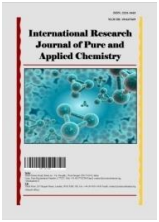

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Seasonal Trend of Polyaromatic Hydrocarbons (PAHs) in Sediments from River Ethiope in the Niger Delta Region of Southern Nigeria

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Authors' contributions

This work was carried out in collaboration among all authors. Author IEA conceptualized and designed the protocol of the study in collaboration with authors OE and GA. Authors SO and UB carried out the sampling and wrote the literature review for the study. Author OE wrote the first draft of the manuscript. Authors SO and UB were responsible for the statistical analysis and converting the raw data to graphics. All authors read and approved the final manuscript.

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ABSTRACT

Seasonal trends of polycyclic aromatic hydrocarbon in the sediment of River Ethiope in Delta State, Southern Nigeria were assessed in this study. Samples were taken from six different points at Ethiope River along its banks during the dry and rainy seasons. Samples were extracted using soxhlet apparatus and analysed with gas chromatography-flame ionization detector (GC/FID). The results obtained for the PAHs concentration ranges from 184.73 µg/kg – 3679.13 µg/kg for dry season and for rainy season, some stations were below detection limit (BDL) to a maximum value of 693.43 µg/kg. The result clearly shows that the total concentration of polycyclic aromatic hydrocarbon detected in the dry season was higher than those of the rainy season. Similarly, more PAHs compound of higher and lower rings were found in the dry season than in the rainy season in sediment samples. Although, the PAHs concentrations were quite low which indicated no danger status from the consumption or dermal contact for humans' point of view, however, the levels can cause adverse effects for lower aquatic organisms which are exposed to the sediments on a daily basis. Therefore, persistent monitoring and strict adherence to responsible waste discharge should

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be upheld by all manufacturing and agro industries located in the study area in order to avoid deleterious effects of the biodiversity in the water bodies as well as ensuring safety of the consumers.

Keywords: PAHs; sediment; River Ethiope; seasons.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic chemicals containing two or more aromatic rings without any heteroatoms or substituents [1]. They are neutral nonpolar compounds with at least two aromatic rings and carbon and hydrogen atoms only [2] are mainly formed during carbonization and incomplete combustion of organic materials [3,4]. PAHs, which is one of the most widely distributed groups of organic pollutants originating from petrogenic, pyrogenic, and natural sources, have long been of environmental concern because of their mutagenic and carcinogenic properties. Waste products containing significant amounts of PAHs are indiscriminately dumped into water, on land or buried at sub-surface sites. Although, these toxic substances can be found in the water, sediments and biota of aquatic environment but for the course of this study, we will be focusing on sediments [5,6]. Airborne particulates resulting from PAHs activities are transported in the atmosphere and are usually deposited in soils and sediments of aquatic system [5-7]. In general, PAHs dissolved in pure water are accumulated in sediments [6] and digestion of sediment may play an important role in the uptake of PAHs by some species.

Aquatic environment, which is a habitat for a large number of organisms, are prone to contamination. These may be because of the fragile nature of the biodiversity of the ecosystem that can be affected by natural and anthropogenic activities that are not favourable to that specific habitat. Continuous anthropogenic input as major contributors of pollutants into the aquatic environment constitutes a potential threat to natural ecosystems because of direct effect on the water quality as well as aquatic organisms since majority of pollutants entering into the marine environment are chemical in nature [8]. A good example is PAHs, and the major entry points of these toxic substances into aquatic ecosystem (i.e. surface water) are usually through point source such as industrial discharges and run offs from polluted areas into water bodies [9,10].

Sediment, which is a part of the aquatic ecosystem is a complex aqueous formation usually at the bottom part of an aquatic environment containing substrates and other compounds that characterise the type of activities in the surrounding aquatic or terrestrial environment in which the sediment is found [11,12]. Sediment therefore remains the potential sink for petroleum hydrocarbons and other organic pollutants, and its contamination could represent a very great health hazard for many aquatic organisms that reside in such an ecosystems [13].

