

COMPOSITIONAL PROFILES AND SPATIAL DISTRIBUTION OF MICROPLASTICS ACROSS THREE SELECTED RIVERS IN RIVERS STATE, NIGERIA

ABSTRACT

Microplastics (MP) are ubiquitous and persistent contaminants in waterbodies and a pervasive and preventable threat to the health of marine ecosystems. These particles are defined as <5 mm in size and can be introduced into the environment via primary sources such as the use and disposal of microbeads in cosmetic, cleaning products and sandblasting largely contribute, as well as secondary sources which include the fragmentation of litter by mechanical or UV light-induced degradation. This study was conducted to investigate the concentration of microplastic contaminants in Imo River, Ntawogba River and New Calabar River as well as the physicochemical and microbial characteristics of the water bodies. Composite sampling technique was used in this study. The physicochemical analysis of the water samples was carried out both *in-situ* and *ex-situ* while the microbiological analysis was performed *ex-situ* to determine the load using APHA 9215B/9610B and ASTM D 5465-93 (Pour plate) test methods where the mean concentration of total heterotrophic bacteria (CFU/mL) was 15900.00 ± 14381.58 , 129333.33 ± 21007.94 , 16666.67 ± 5783.02 ; hydrocarbon utilizing bacteria (CFU/mL) mean load was: 170.00 ± 206.64 , 1103.33 ± 105.04 , 370.33 ± 203.81 ; total heterotrophic fungi (CFU/mL) mean load was: 680.00 ± 589.24 , 10366.67 ± 635.09 , 1.00 ± 0.00 ; hydrogen utilizing fungi (CFU/mL) mean load was: 133.33 ± 57.74 , 1.00 ± 0.00 , 1.00 ± 0.00 for Imo River, Ntawogba River, and New Calabar River respectively. Total heterotrophic bacteria was found to be more predominant in all the rivers than the other microorganisms. Two techniques (Fourier Transform Infrared Spectroscopy, FTIR and Gas Chromatography-Mass Spectrometry, GC-MS) were used to identify the microplastics and their concentrations. The reference spectra for the FTIR results were in the spectral range stretching from $4000\text{--}650\text{cm}^{-1}$ where the prominent absorption peak at 2920 cm^{-1} corresponded to aliphatic C-H (Hydrocarbon) stretching, indicating the presence of CH_2 (Alkene) and CH_3 (Alkane) groups in the microplastic samples, at 1725 cm^{-1} associated with carbonyl (C=O), the band at 1600 cm^{-1} is a characteristic of aromatic C=C stretching, at $1200\text{--}1000\text{ cm}^{-1}$ range suggested C-O stretching vibrations, the region between 800 and 700 cm^{-1} corresponded to out-of-plane bending vibrations commonly seen in aromatic groups while the GC-MS polymer identification library produced results of both qualitative and quantitative assessment of the microplastics. The eight (8) priority MP polymers found in the water samples were polyethylene (PE), polyethylene terephthalate, dioctyl terephthalate, polybrominated diphenyl ether, tetrabromobisphenol A, polypropylene, acrylic fibre, and polystyrene. SEM images of the MPs were acquired at various magnifications to capture their surface features, shapes, and sizes. PE was found to be the most ubiquitous MP (45.74%, 45.84% and 47.76%) across Imo, Ntawogba and New Calabar River, respectively.

Results obtained indicate the pervasiveness of MPs in the studied rivers and signify threat to aquatic organisms and man via their biomagnification through the food chain.

Keywords: Microplastics (MP), Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography-Mass Spectrometry (GCMS), polyethylene (PE), polyethylene terephthalate, dioctyl terephthalate, polybrominateddiphenyl ether, tetrabromobisphenol A, polypropylene, acrylic fibre, polystyrene.

