

Water Quality Assessment of Perak River, Malaysia

Salam, M. A.^{1,2*}, Kabir, M. M.¹, Yee, L. F.², A/I Eh Rak, A.² and Khan, M.S.¹

1. Department of Environmental Sciences and Disaster Management, Noakhali Science and Technology University, Noakhali-3814, Bangladesh

2. Faculty of Earth Science Jeli Campus, University Malaysia Kelantan, Jeli, 17600, Malaysia

Received: 11.01.2019

Accepted: 03.04.2019

ABSTRACT: The present investigation has been conducted to assess the status of physico-chemical parameters as well as the concentrations of some selected heavy metals to understand the present scenario of water quality at Perak River basin, Malaysia. The temperature, turbidity, pH, EC and DO values of all the examined samples have been within the range of 25.0 to 30.5 °C, 39.5 to 168.00 NTU, 6.8 to 7.33, 30.3 to 113.8 µs/cm and 3.62 to 7.01 mg/L, respectively. The concentrations of trace metallic constituents have been determined by means of Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), giving the following ranges: Cr: 0.01 to 0.052 mg/L; Pb: 0.01 to 0.03 mg/L; Zn: 0.11 to 0.92 mg/L; Fe: 1.38 to 5.55 mg/L; Mn: 0.10 to 0.25 mg/L and Ca: 2.55-23.23 mg/L, respectively. The concentrations of heavy metals at downstream of Perak River water were higher than the concentrations of upstream. The order of heavy metallic constituents in the water samples was Fe > Zn > Mn > Cr > Pb. R mode Cluster Analysis (CA) suggests that multiple anthropogenic activities like urban runoff, agricultural runoff, discharges of vehicles washing and workshops, land use changes, unplanned settlements, domestic effluents, wastewater of livestock husbandry farms etc., are influencing the physico-chemical parameters and heavy metals concentrations of Perak River water. The present study is highly significant for providing baseline information of potential hazardous level of heavy metals to human health, environment, and sustainable water resources management for economically and environment friendly uses of Perak River.

Keywords: Surface water pollution, Heavy metals, Cluster analysis, ICP-OES, Physico-chemical characteristics.

INTRODUCTION

The surface water quality is indeed a sensitive concern in the present era because of its effects on human health and aquatic ecosystems. Surface water contamination by chemical, physical, and biological pollutants throughout the world can be considered as a worldwide problem (Noori et al., 2009; Anny et al., 2017). Rivers are extremely

susceptible to pollution providing to their role in assimilating the municipal and industrial wastewater and run-off from agriculture in their large drainage basins. Human induced activities (urbanization, industrial and agricultural activities, increasing consumption of water resources), as well as natural processes (variations in precipitation inputs, erosion and weathering of soil), pollute surface water and hamper their use for drinking, industrial,

* Corresponding Author, Email: s_salam1978@yahoo.com

agricultural, recreation or other purposes (Carpenter et al., 1998; Jarvie et al., 1998). Water quality parameters such as temperature, pH, dissolved oxygen (DO), salinity, and nutrient masses have been conveyed to influence biochemical reactions in surface water systems. Deviations in the value of water quality parameters result changes in the condition of the water system (Hacioglu & Dulger, 2009), which could contaminate the water quality for useful uses. The anthropogenic influences such as urban, industrial and agricultural activities increasing exploitation of water resources as well as natural processes, such as precipitation inputs, erosion, weathering of crustal materials also degrade surface waters and destruct their use for different purposes (Karbassi et al., 2011).

The chemical composition of a water system encompasses interactions of various factors like weathering of rocks, intensity and composition of the rainfall in a specific area, chemical reactions that occur between the water and soil/sediment, and pollution from varying sources (Da Silva & Sacomani, 2001). Chemical contaminants entering into surface water through various sources have been pose a substantial health hazards even at very low levels, especially persistent chemicals (McMichael et al., 2001; Yassi et al., 2001). Pollution caused by heavy metals is considered to be a serious problem due to their toxicity and their ability to accumulate in the biota (Nabi Bidhendi, 2007; Nasrabadi, 2010; Nasrabadi, 2015). Prioritizing the ecological and environmental significance of river systems, much research has been focused on heavy metals pollution and mobility in soil, sediment and in watershed systems in recent decades (Saeedi et al., 2013).

The occurrence of toxic heavy metals such as Pb, Cd, Cr, Hg as well as indigenous pathogenic microorganisms in the environmental systems has been considered a source of vex to environmentalists, government agencies and health practitioners

because of their adverse health effects (Fatoki et al., 2002; Kabir et al., 2018). In order to effectively manage river water environment, obtaining water environment quality parameter data is vital. However, regular measurements needs doing much work, because of spatial and temporal variability of water environment quality data, monitoring by regular measurements, which will provide a representative and dependable estimation of surface water quality, is essential (Chapman, 1992).

In Malaysia, 97 % of the water supply comes from rivers and streams and the demand for residential and industrial water supply has grown rapidly following the country's economic development, increase in population and urban growth (NWRs, 2011). In recent years, the number of polluted rivers are increasing gradually and the condition is deteriorating day by day. In 2008, about 17 rivers out of 186 rivers have been considered as toxic and unsafe for human consumption (Yahya, 2008). Al-Badaii (2013), reported deteriorated water quality of Semenyih River, Malaysia which was mainly due to the industrial and agricultural activities. Hossain et al. (2013) recorded elevated and toxic level of heavy metals (Pb, Hg and CO) in the surface water of Tunggak River. The Perak state of Malaysia where there are 11 major river basins covering over 80 km² area. The Perak River basin is about 760 km long with an area of 14.908 km². Perak River basin is the biggest in this area, which covers about 70% of state area. Water quality status of Perak River falls under Class II status, with the Water Quality Index (WQI) ranging from 74 to 80 over the past six years. If water in the Perak River is further contaminated, it will affect most of the river basin in Perak State and affect the human population as well as the financial income of the local population, where most of the activity in this area is fishing and agricultural activities (Ahmad et al., 2016).