PAHs which are one of the many compounds that could concentrate in sediments have been found to reflect the history of fossil fuel combustion in the environment [11,12]. In aquatic environments, PAHs are mainly derived from atmospheric deposition, municipal and industrial effluents, land run-off, and oil spills or leakages [14-17]. PAHs constitute a major environmental concern on aquatic ecosystems because of their adverse health effects on organisms, including endocrine disrupting activity [18,19]. One of the major risk of PAHs to the environment is that PAH is a persistent contaminant and tends to linger for a long time when it enters the environment [20-22]. In the coastal zones, organic contaminants (PAHs, pesticides, organic-metals) and inorganic (trace elements) accumulate in sediments [23,24]. Thus, the sediment becomes such an important place for storage of pollutants [24]. Sediments are the main environmental sink for PAHs, as PAHs within sediments experience minimal photochemical or biological degradation and well preserved [25,26].

Sediment contamination can be impacted by the temporal variations of anthropogenic activities as well as by the seasonal fluctuations of riverine water discharges [24]. The objectives of this study is to assess the seasonal changes of PAHs in the sediments samples from River Ethiope in Niger Delta region of southern Nigeria.

2. MATERIALS AND STUDY AREA

2.1 Study Area

The study area (Fig. 1) was River Ethiope in Delta State, Niger Delta, Southern Nigeria, which is the second largest Delta in the world and the

largest mangrove swamps in Africa. It spans over 20,000 square kilometers. The Niger Delta region is located between 5º 31' and 5º33'N Latitude and 5º30' and 5º32'E Longitude. The Niger Delta covers an area of 70,000 km^2 of marshland, creeks and tributaries that drains the River Niger into the gulf of Guinea in the Atlantic Ocean. The coastal region cuts across nine (9) states in southern Nigeria. This region has an estimated population of over 30 million people, with fishing and farming as the main source of livelihood and sustenance. Economic activities include oil and gas exploration and exploitation, fishing industries, agriculture and tourism.

2.2 Sampling

Samples were collected from Ethiope River Upstream along its banks at the following towns: Umuaja, Umutu Abraka, Eku, Okpara waterside and Sapele axis during the dry season (December) and rainy season (July). A total of thirty-six (36) sediment samples were collected, made up of eighteen (18) samples in each season, comprising six sampling sites. Wet sediment samples were collected in clean glass bottles and kept cooled during transportation. In the laboratory, samples were frozen awaiting sample preparation and analysis. Sediment samples were air-dried three days and sieved with 0.5 mm mesh size before sample extractions [27,28].

2.3 Extraction of Samples

The process of sample extraction of this study is similar to the extraction process carried out as stated below [29].

2.3.1 Extraction and fractionation of sediment samples

10 g of the sediment sample was blended with 10 g of anhydrous sodium sulphate. The mixture was placed in an extraction thimble and refluxed for 4 hours with 50 ml methylene chloride. Thereafter the solution was cooled, dried with 5 g anhydrous sodium sulphate, and concentrated to 1 ml in a rotary evaporator. The concentrate was fractionated over silica gel column, first eluted with 10 ml hexane and collected as aliphatic fraction, and then with 15 ml methylene chloride, and collected as aromatic fraction.