1. INTRODUCTION

The term microplastic (MP) was formally introduced in 2004 by Thompson *et al.* (2004) who alerted to the growing problem of the plastic release to the seas. The production of plastics has increased tremendously in the last 60 years, from approximately 1.7×10^6 tons in the 1950s, to 3.2×10^8 tons in 2015 (PlasticsEurope, 2016; Hernandez *et al.*, 2017). This increase was fueled by gradual improvements in plastic manufacturing techniques, which resulted in the production of cost-effective, corrosion-resistant, lightweight, and more durable varieties. Globally, plastics play enormous roles in the delivery of comfort, quality, and safety in modern day lifestyles. Consequently, such high plastic production and usage has resulted in increased generation of plastic waste.

Microplastics are plastic debris with its longest diagonal less than or equal to 5mm (Kalčíková *et al.*, 2017) and originate from primary and secondary sources. Primary sources fulfill a specific need or function e.g., microbeads used in personal care products, abrasive cleaning particles, pre-production resin pellets, and microfibers used in manufacturing textiles (Peter *et al.*, 2020) whereas, secondary sources result from degradation, wear and tear, or fragmentation of larger debris. Secondary sources include litter fragments (e.g., plastic bags, bottles, wrappers, Styrofoam containers, cigarette filters), synthetic fibers from textiles, road salt, and tire wear particles (GESAMP, 2019; Rødland *et al.*, 2020). “In 2015, approximately 6,300 million metric tons of plastic waste was generated, of which only 9% was recycled” (Geyer *et al.*, 2017). “Plastic debris items, ranging in size from microscopic to macroscopic, have been detected in benthic and pelagic habitats in almost all aquatic ecosystems, including remote locations such as the Arctic and the deep sea” (Van Cauwenbergh *et al.*, 2015; Browne *et al.*, 2011). “Several human activities potentially introduce microplastic into the aquatic environment, and examples of such activities include the improper disposal of plastics and the intentional use of microscopic plastic particles for personal and industrial uses (e.g., polyester) which are shed during cloth washing” (Browne *et al.*, 2007; Cole *et al.*, 2011). “Some other sources of microplastics in the aquatic ecosystem include loss of pellets during transportation, wastewater effluent, fishing ropes and gears,

cigarette butts, abrasion from sandblasting at shipyards, plastic waste carried by wind or run-off water, and so on” (Rochman, 2013).

“The impacts posed by microplastic debris depend on the debris size. Large plastic debris such as discarded fishing ropes and nets cause entanglement of invertebrates, birds, and mammals. On the other hand, smaller plastic items, such as bottle caps and plastic pellets, can be ingested, causing obstruction of the gut” (Law & Thompson, 2014). “The omnipresent nature of microplastics in the environment, poses a serious threat because of its persistence in the environment. They are carriers of some chemicals that are typically found at their highest concentrations in the sea-surface microlayer, which is, of course, the predominant layer of low-density microplastics” (Desforages *et al.*, 2014; Foekema *et al.*, 2013). “Microplastics have been found to be ingested by some aquatic microorganisms like fishes and other biota and as such, can find its way into the food chain” (Schirinzi *et al.*, 2017). The most identified plastic polymers in environmental samples are polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinylchloride (PVC) (GESAMP, 2015) and their preponderance in water bodies in Nigeria, especially in regions with high concentration of industrial activities has not been investigated. Hence, this study was aimed to investigate the concentration of microplastics, and the physicochemical and microbial characteristics of Imo River, Ntawogba River and New Calabar River, in Rivers State, Nigeria.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 List of Apparatus and Instruments

Beakers, volumetric flasks, conical flasks, Hanna multi-parameter water checker, weighing balance, glass wares, oxygen sensitive membrane electrode, glass rod, nessler’s tube, membrane electrode, burette, pipette, hot plate, fume cupboard, water bath, plastic containers, aluminum containers, sieve mesh, atomic absorption spectrometer(AAS) (LAAS320 Perkin Elmer), cuvettes, UV/VIS spectrophotometer(HAach PR6000), cuvettes, thermometer, dissolved oxygen analyzer(HQ30D Model55, Pro20), COD digester(Model No. IPM-1915), gas chromatograph, mass spectrophotometer(Perkin Elmer HD 2010), Soxhlet extractor(Model

9903600), rotary vacuum evaporator, conductivity meter(Model LEC210), BOD bottle, Oximeter (HQ30D), Magnetic stirrer(Model HP15P), Teflon beaker, dissolved Oxygen meter, GC/MS(Model 7693 ALS/7890/240),electron gun, lenses, scanning coils, detectors, sample stage, data output device, power supply, vacuum system, cooling system, vibration-free floor, room (Free of ambient electric and magnetic fields), Refractometer(DR60007), Incubators (BANN602), IBM SPSS software.