In order to recover the water quality of Perak River basin, the source apportionment of pollutants from various land use activities should be identified. The present research work has been conducted to identify the compositional profile of physico-chemical properties of river water and associated sources in Perak river basin. Investigation on the comparison of concentration and composition of some selected heavy metals has also been carried out in order to provide some baseline information to the policy maker and policy planner of Perak state of Malaysia for better and sustainable management of Perak River's water quality.

MATERIALS AND METHODS

Perak River is called the "River of Life" for Perak State and is the second largest river in Peninsular Malaysia. The Perak River basin is about 760 km long with an area of 14.908 km². Perak River basin is the biggest in this area, which covers about 70% of Perak state (Ahmad et al., 2016). The upper reaches of basin is covered by forest land and the middle and lower reaches of the basin, the agricultural lands consist of mainly rubber and oil palm plantation. The major towns are Gerik, Lenggong, Karai, Kuala Kangsar, Parit, Teluk Intan and Bagan Datuk. Perak River is special for its wide spectrum of functions and perhaps the only one in Malaysia that executes nearly all the purposes expected from a river.

A total of 45 water samples, three replicates from each station along 15 stations starting from upstream to downstream of Perak River were collected. The map of Perak River Basin and the sampling locations along with land use activities has been presented in Fig. 1. Samples were collected during the month of August which is called Southwest Monsoon season. Plastic containers of 500 ml were used for sample collection and all the sampling bottles were thoroughly rinsed with 10% nitric acid (HNO₃) to

avoid contamination (APHA, 1998). The samples were kept in ice boxes and taken to the laboratory as early as possible. In order to determine the heavy metal concentration of the samples, instantly after collection 1 ml of concentrated HNO₃ (65%) was poured to each of the samples and mixed properly to bring the pH below 2 to minimize precipitation and adsorption on container's walls. To prevent the chance of being hydrolysis and oxidation, the samples were preserved at -20 °C in a refrigerator (Kabir et al., 2017). Global Positioning System (GPS) (GARMIN) was used to identify the exact location of the sampling locations.

All the water quality parameters were determined in-situ at the sampling stations along the Perak River. The temperature, electrical conductivity and dissolved oxygen were measured by using digital multimeter (Model- 85, YSI). The pH and turbidity values were measured by means of pH meter (Model- HI 8424, HANNA) and Portable Turbidimeter (Model- 2100 Q IS, Hach). All the instruments were calibrated with standard solution before used and the chemicals used were of analytical grade.

Acid digestion method was used to digest the water samples according for ICP-OES analysis (Hagedorn, 2008). Metal digestion was done according to USEPA Method 200.7, which is acid digestion of water for total recoverable metal analysis by Figure 3.4 showed the digestion procedure of heavy metal analysis. 50 ml of well-mixed acidified sample was transferred to 100 ml Griffin beaker. 2 ml of concentrated HNO₃ and 1 ml of concentrated HCl then were added to the samples. The beaker was placed on the hot plate for evaporation. The samples were covered with elevated watch glass to prevent contaminant from fume hood during the digestion process.