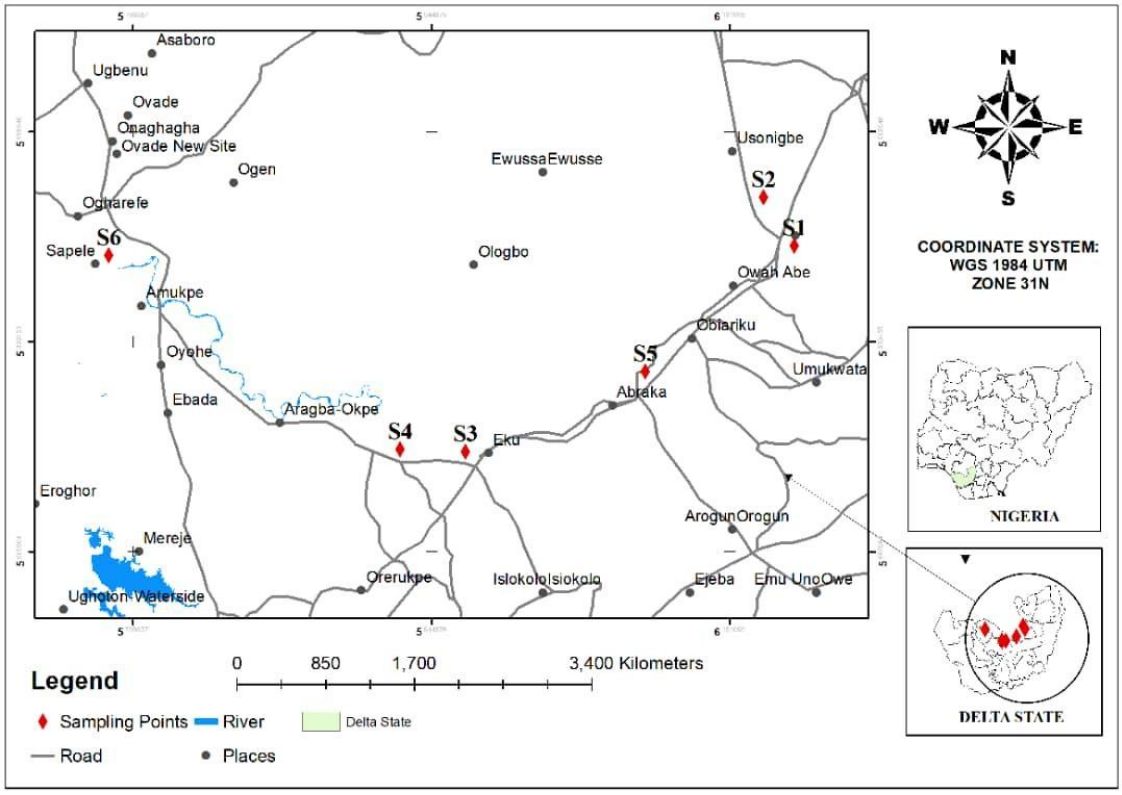

Fig. 1. Map showing the various study areas of River Ethiope

Table 1. Geographical coordinates of the sampled stations

S/No	Sampling locations	Sampling coordinates	
		Northing	Easting
Station 1	Umutu	05°54' 31"	06°13' 58"
Station 2	Umuaja	05°56' 49"	06°12' 30 "
Station 3	Eku	05°44' 43 "	05°58' 20 "
Station 4	Okpare waterside	05°44' 49 "	05°55' 13"
Station 5	Abraka	05°48' 32 "	06°06' 53 "
Station 6	Sapele	05°54' 03 "	05°41' 22 "

2.4 Analysis of Samples

Analysis was done using Gas Chromatography (GC). 1µl of the concentrated sample was injected by means of exmiremicrosyringe through rubber septum into the column. Separation occurs as the vapour constituent partition between the gas and liquid phases. The sample was automatically detected as it emerges from the column by a Flame Ionisation Detector (FID). PAH quantification was carried out by CLARITY-GC interfaced software [29].

3. RESULTS AND DISCUSSION

The results of the sediment samples analysed for dry and rainy seasons are as shown in Figs. 2, 3 and Fig. 4 respectively.

From Fig. 2, the total concentration of the individual PAHs compounds across the six sampling points during the dry seasons are as follows: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace) were below the detection limit (BDL), Fluorene (Flu) 85.5 µg/kg, Phenanthrene (Phen) 376.13 µg/kg, Anthracene (Ant) 100.13 µg/kg, Fluoranthene (FluA) 846.75 µg/kg, Pyrene (Pyr) 343.73 µg/kg, Benzo(a)anthracene (BaA) 819 µg/kg, Chrysene (Chy) 1845 µg/kg, Benzo(b)fluoranthene (BbF) 1777.5 µg/kg, Benzo(k)fluoranthene (BkF) 1803.75 µg/kg, Benzo(a)pyrene (BaP) 2126.25 µg/kg, on the otherhand, Dibenz(a,h)antracene (DahA) Indeno(1,2,3-cd)pyrene (IcdP) and benzo(g,h,i)perylene (BghiP)were also below the detection limit (BDL).