2.1.2 List of Reagents

Nitric acid, hydrochloric acid, deionised water, dichloromethane, hexane, sodium hydroxide, anhydrous sodium sulphate, ethylene diaminetetracetic acid(EDTA) erichrome black T, stannouschloride, glycerol, ethyl alcohol, sodium chloride, silver nitrate, potassium chromate, ammonium hydroxide, ammonium chloride, magnesium salt of EDTA, distilled water, ammonium buffer, ammonium molybdate, phendisulphoric acid, stock nitrate solution, standard nitrate solution, glycerol, barium chloride, sodium sulphate, potassium dichromate indicator, sodium sulphate, isopropyl alcohol, phosphate buffer, magnesium sulphate, calcium chloride, ferric chloride, standards for metals (Fe, Pb, Zn, Ni, Cu, Cd, V). Every of these reagents used were of analytical grade.

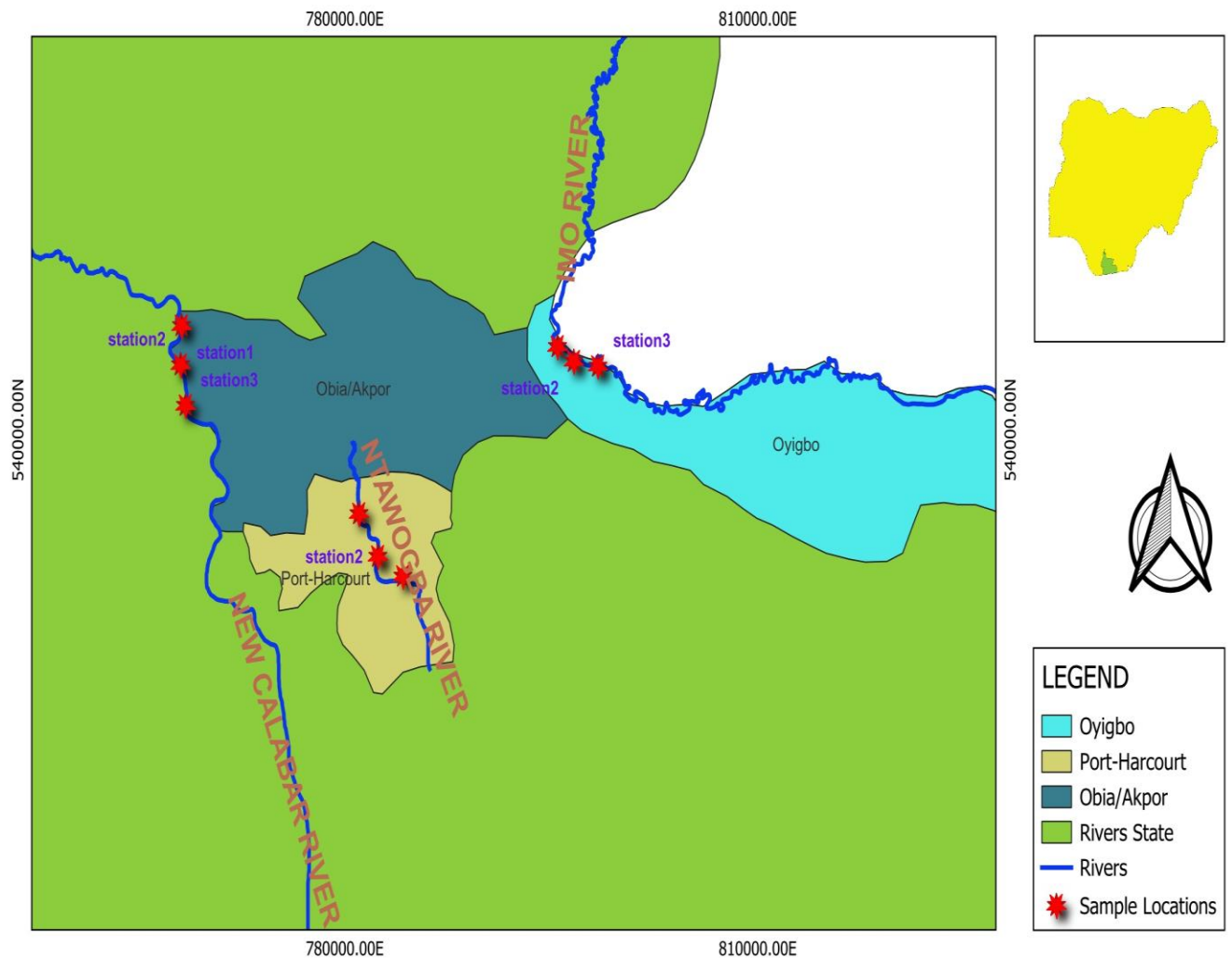
3.1 StudyArea

The study was carried out in Imo River, Ntawogba River and New Calabar River, in Rivers State, Niger-Delta Region of Nigeria.Imo River is in the southern eastern Nigeria and flows 240kilometres (150miles) from Onuimo into the Atlantic Ocean. Its estuary is around 40kilometers (25miles) wide, (Afigbo- Adiele, 2005) and the river has an annual discharge of 4 cubic kilometers (1.0cu/ml) (Menally, 1980) with 26,000 hectares of wetland (Afigbo-

Adiele, 2005). The source location is Okigwe, Imo state and its coordinates are: $5^{\circ}50'56''$ N, $7^{\circ}14'20''$ W.

Ntawogba River is a single-channel low gradient freshwater body (Amangbara & Gobo, 2007) which lies on the extreme west of Port Harcourt Metropolis between the approximate longitude $6^{\circ}58'00''$ to $7^{\circ}06'00''$ E and latitude $4^{\circ}40'00''$ to $4^{\circ}55'00''$ N (Gobo & Abam, 2006). Its upstream is at Rumueme and Rumuepirikom in Obio-Akpor Local Government Area and flows through Government Reserve Area (GRA) Phase III, a less densely populated area to a more densely populated and high economic activity areas of Diobu Axis of Port Harcourt L.G.A. and eventually empties into Amadi Creek.