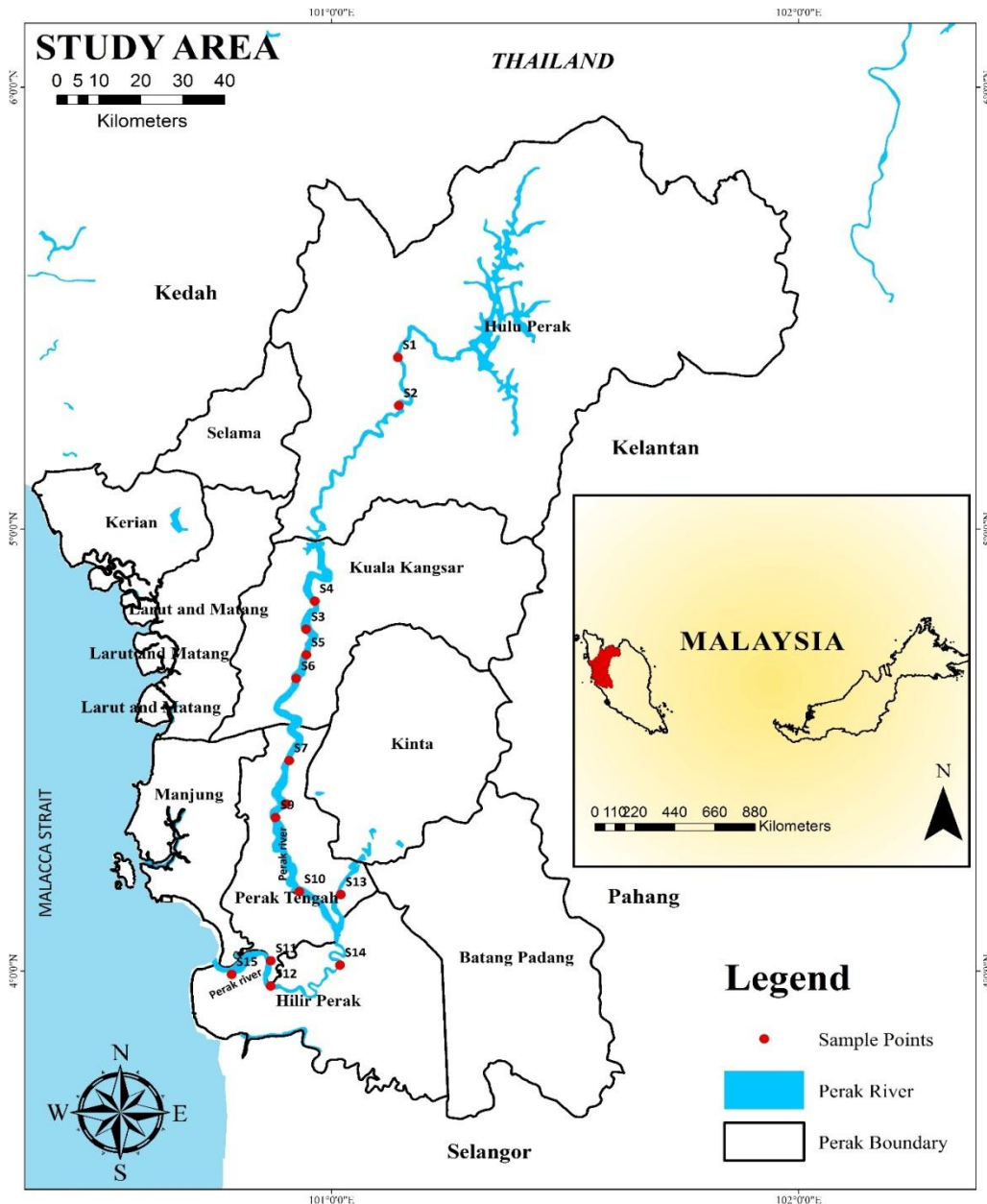


Fig. 1. Map of Perak River basin and sampling locations

The sample was not heated higher than 90°C to avoid the boiling. After 1 hour, the elevated glass was removed to allow evaporation until the volume reduced to 20 ml. The hot plate was turned off and allowed for cooling. Milli-pure water was used to wash down the tube walls and watch glass. The samples were then filtered into 50 ml volumetric flask by using Whatman No. 41 filter paper to remove insoluble materials. The final volume of the sample was adjusted to 50 ml with Milli-pure water. 10

ml of sample was transferred into centrifuge tubes for analysis of targeted heavy metals by ICP-OES. The concentration of heavy metals in water samples were analyzed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), which is linearly calibrated with custom multi-element standards (Faisal et al., 2014). This quantitative method was applied by added ICP Multi Element Standard Solution 4 CertiPUR, follow to the ICP-OES standard

with matrix of nitric acid 1 mol/L. This solution produced from high purity salts and concentration of the elements in this solution was analyzed by ICP-OES real time internal standardization using NIST standard reference materials for calibration. Six heavy metals were targeted to measure by ICP-OES, such as manganese, lead, zinc, calcium, iron and chromium.

For each analytical batch of samples processed, blank samples were carried throughout the entire sample preparation and analytical process. These blanks helped to determine if samples are being contaminated. A set of blank sample was prepared by adding nitric acid and hydrochloric acid for every batch of digestion. Every reading from the ICP-OES was deducted the blank as background reference.

Quality control (QC) can be defined as the procedures that lead to control different steps of measurement process (Al-Badaii et al., 2013). The concept of the sample batch is used to describe the number of samples that are digested prior to ICP analysis and that are accompanied by QC samples that are also digested (Mark, 2010).

The detection Limit and spiked recovery percentage of heavy metal analysis has been given in Table 1. The method accuracy and quality control were carried by triplicate analysis. The spiked recovery percentage of heavy metals was ranging from 103.80 % to 108.20 %. The precision of the analytical procedures expressed as the standard deviation was less than 5 % for all the metals analyzed by ICP-OES. All analyses were carried out in triplicate

and the results were expressed as the mean. The recovery rate of target heavy metals ranged from 104% (Cr) to 108.2% (Mn). This result indicated that the results obtained from the current study were valid.

Statistical analysis

Statistical analysis of data or variable was determined by Cluster Analysis (CA). Cluster Analysis (CA) used to determine the similarities between the sampling stations using Ward's method with Euclidean distances (Varol & Bulent, 2012). All analyzed data was standardized by scale transformation to ensure normal distributions for CA. (Al-badaii et al., 2013). Each set of experiments were carried out in triplicate. Experiments were repeated separately to ensure reproducibility. All the results are expressed by Mean \pm SD (Standard deviation) values.

RESULTS AND DISCUSSION

The physical and chemical properties of water at Perak River basin has been presented in Table 2. The temperatures in the Perak river water varied between 25.0 to 30.5 °C with the average value of 28.2 °C. Upstream of Perak River was recorded the lowest temperature (25°C) whereas downstream of Perak River recorded the highest temperature (30.5°C). The time of measurement and weather condition determine the temperature's range of a water body (Muhammad et al., 2008). Water samples collection was carried out from morning to afternoon under the cloudy weather condition.

Table 1. Detection Limit and spiked recovery percentages of heavy metal analysis

| Heavy Metals | Detection Limit (mg/L) | Spiked concentration of multi-element solution (mg/L) | Measured value of solution (mg/L) | Recovery (%) |
|---------------------|-------------------------------|--|--|---------------------|
| Fe | 0.10 | 0.50 | 0.519 | 103.80 |
| Mn | 0.10 | 0.50 | 0.541 | 108.20 |
| Pb | 0.01 | 0.50 | 0.528 | 105.60 |
| Zn | 0.10 | 0.50 | 0.527 | 105.40 |
| Ca | 0.50 | 0.50 | 0.522 | 104.40 |
| Cr | 0.01 | 0.50 | 0.520 | 104.00 |