From Fig. 3, the total concentration of the individual PAHs compounds across the six sampling points during the rainy season are as follows: Napthalene (Nap), Acenaphthylene (Acy), Anthracene (Ant), Benzo(b)fluoranthene (BbF), Dibenz(a,h)antracene (DahA), Benzo(a)pyrene (BaP), Benzo(k)fluoranthene (BkF), Acenaphthene (Ace), Indeno(1,2,3-cd)pyrene (IcdP) and Benzo(g,h,i)perylene (BghiP) were BDL. While Fluorene (Flu) 83.5 µg/kg, Phenanthrene (Phen) 97.23 µg/kg, Fluoranthene (FluA) 222.96 µg/kg, Pyrene (Pyr) 26.41 µg/kg, Benzo(a)anthracene (BaA) 185.57µg/kg and Chrysene (Chy) 185.87 µg/kg.

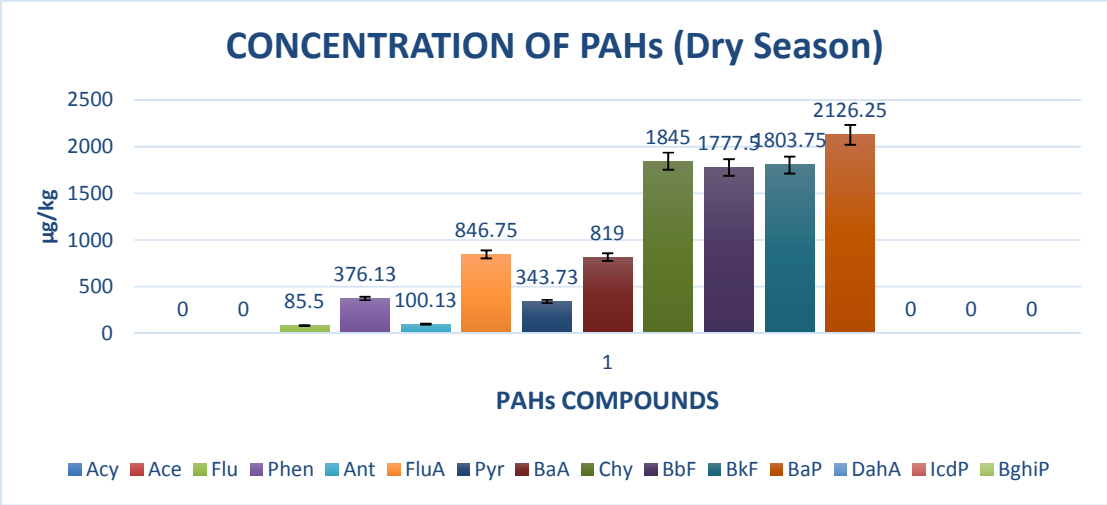

Fig. 2. Bar chart showing the PAHs concentration of the sediment during dry season