New Calabar River and its tributaries are one of the series of low-lying delta river which empty into coastal lagoons and creeks bordering the Atlantic Ocean (Vincent-Akpu & Yanadi, 2014). New Calabar river lies between $4^{\circ}30'00''$ and $4^{\circ}49'00''$ N and $6^{\circ}59'00''$ and $7^{\circ}00'00''$ and empties into the Atlantic Ocean (Stanley *et al.*, 2017). The river is freshwater and acidic at the source, but gradually becomes brackish, tidal, and slightly alkaline at the lower zone near its mouth. Figure 1 presents the locations of the studied rivers.



Data Source : SEPRET LIDAR (2015), Google Earth (2022) and ground truth verification.

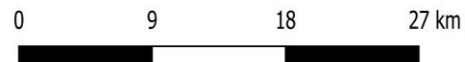


Figure 1. The location of the three rivers studied in Rivers State

3.2 Collection of Water Samples

Using sterile aluminum containers, water samples were collected from three (3) different points in each river. Surface water 1 (SW-1) was collected 100m away from each of the bridges crossing the various rivers: Imo River, Ntawogba River and New Calabar River. Surface water 2 (SW-2) was collected 200m away from SW-1, and surface water 3 (SW-3) was collected 200m away from SW-2 by dipping the sample container 10cm below the water surface against the flow direction. Aluminum sample bottles were conditioned by washing with methanol and allowed to dry under room temperature for 5 days. The pre-cleaned aluminum sampler was immersed 10cm below the water surface and 0.5L of water taken.

