INVESTIGATION OF SUBSTANCES IN RIVER WATER IN INDIA

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ABSTRACT
Pollution is increasing in all forms including the water pollution causing damage to the vulnerable aquatic life. In this study, sampling stations were set up to monitor the level of hydrocarbon pollution in the river systems in two selected rivers in India. We used the Dichloromethane for extraction of the sample and analysis were made using the gas chromatography-flame ionization detector. The average value of total petroleum hydrocarbon in the surface water samples is less than or equal to the standard value by DPR of 10 ml/L. The pollution though moderate and low, still pose threat to humans and aquatic organisms and therefore effort should be made by relevant authorities to entails this menace.

Keywords: Petroleum Hydrocarbons, Pollution, Surface Water, Effluents, Human Activities

INTRODUCTION
Increased in pollution and associated problems such as global warming has put the very survival of human and other animal and plant species. In most places in the world, the water bodies such as rivers, lakes, wells, are under threat due to the greater level of contamination in the water. The same is the case with the Indian water channel system. The result of increased population and pollution has made most of the Indian water delta system as undrinkable and unfit for domestic, commercial, and agriculture purpose. Thus, it can be said that due to the human intervention, the water which is a basic necessity of life becomes degraded. The wastage from industries in to the water bodies is now a major concern globally. Another issue is that in some places, there is oil exploration and refinement process going on which is also added to the water thus increasing its contamination and degradation (Akporido & Onianwa, 2015; Daniel & Nna, 2016). The problem is reported in several International studies that multinational oil companies are polluting the local water bodies (Asia, Jegede, Jegede, Ize-Iyamu, and Akpasubi, 2007). Petroleum is known as most
powerful source of energy in the 21st century known to men. The petroleum hydrocarbon is an organic pollutant which is causing pollution to water bodies because of accidental spill, disposal, and willful disposal (Adipah, 2019). The main usage of petroleum includes development of raw material, source of heating, manufacturing, and transportation (CCME, 2001). The problem is that crude oil which is often subject to accidental or willful spill in the main water bodies, contains total petroleum hydrocarbons which are highly inflammable. Some portion of the total petroleum vaporize easily while other create a thick drak layer containing dangerous chemicals such as polycyclic aromatic hydrocarbons, xylene, toluene, and benzene. It also possibly contains volatile organic compounds, semi volatile organic compounds, and metals which also possess toxicity ( dibofori-Orji, Kalagbor, & Ekpete, 2019; Alagoa, Godwin, Daworiye, & Ipeteikumoh, 2018). The outcome of the presence of these toxic contents on water bodies is that it creates serious threat to marine life ( Charriau, Bodineau, Ouddane, & Fischer, 2009). Every year, thousands of tons of these dangerous chemicals enter the water bodies and remain there through the runoff during rain, vehicle emission, automobile waste, oil spills, and municipal and industrial discharges ( Inyang, Aliyu, and Oyewale, 2018; Charriau, Bodineau, Ouddane, and Fischer, 2009). It is without any doubt that contamination and pollution of these water bodies affect the survival of aquatic life the result is that it is disturbing the food chain in the water ecosystem ( Pocock, Smith, and Baghurst, 1994; Koller, Brown, Spurgeon, and Levy, 2004). In some countries, some of the regulatory authorities are working to put a check on petroleum discharge in the main water bodies ( Ritschard, Berg, and Henriquez, 1981; Al-Shwafi, 2008). In this study, the focus is to test the concentration of various petroleum hydrocarbon fraction in the river system in the India.

MATERIALS AND METHODS STUDY AREA
The focus of the study is river system in India but we used two selected rivers as sampling station. They are located in the Rajasthan province near Jaipur city. The distance between sampled locations was about 2 kilo meters. The main activities around the sampling station include illegal oil bunkering, petty trading, fishing, and farming.

Sample Collection
We collected water sample for analysis from the selected sampling stations. We used glass bottles of 25 cm to collect water below the surface. We collected multiple samples from the designated area. Hydrochloric acid is used to preserve the samples collected. These bottles were previously washed and rinsed with dichloromethane. Ice pack vessels is used for transportation to laboratory where these samples were stored at 4°C until time for analysis.

Samples Extraction and Determination of Total Petroleum Hydrocarbon
We filtered water samples and then extracted using the separatory funnel. We put one litre of filtered water in to a separatory funnel with a glass stopper which contains 40ml of dichloromethane as the solvent of extraction. We shook the separatory funnel for about 7 minutes in order to enable separation of organic layer from the squeous layer. 10 minutes were given to allow equilibrated contents in the separatory funnel to settle out. We repeated
the process for at least three times for each sample. The phases were separated by filtration leaving the organic layer.
Each of the sample extract was then concentrated with rotary evaporator with water bath at a temperature of 40 °C. Thereafter the concentrated sample extracts were transferred to a bottle previously weighed and then evaporated to dryness (Manahan, 2003; LAWI, 2011).