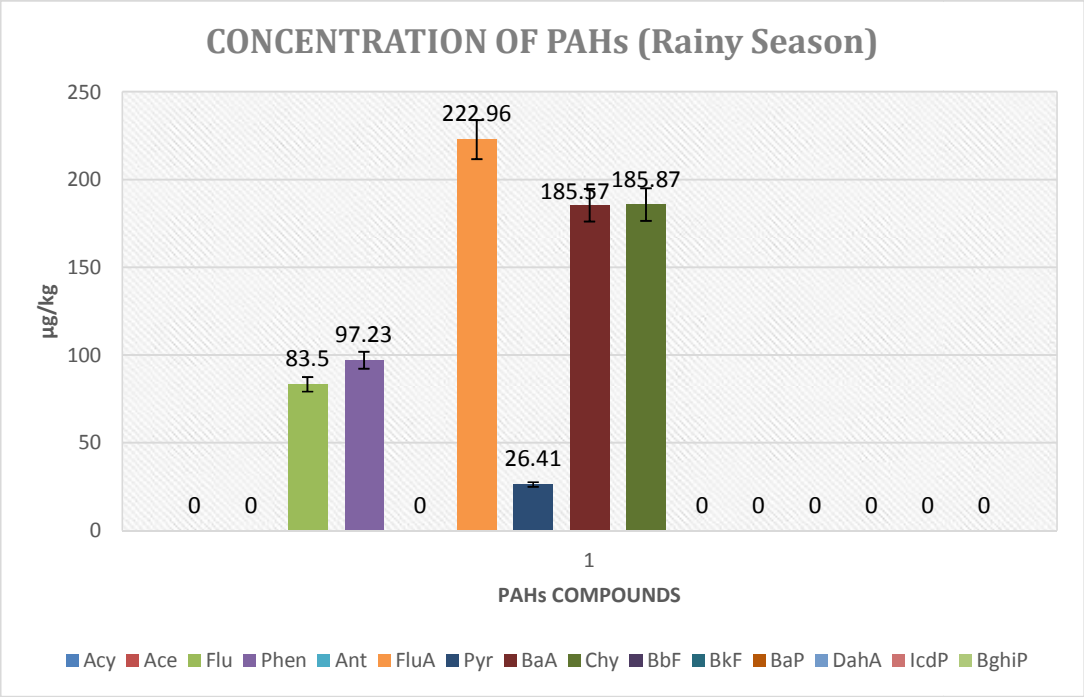

Fig. 3. Bar chart showing the PAHs concentration of the sediment during rainy season

In general, the mean total PAHs levels from the various sample locations analysed as shown in Fig. 4, ranged from 184.73 µg/kg – 3679.13 µg/kg during the dry season. While for the rainy season, some of the samples ranged from below detection limit (BDL) to 693.43 µg/kg for the rainy season. Generally, the dry season recorded elevated PAHs levels in sediment than the rainy season. This may be attributed to the fact that during dry season water bodies dries up through evaporation and therefore PAHs present in the water get concentrated settles at the bottom and adhere to the surface of the water, sediments of biota of aquatic environment [30].

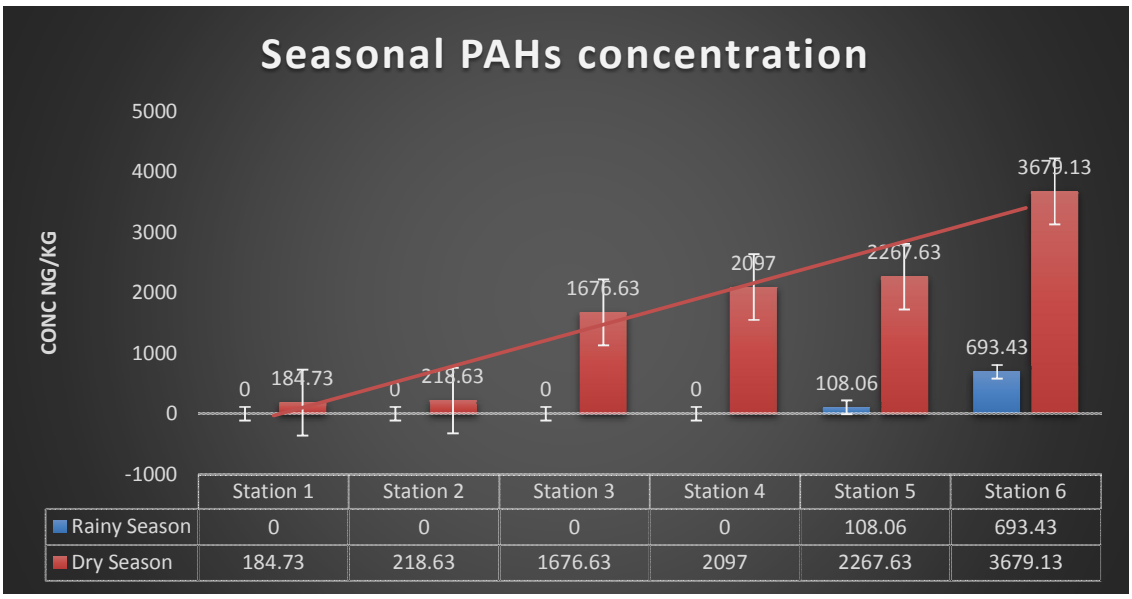

Fig. 4. Bar-chart showing the seasonal variation of PAHs sediment in all stations

During the rainy season, most of the PAHs compounds were not present at most sampling locations, which shows that they were below the detection limit, with over 70% of the sample location having a PAHs total concentration lower than limit of detection (<LOD). This is contrary to the result of the concentration of PAHs obtained during the dry season. Although some PAHs compounds such as Naphthalene, Acenaphthylene, Acenaphthene, Anthracene, Dibenz(a,h)antracene, Indeno(1,2,3-cd)pyrene, Benzo(g,h,i) perylene were found not to be detected (ND) in both seasons.