Water samples (0.5L) were collected at each sampling location and homogenized to form a composite sample. All sampling points were however geo-referenced, and the coordinates are as presented in Table 1. At each sampling site, the aluminum sampler was rinsed three times before sample collection. Samples for different parameters were taken and preserved according to the method of APHA (2005) and Aiyesanmi (2006) to ensure accuracy and reliability of results and implementing quality control measures to minimize contamination during water sample analysis at the laboratory.

Table 1: GPS coordinates of the different sampling stations

	Imo River	Ntawogba River	New Calabar River
SW-1	7° 8' 44" N 4° 53' 19" E	4° 48' 33" N 7° 00' 56" E	4° 53' 19" N 6° 53' 53" E
SW-2	4° 53' 17" N 7° 8' 45" E	4° 48' 32" N 7° 00' 56" E	4° 53' 20" N 6° 53' 54" E
SW-3	4° 53' 15" N 7° 8' 46" E	4° 48' 31" N 7° 00' 56" E	4° 53' 21" N 6° 53' 55" E

3.3 Analysis of Samples

3.3.1 Physicochemical Analysis

The Hanna Multi-parameter water checker was used to determine pH, temperature, electrical conductivity, turbidity, dissolved oxygen, salinity, and dissolved solutes in the water samples. The probe was first calibrated, then dipped into each sample and the displayed reading was allowed to stabilize before recording. The temperature of the sample was measured in degree Celsius while the electrical conductivity of samples was measured in milliSiemens per meter (mS/m). The turbidity of the samples was measured and reported in NTU (Nephelometric Turbidity Units). Dissolved oxygen, salinity and dissolved solids of the water samples were measured in milligrams per litre (mg/L).

The APHA 2540D test method was used for the determination of total suspended solids (TSS). Deviation from the method was that Whatman filter paper (0.45µm) was used instead of glass fibre filter and the TSS content was calculated using Equation (1):

$$TSS \left(\frac{mg}{L} \right) = \frac{(A - B)1000}{Sample Volume (mL)} \quad (1)$$

Where A is the weight of filter paper + residue (mg) and B is the weight of filter paper (mg).

APHA 5220 D/ HACH 8000 method was employed for the determination of chemical oxygen demand (COD) and the COD results were defined as the mg of O₂ consumed per litre of sample under conditions of this procedure. The 5-day BOD test method (APHA 5210B) was used for BOD₅ determination. Samples for the BOD₅ test were incubated in the dark for 5 days at 20°C. The residual dissolved oxygen was determined electrometrically after the incubation period and the BOD₅ calculated afterwards. APHA 4500-Cl⁻ B test method was used in the titrimetric determination of the concentration of chloride. In a neutral or slightly alkaline solution, with potassium chromate as indicator for the end point of silver nitrate titration of chloride, silver chloride is precipitated quantitatively before red silver chromate is formed.

3.3.2 Microbiological Analysis

Counts of total heterotrophic bacteria and fungi in the water samples were determined using APHA 9215B/9610B and ASTM D 5465-93 (pour-plate) test methods. Serial dilution of the water samples was carried out using sterile normal saline. Aliquots (1mL) of the 10-fold dilutions were plated on nutrient agar and Sabouraud dextrose agar for the enumeration of heterotrophic bacteria and fungi, respectively. Bacterial plates were incubated at 35±2°C for 24-48 hours whereas fungal plates were incubated at 25±2°C for 3-5 days. Counts of microorganisms in samples were presented as colony-forming units per millilitre (cfu/mL) of water sample.

Counts of hydrocarbon utilizing bacteria were determined using APHA 9215C/ASTM 5465-93 (spread plate) test method. Serial dilution of the water samples was carried out using sterile normal saline. Aliquots (0.1mL) of the 10-fold dilutions were spread on minimal medium containing the appropriate mineral salts for bacterial growth. Crude oil-moistened filter papers placed on the lid of the inverted plates provided the carbon source for growth. The plates were incubated at 25±2°C (for bacteria & fungi) for 7-10 days. After incubation, colonies that developed were counted and presented as cfu/mL of water samples.