Table 2. Physico-chemical parameters of water at Perak River Basin

| River Positions | Sampling Stations | Temperature (°C) | pH | Turbidity (NTU) | Conductivity (µS/cm) | Dissolved Oxygen (mg/L) |
|---|-------------------|------------------|-----------------|-------------------|----------------------|-------------------------|
| Upstream | S1 | 25.0 | 7.26 | 57.4 | 75.1 | 6.72 |
| | S2 | 25.6 | 7.21 | 39.5 | 34.1 | 7.01 |
| | S3 | 25.0 | 6.82 | 166.0 | 61.2 | 5.09 |
| | S4 | 28.5 | 6.80 | 113.0 | 55.8 | 4.98 |
| | S5 | 27.4 | 6.93 | 168.0 | 30.3 | 3.62 |
| | S6 | 28.4 | 7.30 | 114.0 | 54.3 | 3.82 |
| | S7 | 27.8 | 7.16 | 158.0 | 72.7 | 3.78 |
| Average concentration | | 26.8±1.6 | 7.07±0.2 | 116.6±52.1 | 54.8±17.3 | 5.0±1.4 |
| Downstream | S8 | 28.9 | 7.06 | 116.0 | 57.8 | 5.18 |
| | S9 | 30.0 | 7.02 | 95.8 | 60.3 | 4.78 |
| | S10 | 29.2 | 7.33 | 79.9 | 54.5 | 5.54 |
| | S11 | 29.7 | 7.26 | 131.0 | 113.8 | 4.19 |
| | S12 | 30.5 | 7.16 | 95.1 | 95.2 | 4.34 |
| | S13 | 28.7 | 7.20 | 66.4 | 87.6 | 4.17 |
| | S14 | 28.9 | 7.30 | 78.4 | 81.4 | 4.26 |
| S15 | 29.9 | 7.26 | 150.0 | 82.87 | 4.17 | |
| Average concentration | | 28.2±1.8 | 7.14±0.2 | 108.6±40.4 | 67.8±22.4 | 4.8±1.0 |
| Overall | Range | 25.0-30.5 | 6.8-7.33 | 39.5-168.00 | 30.3-113.8 | 3.62-7.01 |
| | | 28.2±1.8 | 7.1±0.2 | 108.6±40.4 | 67.8±22.4 | 4.8±1.0 |
| Standard permissible limits (MOH, 2004) | | - | 6.5 - 9.0 | 5.0 | - | - |
| WHO (2004) standard | | 25.0 | 6.5-8.5 | 1000.0 | 150.00 | - |

WHO= World Health Organization, MOH= Ministry of Health Malaysia

The pH values of the Perak River water ranged within 6.80 to 7.33. The lowest pH value was 6.80 which were found in station 4 at upstream. The highest pH value was 7.33 that were found at station 10 at the downstream of Perak River. The pH in a water body is controlled by the dissolved carbon dioxide (CO₂) which forms carbonic acid in water, besides high concentrations of heavy metals in water are associated with acidic and oxidizing conditions (Hem, 1985; Voica et al., 2011). The pH of the Perak River water was normal compared to the regulation set by Ministry of Health which are in the range 6.5-9.0 (MOH, 2004).

The turbidity was varying within the range of 39.5 to 168.0 NTU with the mean value of 108.6 NTU. Overall, the turbidity at upstream river position was higher than that of downstream river position with the values of 116.6 ± 52.1 and 108.6 ± 40.4 NTU, respectively. The highest value (168 NTU) was found at station 5 of upstream of Perak River basin. This may be due to the reason of heavy rainfall before the day of sampling. Heavy rainfall causes surface runoff and soil particular to be drained into the water thus increase the turbidity of water. The electrical conductivity (EC) values ranged from 30.3 to

113.8 µS/cm with the average values of 67.8 µS/cm. The conductivity values of the downstream were higher than the values of upstream which recorded as 67.8 and 54.8 µS/cm, respectively. The average concentration of EC values were within the range of WHO's drinking water quality standard. The DO concentrations were ranged from 3.62 to 7.01 mg/L. The highest DO value (7.01 mg/L) was recorded at Station 2 and the lowest DO value (3.62 mg/L) was recorded at station 5. Both stations were situated at the upstream of Perak River. The higher DO value can be attributed by the high river flow which leads to high dissolved oxygen (Muhammad et al., 2008).

The total concentration of trace metals in water from different sampling stations of the Perak River has been has been illustrated in Table 3. The upstream of Perak River basin include station 1 to 7 whereas downstream of Perak river included station 8 to 15. The highest concentrations of heavy metals at the upstream were at station 3 whereas at downstream it was at station 15. The total concentration of metals in station 3 and station 15 were 15.53 mg/L and 27.23 mg/L, respectively in Perak River water.

Table 3. Concentration of heavy metals in Perak River water

| River Locations | Sampling stations | Concentration (µg/L) | | | | | |
|------------------------------|-------------------|----------------------|-----------------|-----------------|-----------------|------------------|----------------|
| | | Fe | Mn | Pb | Zn | Ca | Cr |
| Upstream | S1 | 3620 | BDL | 33 | 633 | 9505 | 16 |
| | S2 | 1743 | BDL | 14 | 202 | 2552 | 52 |
| | S3 | 1382 | 169 | 10 | 184 | 13610 | 10 |
| | S4 | 5549 | 120 | 11 | 229 | 5378 | BDL |
| | S5 | 4541 | 245 | 10 | 247 | 6.079 | BDL |
| | S6 | 3008 | 103 | 12 | 264 | 5210 | BDL |
| | S7 | 4507 | 130 | 14 | 118 | 5365 | BDL |
| Average Concentration | | 3480±1.53 | 150±0.06 | 20±0.008 | 270±0.17 | 6081±3.63 | 30±0.02 |
| Downstream | S8 | 3441 | 0.101 | 0.010 | 0.167 | 5.056 | BDL |
| | S9 | 3136 | 0.148 | 0.011 | 0.484 | 5.385 | BDL |
| | S10 | 2739 | 0.100 | BDL | 0.918 | 4.669 | BDL |
| | S11 | 4161 | 0.100 | 0.012 | 0.130 | 7.543 | BDL |
| | S12 | 3326 | 0.103 | 0.010 | 0.157 | 7.513 | BDL |
| | S13 | 2232 | BDL | 0.015 | BDL | 8.025 | BDL |
| | S14 | 2462 | BDL | 0.010 | 0.109 | 8.183 | BDL |
| S15 | 4110 | 0.100 | 0.010 | 0.237 | 23.233 | BDL | |
| Average Concentration | | 3200±0.71 | 110±0.02 | 10±0.002 | 320±0.29 | 8700±6.04 | BDL |
| Overall concentration | | 3330±1.13 | 130±0.05 | 10±0.01 | 300±0.23 | 7800±5.0 | 30±0.02 |
| Range | | 1380-5550 | 100-250 | 10-30 | 110-920 | 2550-23230 | 10-52 |
| MOH (2004) standards | | 300 | 100 | - | 3000 | - | 50 |
| USEPA (2012) standards | | 300 | 50 | - | 5000 | - | 100 |

