessment due to the potential sources from natural and anthropogenic sources at the case study. Sampling was conducted twice which was on April 2019 and July 2019 at eight (8) sampling points in Benut River. Eight (8) sampling points were chosen due high potential of pollutant at point sources include chicken farm, landfill, oil palm plantation and residential. Heavy metals were analysed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) followed the APHA (2012) standard. It can be concluded the Cu, Zn, Cd, Mn, Ni, Cr, As and Al are detected at Benut River and most of the heavy metals are within allowable standard by INWQS Class II and DWQS except for Al concentration. Therefore, concentration of heavy metals is low in Benut River for both sampling. However, continuous monitoring is needed to maintain the quality of Benut River and advance treatment could apply to the water treatment facility for this river water for household purpose.

1. Introduction
The rapid development of economic activities in Simpang Renggam including landfill, chicken farms, oil palm plantations, and residential area has led to deterioration of river water quality. There have been several series of water supply disruption at Simpang Renggam, Johor since 2013 which lead to complaints and unpleasant condition to 75,000 residents [1]. The most recent case is in March 2019 which has prompted the temporary closure of the water treatment plant. This is due to high ammonia readings, most probably due to illegal dumping and leachate from a landfill. The problems have been reported by several of Malaysian news [1-3]. It is revealed that the ammonia contamination ranges between 1000-3000 mg/L, exceeding the standard. It needs to be treated around 5 mg/L as according to the Environment Quality Regulation 2009. Water operator needs to cut off the water supply because the quality of poor quality of raw water resources. However, the heavy metals amount still did not reported yet. Hence, the immediate water quality monitoring of heavy metals assessment is needed to find the possible pollutant sources and mitigating measures.

Heavy metals such as copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), aluminum (Al), nickel (Ni), chromium (Cr) and Arsenic (As) are found in river water [4-6]. Heavy metals are available in the water system from natural and anthropogenic sources around the drainage basin of rivers [5]. Nizami and Rehman [2] conducted a pollutant assessment at Ganga River in Allahabad and Varanasi, India which is known as polluted river in the world [4]. They found Ganga River in Allahabad have high
concentration of heavy metals with Cr 0.290 mg/L, Cd 0.290 mg/L, Ni 1.939 mg/L and Mn 0.055 mg/L while Ganga River in Varanasi give heavy metal concentration with Cr 6.280 mg/L, Cd 18.650 mg/L, Ni 5.900 mg/L, Cu 57.860 mg/L and Zn 447.500 mg/L respectively. The high concentration is might be due to the rapid urbanization and industrialization activities around Ganga River. Concentration of heavy metals Cr, Fe, Cu and Cd were detected at Sungai Muda and Sungai Kerian, Penang, Malaysia with 0.003 and 0.002 mg/L, 0.549 and 0.321 mg/L, 0.004 and 0.006 mg/L, 0.001 mg/L respectively due to chemical industry discharge into river water [7]. Mn and Ni are not detected in these rivers while Zn only found in Sungai Jarak with 0.004 mg/L [7]. Those studies proven the heavy metals are presence in the river water.

The type of pollutants especially by heavy metals contamination brought into the aquatic ecosystem are largely influenced by the various anthropogenic activities such as disposal of untreated and partially treated effluents, metal chelates from different industries, metals usage in chicken farm industries and indiscriminate use of heavy metal-containing fertilizers and pesticides in agricultural fields [8-9]. Benut River has various potential sources of pollution which comes from agriculture area, chicken farm area, residential area and leachate from landfill. Heavy metal contamination in aquatic ecosystems is persistence and abundance in the environment caused a worldwide environmental problem especially on Al, Cr and Cd [7-10]. Generally, the residues of heavy metal in polluted habitats can be accumulated in microorganisms, aquatic fauna and flora, which, in turn, may result in health problems to human through the food chain or water supply [5, 7, 10]. A long-term exposure to heavy metals can be carcinogenic, affecting human health especially central and peripheral nervous system and circulatory effects as heavy metal is easy to accumulate into the living tissues [5].

The standard for heavy metals pollutant in Malaysia was referred according to Department of Environment Malaysia (DOE) and Malaysia Interim National Water Quality Standard (INWQS) [11] are shown in Table 1. The INWQS in the table defined six classes (I, IIA, IIB, III, IV and V) in descending order referred to the classification of rivers or river segments. Table 2 shows the water classes and their suitable usage in terms of the classes. The river should maintain in Class I category or at least in Class II which suitable for household usage with conventional treatment.

| Parameter          | Unit | Classes       |
|--------------------|------|---------------|
| Copper (Cu)        | mg/L | 0.02          |
| Zinc (Zn)          | mg/L | 5             |
| Cadmium (Cd)       | mg/L | 0.01          |
| Manganese (Mn)     | mg/L | 0.1           |
| Aluminum (Al)      | mg/L | 0.05          |
| Chromium (Cr)      | mg/L | 0.05          |
| Nickel (Ni)        | mg/L | 0.05          |
| Arsenic (As)       | mg/L | 0.05          |

The standard for heavy metals pollutant Malaysia according to Ministry of Health Malaysia and Drinking Water Quality Standards Malaysia (DWQS) are as in Table 3. The standard is vital as referred in this study since the water river is source of water supply in Simpang Renggam.