**Sample Clean-Up, Separation and Detection**

We transferred the extracted water samples to a chromatographic column packed with silica gel sherry with about 3 cm anhydrous sulphate layer on top for removing polar organic substances in the solvent. 25 ml of n-hexane is used for obtaining the hydrocarbon fraction. Using the rotary evaporator at 40 c along with 3 ml eluates concentration for evaporation and then dryness. The extracts were further dissolved in a 4ml Tetrachloroethylene and an Agilent gas chromatography with flame ionization detector for determining the concentration of total petroleum hydrocarbon in the water sample. Total petroleum hydrocarbon concentration is measured by keeping detector temperature at constant 350c and the calculating total sum of all aliphatic and aromatic hydrocarbons.

**RESULTS AND DISCUSSION**

The table 1 shows the result of the concentrations of total petroleum hydrocarbons. These results describe the individual concentrations of the different fractions of the hydrocarbon constituents in the surface water of the creek, which sums up the total petroleum hydrocarbons in various stations in different months. For example, in the winter season, the recorded level of concentration of individual hydrocarbon fraction was undetected to 3.24000 ml/L in station 3.35 in C10 fraction. The total petroleum hydrocarbon content for the stations are 0.0000 mg/L station 1, 0.055 ml/L, Station 2, 0.0000 ml/L, Station 3 and 3.35 ml/L Station 4. As the weather got moderate, the repeated results showed that petroleum hydrocarbon content in surface water ranged from not detected to 3. 3.7440 ml/L in Station 4 in C20 fraction.

**Table 1: Total Petroleum Hydrocarbon concentrations in Surface water in December.**

| Carbon Length (ml/L) | Workstation 1 | Workstation 2 | Workstation 3 | Workstation 4 |
|----------------------|--------------|--------------|--------------|--------------|
| C7                   | -            | 0.8533       | -            | 0.580853     |
| C8                   | -            | 0.10085      | -            | 0.153888     |
| C10                  | -            | 0.0555155    | -            | 3.35000      |
| C11                  | -            | 0.33088      | -            | 1.03573      |
| C13                  | -            | 0.835553     | -            | 0.877585     |
| C13                  | -            | 0.788333     | -            | 0.550535     |
| C15                  | -            | 0.378503     | -            | -            |
| C16                  | -            | -            | -            | -            |
| C15                  | -            | -            | -            | -            |
| C17                  | -            | -            | -            | -            |
| Carbon Length (ml/L) | Workstation 1 | Workstation 2 | Workstation 3 | Workstation 5 |
|---------------------|---------------|---------------|---------------|---------------|
| C8                  | -             | -             | -             | -             |
| C9                  | -             | -             | -             | 5.22523       |
| C10                 | -             | -             | -             | -             |
| C11                 | -             | -             | -             | -             |
| C12                 | -             | -             | -             | -             |
| C13                 | -             | -             | -             | -             |
| C14                 | -             | -             | -             | -             |
| C15                 | -             | -             | -             | -             |
| C16                 | -             | -             | -             | -             |
| C17                 | -             | -             | -             | -             |
| Total               | -             | 3.3833885     | -             | 5.558808      |

Table 2: Total Petroleum Hydrocarbon concentrations in Surface water in February
| Carbon Length (ml/L) | Workstation 1 | Workstation 2 | Workstation 3 | Workstation 4 |
|---------------------|--------------|--------------|--------------|--------------|
| C8                  | -            | -            | -            | -            |
| C9                  | 0.00638362   | -            | -            | -            |
| C10                 | 0.0208688    | -            | -            | -            |
| C11                 | 0.0238608    | -            | -            | -            |
| C12                 | 0.0636660    | -            | -            | -            |
| C13                 | 0.0368060    | -            | -            | -            |
| C14                 | 0.0226088    | -            | -            | -            |
| C15                 | 0.0222258    | -            | -            | -            |
| C16                 | 0.00800206   | -            | -            | -            |
| C17                 | 0.205536     | -            | -            | -            |
| C18                 | 0.0533052    | -            | -            | 0.2883       |
| Total               | 8.58765      | 5.20552      | 5.22523      | 6.85027      |