BDL= Below Detection limit

The Fe value ranged from 1380-5550 µg/L with mean value of 3480 µg/L at upstream whereas mean value of downstream was 3200 µg/L from overall mean value of 3330 µg/L out 15 sampling stations. The highest concentration of Fe was detected at station 4 which was under the bridge. The rusting of bridge experiences oxidation then diffused into water. The high concentration of Fe may also be attributed by domestic wastewater discharges and high concentrations of total suspended solids at this site (Memet et al., 2013). The mean value of Fe was far exceeding the standard permissible limit set by Ministry of Health (200 µg/L). The concentration of Mn ranged from 100-250 µg/L with the overall mean value of 130 µg/L. The concentration of Mn at upstream with the mean value of 150 µg/L was higher than the downstream with the mean value of 110 µg/L. The highest concentration of Mn was found at upstream of station 5. The concentration of Mn in river water may be contributed by Mn rich soil in the surroundings due to the excavation activities of river bank observed during sampling period.

The Pb concentration ranged from 10-30 µg/L with the overall mean value of 10 mg/L. The concentration of Pb at upstream with the mean value of 200 µg/L was higher than the downstream with the mean value of 10 µg/L. The highest concentration of Pb was found at upstream of station 1 with mean value of 30 µg/L. Leakages or spillages of leaded petrol from vehicles during excavation activity of river bank at station 1 may the possible anthropogenic sources of Pb. The Zn concentration ranged from 110-920 µg/L with the overall mean value of 300 µg/L. The concentration of Zn at downstream with the mean value of 320 µg/L was more than upstream with the mean value of 270 µg/L.

The Ca concentration ranged from 2550-23230 µg/L with the overall mean value of 7800 µg/L. The concentration of Ca at downstream with the mean value of 8700 µg/L was higher than upstream with the mean value of 6810 µg/L. The highest concentration of Ca was at downstream of station 15 which have 23230 µg/L. This may due to the location of station 15 near to mouth of river, the decaying of aquatic living things such as shell or exoskeleton increased

the concentration of calcium in the river water. The Cr was detected only at station 1, 2 and 3 and the concentrations were 16, 52 and 10 µg/L, respectively. The overall mean value of Cr was 30 µg/L from the above mentioned stations. The concentration of Cr was below detection limit of all the downstream stations. The detection of Cr in river water at upstream was probably due to rain water runoff. Sewage containing electroplating and painting wastes may another major anthropogenic sources of Cr into river water.

The Fig. 2 illustrates the distribution of each heavy metal concentration along stations in Perak River water. The total heavy metals concentration including iron, manganese, lead, zinc, calcium and chromium at downstream were higher than that of upstream of Perak River. Concentration of total heavy metals at downstream was 85690 µg /L whereas the value at upstream was 53920 µg /L. The results indicate that increasing anthropogenic activities such as agriculture and mineral process at downstream increase the concentrations of heavy metals when compared with little industrial area at upstream. The anthropogenic activities at upstream such as

excavation activity of river bank, wastewater from residential areas and fertilizer from palm oil plantation lead to high concentration of heavy metals. The major sources of heavy metals attributions at downstream were from shipping activities. Perak River especially at downstream become the main shipping route in transporting the products or materials between factories and fishing activities. The point source input from industrial zone which was located adjacent to the river also increases heavy metals pollution within this area.

The concentration of calcium was considered to be the highest in water whereas the concentration of lead was considered to be the lowest in water of Perak River. The more proportion of metals in water, the more mobile they are, and the higher risk they could pose to the environment (Saiful et al., 2015). The relative variability of the studied heavy metals from Perak River basin was in the order of Fe > Zn > Mn > Cr > Pb. The concentration of Ca, Fe in water was found to be highest and the concentration of Zn, Mn, Cr and Pb was the lowest. Zn, Mn, Cr and Pb concentrations were less than 1.0 mg/L in Perak River water.

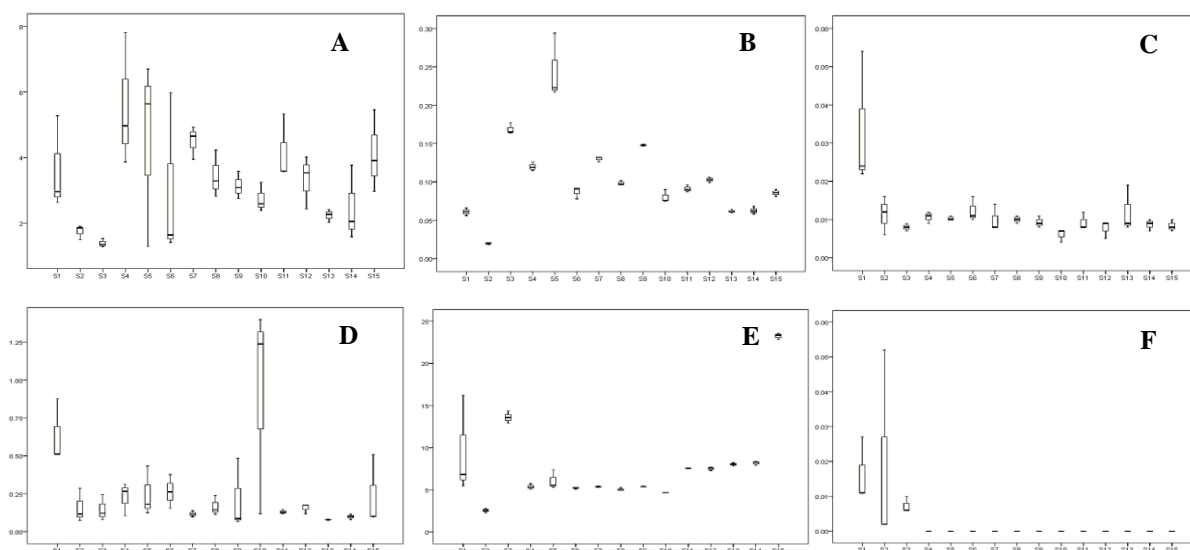


Fig. 2. Distribution of each heavy metal concentration (mg/L) along the stations in Perak River water samples: A) Fe, B) Mn, C) Pb, D) Zn and E) Cr. Values are mean numbers ± standard deviations generated from three independent experiments.