Hence, this study provides a preliminary data on the heavy metals concentration in selected sampling stations in Benut River, Simpang Renggam, Johor. This finding is beneficial to authorities to develop strategies to deal with the river water quality problem.
Table 2. Water classes and uses [11]

| Class   | Uses                                                                 |
|---------|----------------------------------------------------------------------|
| Class I | Conservation of natural environment.                                 |
|         | Water Supply I – Practically no treatment necessary.                 |
|         | Fishery I – Very sensitive aquatic species.                          |
| Class IIA| Water Supply II – Conventional treatment required.                   |
|         | Fishery II - Sensitive aquatic species.                               |
| Class IIB| Recreational use with body contact.                                   |
| Class III| Water Supply III – Extensive treatment required.                      |
|         | Fishery III – Common, of economic value and tolerant species; livestock drinking. |
| Class IV | Irrigation.                                                          |
| Class V  | None of above.                                                       |

Table 3. Drinking water quality standard [12]

| Parameter         | Unit | Maximum Acceptable Value (unless otherwise stated) |
|-------------------|------|---------------------------------------------------|
| Copper (Cu)       | mg/L | 1.0                                               |
| Zinc (Zn)         | mg/L | 3.0                                               |
| Cadmium (Cd)      | mg/L | 0.003                                             |
| Manganese (Mn)    | mg/L | 0.1                                               |
| Aluminium (Al)    | mg/L | 0.2                                               |
| Chromium (Cr)     | mg/L | 0.05                                              |
| Nickel (Ni)       | mg/L | 0.02                                              |
| Arsenic (As)      | mg/L | 0.01                                              |

2. Materials and methods

2.1. River water sampling
Eight sampling stations were identified along Benut River at Simpang Renggam, Johor which most of sampling stations are the main point sources and activity at surrounding sampling stations (Figure 1 and Table 4) with most of them are agriculture area, chicken farm area and residential area. Google map and Geographic Information System (GIS) technology was implemented for mapping the sampling points. GIS technology is the framework for capture maps, gathering, managing and analyzing data using the maps. Two samplings of the river water samples were collected at first sampling on April 2019 (14.4.2019 [10.25 a.m.-2.15 p.m.]) and second sampling on July 2019 (17.7.2019 [10.00 a.m.-12.15 p.m.]) with three months times interval. 250 mL of raw river water samples were collected using glass bottles (rinsed with nitrite acid, HNO₃) and transported to the Environmental Engineering Laboratory and Wastewater Laboratory in the ice box. Sampling were followed the Standard Method of Examination of Water and Wastewater, APHA standard (2012) [13].

2.2. Heavy metals analysis
River water samples were kept at the temperature 4°C or below but not freeze the sample in the chill room which normally can be used after 24 hours stored. Samples were filtered immediately with addition of HNO₃ and pH must be below than 2 as preservation for dissolved metals. Sample dilutions were prepared for the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) instrument which measure heavy metals have a part per billion of detection limit. The samples required 10 times dilution factor to achieved 1ppb. Heavy metals which are copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), aluminium (Al), nickel (Ni), chromium (Cr) and Arsenic (As) were analyzed by ICP-MS. Storage and testing procedure (Method 3020B for ICP-MS) were followed the APHA standard [13].
Figure 1. Mapping of sampling stations using GIS [14]

| Sampling stations | Location of sampling                                      | Activity at surrounding area                                      |
|-------------------|-----------------------------------------------------------|-------------------------------------------------------------------|
| ST1               | Point from Machap dam (1.9014, 103.36925)                 | Agriculture area (oil palm and banana)                             |
|                   | Machap River before combined with Upstream Benut River (1.87338, 103.27816) | Agriculture (oil palm), residential, chicken farm areas           |
|                   | Upstream Benut River before combined Machap River (1.85837, 103.29419) | Agriculture, chicken farms and residential area                   |
|                   | Tributaries of Machap River and Upstream Benut River at Parit Jepun (1.83028, 103.29749) | Agriculture area                                                  |
| ST5               | Point at Benut River after CEP Landfill (1.89295, 103.36515) | Landfill area (leachate), agriculture area                        |
| ST6               | Final release point of Simpang Renggam Prison Sewage Pool (1.8437, 103.34343) | Prison area, agriculture area                                     |
| ST7               | Outlet Berembong River to Upstream Benut River (1.83316, 103.30208) | Residential area, shoplots, agriculture and orchard area          |
| ST8               | Intake Water Treatment Plant Simpang Renggam (1.82618, 103.29612) | Agriculture area, residential and public market area               |
3. Results and Discussion