3.3.3 Concentration of Microplastics in Water Samples

A Fourier transform infrared (FT-IR) spectroscopy was used for identification of the polar functional groups of the microplastics polymer. The samples were subjected to contact with

infrared (IR) radiation. The IR radiations then had impacts on the atomic vibrations of molecules in the sample. The wavelength of incident laser was set to 532nm, and the FT-IR spectra were from 650 to 4000 cm^{-1} . The FT-IR images of the samples were analyzed to identify and quantify the functional groups of the microplastics present.

Gas Chromatography-Mass Spectrometry (GC-MS) analysis was carried out using an Agilent 6890 gas chromatograph with a 5973 MS detector equipped with 30-m x 0.25-mm and 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), and 1- μm film thickness. (Agilent). The following temperature ramp was used: injector at 250°C, oven initially at 200°C, held for 1 min and heated to 230°C (1.5°C min^{-1} , then held for 10min). Helium was used as the carrier gas at a flow rate of 1 mL min^{-1} . The split ratio was 50:1, and the sample size was 2 μL . The characterization and identification of the microplastics, from the sample was completed in the thermo Excalibur2.1 0.114 acquisition software.

In SEM imaging, the specimen was rastered using a collimated beam of electrons (also called electron probe) emerging from the microscope column. The information about every discrete location on the specimen is encoded in the intensity of the signal of the secondary electrons (SE) and backscattered electrons (BSE). To each pixel on the finished image exists a corresponding picture element on the specimen. The size of those picture elements depends on the magnification during the imaging. If the signal generating area, which is dependent on probe diameter, is smaller than the respective picture element (dependent on magnification) the picture will be sharp. However, if the signal generating area is bigger than the picture element, the image will appear blurry and out of focus because information from neighbouring picture elements will overlap. So, to gain 5 maximum performances, the spot size should be adjusted depending on the magnification. SEM images of the MPs in this study were acquired at various magnifications to capture their surface features, shapes, and sizes. Different imaging parameters were experimented to achieve the best contrast and resolution.

3.4 Statistical Analysis

The results were subjected to descriptive analysis and Pearson's correlation. Pearson's correlation was used to assess the relationship between the microplastics, and some physicochemical properties of the water samples collected.

4. RESULTS AND DISCUSSION

Water has a neutral pH of 7 which indicates that it is neither acidic nor basic where scale ranges from 0 (very acidic) to 14 (very alkaline). The results in Table 2 showed that New Calabar River with a mean pH of 5.66 was slightly acidic compared to Imo River and Ntawogba River with mean pH values of 6.57 and 6.44 respectively which are closer to the pH neutral value of 7 for water. The U.S. Environmental Protection Agency (EPA) recommends that the pH of water sources should be between 6.5 to 8.5. Going with EPA standard, water source from New Calabar River is unfit for domestic use unless it undergoes further treatment to take care of the acidity. The results in this study agreed with the report of Nzeakoet *al.* (2014) in their assessment of freshwater body in Niger-Delta, Nigeria with pH of 5.15 to 5.82. “This acidic nature of New Calabar River is probably due to industrial discharges, illegal sand mining, burning of tyres to roast cow-skin, and direct refuse disposal into the water body. Water with pH outside the normal range (6.5 to 8.5) can adversely affect the growth and development of aquatic life” (Kalagboret *al.*, 2020). “The aggregation behaviours of MPs regulate their fate and ecological risks in aquatic environments, and it is described that attachment efficiency of heteroaggregation depends on surface interaction of aggregating particles, characteristics of plastic particles, and features of surrounding medium such as pH, natural organic matter, and ionic strength” (Atugoga, *etal.*, 2021). However, these phenomena were not investigated in this study.

“Salinity of surface water is relatively uniform as it is generally well mixed by waves, wind, and tides” (Chikwe,2020). It is an important factor in understanding the properties and characteristics of waterbodies. For this study, New Calabar River had a mean salinity of 0.44mg/L (Table 2) which agreed with the report of Chikwe (2020) in her assessment of pollution status of Imo River, Southeastern Nigeria with mean salinity of 0.48mg/L in Asa sampling station, during dry season. This could be attributed to the human activities there such as industrial discharge, and illegal sand mining. Physicochemical properties of the water samples may provide insights into the conditions that influence the presence and transport of MPs. “The increase in salinity may enhance the MP adsorption capacity for organic pollutants by causing a change on the strength of electrostatic interaction and the degree of ion

exchange in the adsorption process” (Gaoet *al.*, 2023). As shown in Table 2, salinity level was highest in New Calabar River (NCR) with a mean value of 0.44mg/L; the probable reason why polyethylene obtained from New Calabar River was also highest at 44.40%.