Table 4. Pearson correlation matrix between physico-chemical parameters with heavy metals of Perak River water

| | Temp. | pH | Turb. | Cond. | DO | Fe | Mn | Pb | Zn | Ca |
|-------|---------------|---------------|----------------|-------|-------|-------|-------|-------|-------|------|
| Temp. | 1.00 | | | | | | | | | |
| pH | 0.24 | 1.00 | | | | | | | | |
| Turb. | 0.08 | -0.47 | 1.00 | | | | | | | |
| Cond. | 0.45 | 0.39 | -0.01 | 1.00 | | | | | | |
| DO | -0.57* | 0.05 | -0.64** | -0.30 | 1.00 | | | | | |
| Fe | 0.33 | -0.22 | 0.41 | 0.09 | -0.35 | 1.00 | | | | |
| Mn | 0.12 | -0.62* | 0.83** | -0.32 | -0.48 | 0.39 | 1.00 | | | |
| Pb | -0.53* | 0.10 | -0.30 | 0.16 | 0.38 | 0.08 | -0.43 | 1.00 | | |
| Zn | -0.08 | 0.21 | -0.28 | -0.28 | 0.46 | -0.02 | 0.04 | -0.03 | 1.00 | |
| Ca | 0.06 | 0.04 | 0.38 | 0.37 | -0.19 | 0.02 | 0.04 | 0.06 | -0.11 | 1.00 |

* Correlation is significant at the 0.05 level (2-tailed)

** Correlation is significant at the 0.01 level (2-tailed)

The correlation analysis among physico-chemical properties (temperature, turbidity, pH, DO, conductivity and turbidity) of water with different heavy metal concentrations (Mn, Pb, Zn, Fe and Ca) was presented in Table 4. The relationships between variables were analyzed by Pearson correlation matrix (Wang et al., 2011). The correlation analysis was conducted to determine the relationship between heavy metals concentration in water and the influence of physico-chemical parameters of water on metals distributions.

Present study showed that most of the heavy metals in water were significantly correlated with temperature, DO, pH and electrical conductivity indicating that these parameters were the vital factor in metal solubility and controlling metals speciation and thus their distribution in river environment. From the analysis, temperature showed significant positive correlation with pH ($r=0.24$), turbidity ($r=0.08$), conductivity ($r=0.45$), Fe ($r=0.33$), Mn ($r=0.12$) and Ca ($r=0.06$) at the level of $p<0.05$. This signify that as temperature increased so did the binding of Fe, Mn and Ca in the water column. On the other hand, temperature showed negative correlation with DO ($r=-0.57$) and Pb ($r=-0.53$) at the level of $p<0.05$. The pH also suggesting a negative correlation with Mn ($r=-0.62$) at the level of $p<0.05$. The correlation coefficient of turbidity with Mn was

($r=0.83$) at the level of $p<0.01$ which suggesting a positive correlation whereas turbidity with DO was ($r=-0.64$) at the level of $p<0.01$ which suggesting a negative correlation. The Pearson correlation matrix showed that these heavy metals may come from the same sources or were influenced by the same factors. The highest extent of correlation between element concentrations reflect either a common or a similar geochemical sources of origin (Wang et al., 2011). Low concentration of heavy metals in water might not necessarily reveal that the area is pollution-free. Some metals in water tend to bind with sediment, and it might be accumulated from time to time and pose health hazard to aquatic biota (Lim et al., 2012).

Cluster analysis (CA) can be defined as a group of multivariate methods whose primary purpose is to gather objects based on the characteristics they hold. Cluster analysis classifies objects, so that each object is analogous to the others in the cluster with regard to a prearranged selection criterion. The resulting clusters of objects are supposed to show high internal homogeneity and high external (between clusters) heterogeneity. Each cluster thus demonstrates, in terms of the data collected, the class to which its members belong; and this description may be abstracted through use from the particular to the general class or type (Einax et al., 1997). Hierarchical

agglomerative clustering (HCA) is the most common approach, which offers perceptive similarity between any one sample and the entire data set, and is usually represented by a dendrogram (McKenna, 2003). The dendrogram illustrates a visual framework of the clustering processes, presenting a picture of the groups and their proximity, with a dramatic minimization in dimensionality of the original data. The Euclidean distance usually provides the similarity between two samples and a distance can be symbolized by the difference between analytical values from the samples (Otto, 1998).

The dendrogram derived from R-mode CA (Fig. 3) shows that all the sampling stations of Perak River are grouped into two statistically significant clusters. In cluster 2 (Fig. 4A), station 15 can be grouped separately from other stations, indicating

different sources of heavy metals. The large industrial clusters were responsible for the abrupt increase in the heavy metals concentrations at this station, which was reflected in the statistical results. In cluster 1, the sub-cluster which included stations 13, 14, 11, 12 and 1 can also be grouped together into another separate group and mostly the stations were from downstream possibly due to the influence by urban runoff and anthropogenic activities. Those stations were located in the downstream and affected by palm plantation, agricultural runoff and discharge of vehicles washing and workshops. In sub-cluster 1(b), the sampling stations were mostly from upstream and had similar characteristic which was impacted by parallel pollution sources in consequence of the land use changes like forest to agriculture and unplanned settlements.