From Fig. 4, it is observed that station 4, during the rainy season, there was no PAHs concentration within detection limit, while during the dry season a total of 7 PAHs compounds were above the detection limit, with a sum concentration of 2097 µg/kg. This result was similar to that of station 5 but only 6 PAHs compounds were within the detection limit, with a sum concentration of 108.06 µg/kg and 2267.03 µg/kg for both rainy and dry seasons respectively. In station 1, there was no PAHs compound as follows to the previous station during the rainy season and with only two PAHs compounds out of the 16 compounds analysed for were within the detection limits with a total concentration of 184.73 µg/kg and a similar result was obtained for station 2.but the total concentration level during the dry season was a bit higher, with a total concentration of 218.63 µg/kg. It could be said that station 1 and station 2 are less contaminated when compared to other sampled stations. The concentrations recorded in the stations that have no oil formations could imply input result from other sources like domestic wastes, discharge of sewage, drifts from polluted areas and other activities [29,31].

Station 6 on the other hand, was observed to have the highest number of PAHs compounds above the detection limits and a maximum concentration of 3679.125 µg/kg, only six compounds were below the detection limits. From the results obtained, it could be said to be the most polluted station from this study with the highest total concentration of PAHs within the detection limit during the rainy season. It is the only station found to have more than one PAHs compound above the set limit. The total concentration value was 693.43 µg/kg from five PAHs compounds within the detection limit. The pollution of this station could be as a result of the industrial and domestic activities along these areas which have run off to the shores of the River Ethiope.

For station 3, there was no PAHs compound above the detection limits during the rainy season but during the dry season, seven compounds of PAHs were above the detection limit with a total concentration of 1676.63 µg/kg. These were a similar output of 60% of the sediment sample from the various stations analysed during rainy and dry seasons.

Chrysene was found to be highest in all PAHs concentration detected in both rainy and dry seasons with a concentration level of 185.875 µg/kg and 1357.5 µg/kg respectively. Although individual PAHs concentration was high at some locations in the rainy season, most of the lower molecular weights PAHs were below detection limits in the rainy season. This is believed to be responsible for the overall lower result in the season.

The results obtained in this study was higher than the result reported by Essumang et al. [30] This shows the extent of the pollution of Ethiope River when compared to the lagoon analysed by Essam et al. [32] It was found to be lower than the concentration of PAHs level reported by Gilbert et al. [33] in which the total PAHs concentration ranged from 254 mg/kg -558 mg/kg in the sediments from Fosu lagoon [30]. When compared with the water bodies in this study shows that it was relatively less polluted to Fosu lagoon. The values obtained in this study were similar when compared to the study carried out by Bayowa & Agbozu [12], which has a mean PAHs total concentration 0.125 mg/kg – 0.283 mg/kg for dry season but was much lower to the result obtained during the wet season that has a range of 0.065 mg/kg – 0.189 mg/kg as against BDL mg/kg – 0.069 mg/kg.

On the contrary, the results obtained from this study are different from those observed in surface sediments collected in a tropical coastal lagoon (Grand – Lahou Lagoon) in Côte d'Ivoire [2]. In their study, lower concentrations of PAHs were detected in the dry season than in the rainy season [2].

4. CONCLUSION

The study has shown that the total concentration of polycyclic aromatic hydrocarbon detected in the dry season was higher than those of the rainy season, likewise more PAHs compound of higher and lower rings were found in the dry season than in the rainy season in sediment samples collected from Ethiope River, Delta state. This

may be attributed to the fact that during dry season water bodies dry up through evaporation and therefore PAHs present in the water get concentrated settles at the bottom and adhere to the surface of the water, sediments or biota of aquatic environment. Although, the polycyclic aromatic hydrocarbons were below the threat level, which indicated no danger status from the consumption or dermal contact for humans but the levels observed in this study can cause adverse effects for lower aquatic organisms. Therefore, persistent monitoring and strict adherence to responsible waste discharge should be upheld by all industries near these waters in order to avoid deleterious effects of the biodiversity in these water bodies as well as ensuring safety of the consumers.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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