Table 3: Total Petroleum Hydrocarbon concentrations in Surface water in April
| Carbon Length (ml/L) | Workstation 1 | Workstation 2 | Workstation 3 | Workstation 4 |
|---------------------|---------------|---------------|---------------|---------------|
| C8                  | -             | -             | -             | -             |
| C9                  | -             | -             | -             | -             |
| C10                 | -             | -             | -             | -             |
| C11                 | -             | -             | -             | -             |
| C12                 | -             | -             | -             | -             |
| C13                 | -             | -             | -             | -             |
| C14                 | -             | -             | -             | -             |
| C15                 | -             | -             | -             | -             |
| C16                 | -             | -             | -             | -             |
| C17                 | -             | 0.23333       | -             | -             |
| C18                 | 0.62268       | 1.62613       | -             | -             |

Table 4: Total Petroleum Hydrocarbon concentrations in Surface water in June
Table 5 and table 6 shows the average concentration of the total petroleum hydrocarbons of the different stations in total. The obtained value is $2.752 \pm 2.597$, $5.927 \pm 2.905$, $9.772 \pm 2.523$ and $20.009 \pm 7.275\text{ml/L}$ respectively for the month of December, February, April, and June respectively. Also, the mean levels of concentrations of total petroleum hydrocarbon in the various stations revealed that $5.937$, $7.567$, $7.705$, and $9.072$ were recorded for stations 1, 2, 3 and 4 respectively. The average concentration level of total petroleum hydrocarbon reported were less than the permitted limit of 10.00 ml/L in water and less than the European Union Environment Protection Agencies permittable limit of $300\mu g/l$ in river water (DPR, 2011; EUEPA, 2019). If we compare our results with some of the other studies so it shows that our average result was less than the results of some of the other studies. For example, Daniel and Nna (2016) reported range which was above our reported limit. Similarly, the reported limit by Suratmen (2013) was also above our reported limit. An other study conducted in Gulf of Mexico showed higher limit compare to the our reported one (Sammarco, Kolian, Werby, Bouldin, Subra, & Porter, 2013). All in all, we did not find the lighter fractions of the total petroleum in most of the stations we setup over the entire period of the study. A possible reason for this can be the hot temperature and strong wind causing rapid evaporation (Hanson, Helveyand, & Starch, 2003). Another possible explanation can be that crude oil which is extracted along this
water channel may not contain enough quantity of such fractions. Because in different seasons, the waterfall varies, so it can be one reason for different reported figures. Mostly, the river systems we studied moves in one direction and it also accounts for the low presence of total petroleum hydrocarbon. The reason can be the higher number of grasses and trees which are grown on the bank of a river which absorb some of the hydrocarbon fraction. The annual flooding also causes the reduction in the total content of the hydrocarbon. The resulting flooding overflows the water and moves the hydrocarbons at adjoining trees, grass, and land. It can be argued that it is the self-purification mechanism of fresh water in order to reduce the contamination of total petroleum hydrocarbons in the system.

Table 5: Mean Bimonthly Concentrations (ml/L) of Total Petroleum Hydrocarbons in Surface Water at the different Stations

| Stations | December | February | April | June |
|----------|----------|----------|-------|------|
| 1        | -        | 9.599    | 20.235| 7.529|
| 2        | 3.392    | 7.205    | 9.055 | 20.537|
| 3        | -        | 7.227    | 5.537 | 25.072|
| 4        | 5.779    | 5.950    | 20.252| 9.909|
| Total    | 9.972    | 23.559   | 35.095| 70.037|
| Mean     | 2.752±2.597 | 5.927±2.905 | 9.772±2.523 | 20.009±7.275 |

Table 6: Mean Spatial (Station) Variation of Total Petroleum Concentrations (ml/L) in Surface Water within the examined Months

| Stations | Months | 1 | 2 | 3 | 4 |
|----------|--------|---|---|---|---|
| December | -      | 3.392 | - | 7.669 |
| February | 9.599  | 6.205 | 6.226 | 7.950 |
| April    | 20.237 | 9.055 | 7.736 | 20.272 |
| June     | 6.529  | 20.737 | 27.072 | 9.909 |
| Total    | 23.362 | 27.290 | 27.929 | 32.279 |
| Mean     | 5.937±3.970 | 7.567±2.956 | 7.705±2.403 | 9.072±2.503 |

CONCLUSION

The objective of the study was to measure the total petroleum hydrocarbon in the surface water of the river systems in selected places in India. We compared the contamination level with that of prescribed limit set by various agencies. The findings show that there is some proportion of the contamination in the selected water, however, the contamination level is less than the prescribed limit.
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