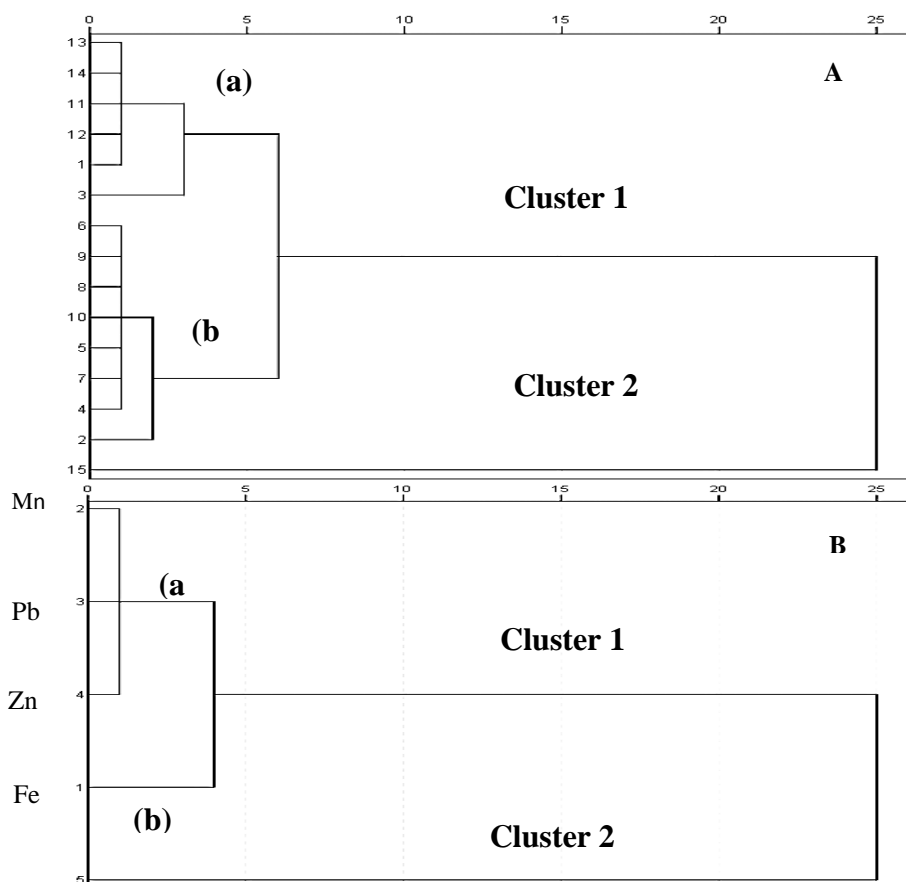


Fig. 3. Dendrogram obtained with the Hierarchical cluster analysis (HCA): A) Sampling in the Perak River; B) Heavy metals at Perak River water

The CA results for the heavy metals shown in Fig. 4 (B) illustrates that Ca was at cluster 2 and grouped separately from other heavy metals, indicating that its origins was basically different from those of Mn, Pb, Zn, Fe and Cr which grouped in cluster 1. The Mn, Pb and Zn which in sub-cluster (a) can also be grouped together, indicating the sources of these metals were same. These metals were released from point sources and non-point sources such as untreated domestic effluents, wastewater of livestock husbandry farms, agriculture and urban runoff.

CONCLUSIONS

Water quality assessment can be considered as one of the major prerequisites for sustainable water resources management in the developing as well as developed countries. Except temperature, all the physico-chemical parameters in the present study were within the acceptable limits as per the guideline values recommended by MOH (2004) and USEPA (2012). Perak River water is significantly contaminated with Fe which is approximately eleven times higher than the standard value set by MOH (2004) and USEPA (2012), the rest of the heavy metals (Zn, Pb, Cr and Mn) were within the standard limits. Pearson correlation matrix showed that most of the heavy metals in water were significantly correlated with temperature, DO, pH and electrical conductivity indicating that these parameters are the major influential factors in metal solubility and governing metals speciation and thus their distribution in river environment. However, further investigation related to seasonal variations of physico-chemical parameters and metallic constituents, preparation of water quality index of Perak River water are highly recommended. Moreover, regular monitoring of water quality is essential for sustainability of environment and maintaining functional human health.

ACKNOWLEDGEMENT

The authors are grateful to Shihab Ahmad Shahriar, Department of Environmental Science and Disaster Management, Noakhali Science and Technology University, Noakhali-3814, Bangladesh, for his technical co-operation regarding study area preparation by GIS methodology.

REFERENCES

- Ahmad, Z., Rahim, N. A., Bahadori, A. and Jie, Z. (2016). Improving water quality index prediction in Perak River basin Malaysia through a combination of multiple neural networks. *Int. J. Riv. Bas. Manag.*, 15 (1), 79-87.
- Al-badaii, F. M., Othman, S and Gasim, M. B. (2013). Water quality assessment of the Semenyih River, Selangor, Malaysia. *J. Chem.*, Article ID 871056, 10 pages.
- Anny, F., Kabir, M. M. and Bodrud-Doza, M. (2017). Assessment of surface water pollution in urban and industrial areas of Savar Upazila, Bangladesh. *Pollution*, 3(2), 243-259.
- Carpenter, S. R., Caraco, N. F., Correll, D. L., Howarth, R. W., Sharpley, A. N. and Smith, V. H. (1998). Non-point pollution of surface waters with phosphorus and nitrogen. *Ecol Appl.*, 8(3), 559-568.
- Chapman, D. (1992). *Water Quality Assessment*. In: Chapman D. On behalf of UNESCO, WHO and UNEP. London: Chapman & Hall, 585.
- Da Silva, A. M. M. and Sacomani, L. B. (2001). Using chemical and physical parameters to define the quality of Pardo River water (Brazil). *Water Res.*, 35, 1609-1616.
- Einax, J. W., Zwanziger, H. W. and Geib, S. (1997). *Chemometrics in environmental analysis*, Wiley, Weinheim.
- Faisal, B. M. R., Majumder, R. K., Uddin, M. J. and Halim, M. A. (2014). Studies on heavy metals in industrial effluent, river and groundwater of Savar industrial area, Bangladesh by Principal Component Analysis. *Int. J. Geomat. Geosci.*, 5(1),182-191.
- Fatoki, O. S., Lujiza, N. and Ogunfowokan, A. O. (2002). Trace metal pollution in Umtata River. *Water SA.*, 28, 183-190.
- Hacioglu, N. and Dulger, B. (2009). Monthly variation of some physicochemical and microbiological parameters in Biga stream (Biga, Canakkale, Turkey). *Afr. J. Biotechnol.*, 8, 1927-1937.
- Hagedorn, B. (2008). Acid digestion of waters for total recoverable metals (following EPA method