The mean conductivity value of New Calabar River is 905.33 $\mu\text{S}/\text{cm}$ (Table 2) and slightly exceeded the WHO recommended standard. WHO requirement for aquatic life is 900 $\mu\text{S}/\text{cm}$. Since conductivity is a useful indicator of mineralization and salinity in water, this could be a reason why salinity value (Table 2) is also highest in New Calabar River compared to the other rivers studied. Conductivity qualitatively reflects the status of inorganic pollution and is a measure of total dissolved solid and ionized species in the water (Chikwe, 2020).

Ntawogba River with a COD mean value of 75.67mg/L (Table 2) was highest amongst the studied rivers. This could be attributed to its lentic nature, indiscriminate refuse dumping of wastes, open defecation, and construction activities happening around this waterbody. This trend was also observed by Ogunfowakanet *al.* (2005) in their study. The values obtained in this study are also similar with those reported by Amadi (2010), in his study of water quality indices of Otamiri and Oramiriukwa Rivers. High COD values suggest the presence of a significant amount of organic matter in a waterbody, which can include fecal matter, sewage, industrial effluents, and agricultural runoff.

From Table 2, chloride concentrations for the rivers studied met the WHO recommended limit of 250mg/L for aquatic life. New Calabar River with a mean chloride value of 230.33mg/L had the highest chloride concentration which gave credence to the benign salinity of the water samples.

The mean BOD value as stated in Table 2 for Imo River was 8.25mg/L and 33.50 mg/L for Ntawogba River while New Calabar River was 15.67mg/L. Although these values are in consonance with the report of Chindahet *al.* (2011), they are higher than WHO recommended standard of 5.0mg/L. Ntawogba River showed the highest mean BOD value (33.5mg/L), which could be likely attributed to the presence of a significant amount of readily biodegradable organic matter in the river which indicated pollution from sources like untreated sewage, industrial effluents, and agricultural runoff. Oxygen is required for respiration by microorganisms involved in the decomposition of these organic materials (Nartey *et al.*, 2012).

THB were found in high numbers in all the water samples analyzed (Table 2) and was expressed in colony-forming units per millilitre (CFU/mL) of water sample. Mean THB count was highest in Ntawogba River (1.29×10^5 CFU/mL) when compared to the other rivers studied. Likewise, mean HUB count was highest (1.10×10^3 CFU/mL) in Ntawogba

River (Table 2) indicating the probable contamination of the water by petroleum hydrocarbons. HUBs proliferate in environments contaminated with petroleum hydrocarbons since they possess the metabolic capability for assimilation and utilization of these compounds as sources of carbon and energy. Hence, they are important players in the natural breakdown of hydrocarbon pollutants and restoration of polluted environments. Several anthropogenic activities occurring around the Ntawogba river could have predisposed the river to hydrocarbon pollution.

Figs. 2 – 4 indicate the concentrations of MPs in the three rivers in Port Harcourt studied. MPs were detected in all water samples from the rivers studied with polyethylene (PE) being the predominant microplastic type in the surface water bodies with average abundance of 45.91%, 40.18%, 44.40% across the Imo River, Ntawogba River and New Calabar River respectively. Polyethylene terephthalate (PET) was next to PE in predominance as indicated on the GC-MS chromatograms (Figs. 5–7). This phenomenon can be linked to the vast consumption of plastic products (e.g., single-use plastics), littering and poor waste management culture which result in microplastics ending up in the waterbodies via storm water runoff or wind. Among the microplastics detected in the rivers, tetrabromobisphenol A (TBA) and polybrominated diphenyl ether (PBDE) were the least in magnitude obtained. Both forms of plastic are used as flame retardant coatings of electronic devices such as televisions, mobile phones, and computers and become e-waste at the end of their life cycle. Most of these devices end up in landfills which could be the reason why their concentrations were low in surface water of the three rivers.