Eight heavy metals which are copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), aluminum (Al), nickel (Ni), chromium (Cr) and Arsenic (As) were measured from eight sampling stations at Bentu River samples. Figure 2 illustrates the result of Cu concentration at eight sampling station with comparison between the result and INWQS (Class II because the water used as water supply). It shows that both sampling time (on 1st and 2nd sampling) are below the INWQS limit, even the values of Cu on 2nd sampling are higher compared to 1st sampling for every sampling stations. Besides that, the Cu concentration are also determined to be within the limits sets for drinking water since the DWQS for Cu is 1.0 mg/L. The anthropogenic sources related to the discharge of domestic sewage and industrial effluents generally result in pollution with Cu in river water samples. Concentration of Cu from Machap dam and flow along the Bentu River might be from agricultural activities at surrounding sampling stations area use Cu as a pesticide, fungicide and an algaecide [10].

The existence of Zn concentration is few in each sampling stations which is less than 0.25 mg/L and most of them are around 0.04 – 0.08 mg/L caused the level of bar chart seem like absent in the graph. Zn concentration on first sampling is higher compared to second sampling. In Bentu River, Zn is allegedly attributed to industrial and municipal activities [10]. Zn concentration in all sampling stations is under allowable standard by INWQS (5.00 mg/L) and DWQS (3.00 mg/L) respectively and it safe for residents to use the water in term of amount of Zn concentration.

Cd concentration was found at each station with the amount is less than 0.0005 mg/L except ST2 in second sampling (0.0011 mg/L). River water samples at ST2 are the wastewater discharged from chicken farms, agriculture and residential area. The result might be higher due to the detergent use during cleaning the chicken farm floor [15]. The presence of Cd concentration also might come from leachate from landfill area caused the Cd were spread and follow the river flow along Bentu River [9]. However, the results are below than INWQS (0.010 mg/L) and DWQS (0.03 mg/L) respectively. The fourth graph shows Mn concentration in each sampling in two different sampling times with comparison of INWQS and DWQS. Mn were determined in every sampling station are due to the Mn fertilizer usage thus the Mn was absorbed in the soils and flow to the river [16]. This can be a reason of existence on Mn concentration since all sampling stations is agriculture area as referred to Table 4. Besides that, leachate is the possible factor affected amount of Mn in the river samples [10]. The graphs show all sampling stations are under allowable standard by INWQS and DWQS which is 0.10 mg/L.

All sampling stations show Al concentration were detected exceed the permissible limits by DWQS which is 0.2 mg/L except ST6. The results also found more than INWQS Class II which is the permissible limit should be 0 mg/L or absent amount of Al. Al concentrations at sampling stations are high caused acidic soils which due to natural sources and precipitation of Al during rainfall when industrial area at Simpang Renggam released Al on air [17]. The amount of Ni concentration at all sampling stations for two different time sampling is at the range 0.0014 to 0.0052 mg/L. The Ni value was influenced by the receiving of significant quantities of anthropogenic discharges from landfill area, urban areas and agricultural areas, which were related to the electrolyte nickel plating activities, livestock manures, inorganic fertilizer and sewage sludge [10]. The results are within permissible limits by INWQS (0.05 mg/L) and DWQS (0.02 mg/L), respectively.

Cr concentration are unstable for all sampling stations but in the low range (0.0011 to 0.0026 mg/L) except second sampling at ST1 which has 0.0066 mg/L. The presence of Cr in the areas might be contributed from the fertilizer used the agriculture area [18]. However, the results are lower than standard by INWQS and DWQS which is 0.05 mg/L. As concentration are at range 0.0014 to 0.0040 for first sampling while 0.0155 to 0.0205 mg/L for second sampling at each sampling stations. However, the As usage in chicken farm for additive to increase weight gain, improve feed efficiency, kill parasites and improve pigmentation of chicken meat are widely used for chicken farm activity [9] caused the amount of As are exist in most sampling stations. The results represent all data are determine within the limit by INWQS (0.05 mg/L) and DWQS (0.01 mg/L) accept second sampling, which was at the range 0.0155 to 0.0205 mg/L.
Figure 2. Heavy metals concentration of Cu, Zn, Cd, Mn, Al, Ni, Cr and As at each sampling station in Benut River, Simpang Renggam.
4. Conclusion

It can be concluded the heavy metals concentration for Benut River, Simpang Renggam, Johor are within allowable standard by INWQS Class II and DWQS except for Al concentration. Al concentration was found to be 2.36±0.15 mg/L, exceed the permissible limits by DWQS which is 0.2 mg/L except ST6. It is suggested that the continuous and detail of the sources that contribute to the high concentration will be investigated thoroughly at Benut River. River water quality model and simulation could apply to monitor the level of heavy metals in the stream for the surveillance purposes. Moreover, industrial and public awareness campaigns about this issue need to be implemented to maintain the quality of river water at Benut River.

5. References

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