- 3005). Applied Science, Engineering, and Technology Laboratory, University of Anchorage Alaska. pp. 1-14.
- Hem, J. D. (1985). Study and interpretation of the chemical characteristics of natural water. 3rd Ed. Washington: United States Geological Survey.
- Hossain M. A., Mir S. I. and Nasly M. A. (2013) surface water quality assessment of Tunggak River Gebeng, Pahang, Malaysia. 4th International Conference on Water & Flood Management, 47-53.
- Jarvie, H. P., Whitton, B. A. and Neal, C. (1998). Nitrogen and phosphorus in east coast British rivers: speciation, sources and biological significance. *Sci Total Environ.*, 210/211, 79–109.
- Kabir, M. M., Fakhruddin, A. N. M., Chowdhury, M. A. Z., Fardous, Z. and Islam, R. (2017). Characterization of tannery effluents of Hazaribagh area, Dhaka, Bangladesh. *Pollution.*, 3(3), 395-406.
- Kabir, M.M., Fakhruddin, A.N.M., Chowdhury, M.A.Z., Pramanik M.K. and Fardous, Z. (2018). Isolation and characterization of chromium (VI)-reducing bacteria from tannery effluents and solid wastes. *World J Microbiol Biotechnol.*, 34, 126.
- Karbassi, A., Mir Mohammad Hosseini, F., Baghvand, A. and Nazariha, M. (2011). Development of Water Quality Index (WQI) for Gorganrood River', *Int. J. Environ. Res.*, 5(4), 1041-1046.
- Lim, W. Y., Aris, A. Z. and Zakaria, M. P. (2012). Spatial variability of metals in surface water and sediment in the langat River and geochemical factors that influence their water-sediment interactions. *Sci. World J.*, Article ID 652150, 14 pages.
- Mark, E.T. and Dulasiri, A. (2010). Optical Emission Inductively Coupled Plasma in Environmental Analysis. *Encyclopedia of Analytical Chemistry*. Pp. 1-13.
- McKenna, Jr., J. E. (2003). An enhanced cluster analysis program with bootstrap significance testing for ecological community analysis. *Environ. Mode. Softw.*, 18 (3), 205-220.
- Memet, V., Bulent, G. and Aysel, B. (2013). Dissolved heavy metals in the Tigris River (Turkey): spatial and temporal variations. *Environ Sci Pollut Res.*, 20, 6096-6108.
- MOH (2004). Ministry of Health Malaysia, National standard for drinking water quality.
- Muhammad, B.G., Mohd, E. H. T., Ahmad, A., Mir, S.I. and Tan, C.C. (2008). Water quality of several feeder Rivers between two seasons in Tasik Chini, Pahang. *Sains Malays.*, 37(4), 313–321.
- Nabi Bidhendi, G.R., Karbassi, A.R., Nasrabadi, T. and Hoveidi, H. (2007). Influence of copper mine on surface water quality. *Int. J. Environ. Sci. Technol.* 4 (1), 85-91.
- Nasrabadi, T. (2015). An Index Approach to Metallic Pollution in River Waters. *Environ Model Assess.*, 17, 411–420.
- Nasrabadi, T., Nabi Bidhendi, G. R., Karbassi, A. R. and Mehrdadi, N. (2010). Partitioning of metals in sediments of the Haraz River (Southern Caspian Sea basin). *Environ. Earth Sci.*, 59, 1111-1117.
- Noori, R., Karbassi, A., Farokhnia, A. and Dehghani, M. (2009). Predicting the longitudinal dispersion coefficient using support vector machine and adaptive neuro-fuzzy inference system techniques. *Environ. Engin. Sci.*, 26 (10), 1503– 1510.
- Otto, M. (1998). Multivariate methods." In: Kellner, R., Mermet, J.M., Otto, M., Widmer, H. M. (Eds.), *Analytical Chemistry*, WileyVCH, Weinheim.
- Saeedi, M., Li, L.Y., Karbassi, A.R and Zanjani A.J. (2013). Sorbed metals fractionation and risk assessment of release in river sediment and particulate matter. *Environ Monit Assess.*, 185, 1737–1754.
- Saiful, I., Kawser, A., Raknuzzaman, M., Habibullah. M. and Kamrul, I. (2015). Heavy metal pollution in surface water and sediment: A preliminary assessment of an urban river in a developing country. *Ecol Indi.*, 48, 282-291.
- Tengku Yahya, T.F. (2008). River Management System: Yes To 'Kg/Day', No To 'Mg/L'
- Varol, M. and Bulent, S. (2012). Assessment of nutrient and heavy metal contamination in surface water and sediments of the upper Tigris River, Turkey. *Catena.*, 92, 1-10.
- Voica, C., Kovacs, M. H., Dehelean, A., Ristoiu, D. and Iordache, A. (2011). ICP-MS determinations of heavy metals in surface waters from Transylvania. *Environmental Physics.*, 57(7-8), 1184-1193.
- Wang, L., Wang, Y., Xu, C., An, Z. and Wang, S. (2011). Analysis and evaluation of the source of heavy metals in water of the River Changjiang. *Environ Monit Assess.*, 173, 301-313.
- WHO (2004). Guidelines for drinking-water quality, Third Ed. WHO, Geneva, Switzerland.