Observations of the spectral (Figs. 8–10) shows that the prominent absorption peak at 2920 cm^{-1} corresponds to aliphatic C-H (Hydrocarbon) stretching, indicating the presence of CH_2 (Alkene) and CH_3 (Alkane) groups in the microplastic samples. The peak at 1725 cm^{-1} is associated with carbonyl (C=O) stretching, suggesting the presence of polymers with carbonyl functional groups. The band at 1600 cm^{-1} is a characteristic of aromatic C=C stretching, indicating the presence of aromatic polymers. The absorption in the $1200\text{--}1000\text{ cm}^{-1}$ range suggests C-O stretching vibrations which can be indicative of polyester and polyethylene plastics. The region between 800 and 700 cm^{-1} corresponds to out-of-plane bending vibrations commonly seen in aromatic groups.

The SEM images presented here (Figs. 11– 13) provide a close-up view of the microstructures and offer a glimpse into the microscopic world of the identified MPs, showcasing their unique structures and surface properties.

“MPs have not only caused physical damage to marine organisms, but they also introduce potential hazards that have had a negative impact on marine ecosystems” (Gaoet *al.*, 2023). “Fishes mostly (80%) ingest blue PE fragments because the colour and size are more like copepods that they usually consume which causes reduced body weight, growth inhibition, impairment of the reproductive systems, reduced mobility, and finally mortality” (Atugoga, *etal.*, 2021).

However, mitigation of MPs in water bodies is a complex challenge that requires painstaking strategies at various levels, from individual actions to policy changes. It is a collective effort involving individuals, communities, industries, government, and the scientific community. By taking proactive steps to reduce plastic use, improve waste management, and advocate for policy changes, it is possible to work towards healthier and more sustainable aquatic ecosystems.

Table 2: Physicochemical characteristics of surface water samples obtained from Imo River (IM-RIV), Ntawogba River (NTW) and New Calabar River (NCR)

Parameter	Imo River	Ntawogba River	New Calabar River	NESREA Limits	USEPA Limits
pH	6.57±0.17	6.44±0.05	5.66±0.04	6.5–8.5	6.5–9
Conductivity(μS/cm)	12.00±5.29	397.33±72.47	905.33±174.00	–	1000
Total Dissolved Solids (mg/L)	6.00±2.65	197.33±35.64	453.00±87.00	–	500
Turbidity(NTU)	41.70±2.55	15.97±1.18	19.17±8.84	–	1
Dissolved Oxygen (mg/L)	7.22±0.46	4.07±0.38	5.48±0.14	6.0	0.05
Salinity(mg/L)	0.01±0.00	0.19±0.04	0.44±0.09	–	–
Temperature(°C)	27.93±0.25	29.97±0.72	29.60±0.17	–	–
Redox Potential(mv)	149.67±26.27	75.73±3.50	143.67±1.53	–	–
Chloride (mg/L)	1.26±0.22	103.33±19.55	230.33±70.85	300	250
BiochemicalOxygen Demand(BOD) (mg/L)	8.25±0.12	33.50±1.78	15.67±0.60	3.0	–

Chemical Oxygen Demand (mg/L)	23.67±1.53	75.67±3.06	33.67±1.53	30	250
Total Suspended Solids(mg/L)	21.33±1.53	31.33±2.52	26.33±1.53	0.25	–
Total Oil and Grease(mg/L)	0.64±0.11	1.24±0.26	0.47±0.04	0.01	–
THB (CFU/mL)	15900.00±14381.58	129333.33±21007.94	16666.67±5783.02	–	–
HUB (CFU/mL)	170.00±206.64	1103.33±105.04	370.33±203.81	–	–
THF (CFU/mL)	680.00±589.24	10366.67±635.09	1.00±0.00	–	–
HUF (CFU/mL)	133.33±57.74	1.00±0.00	1.00±0.00	–	–

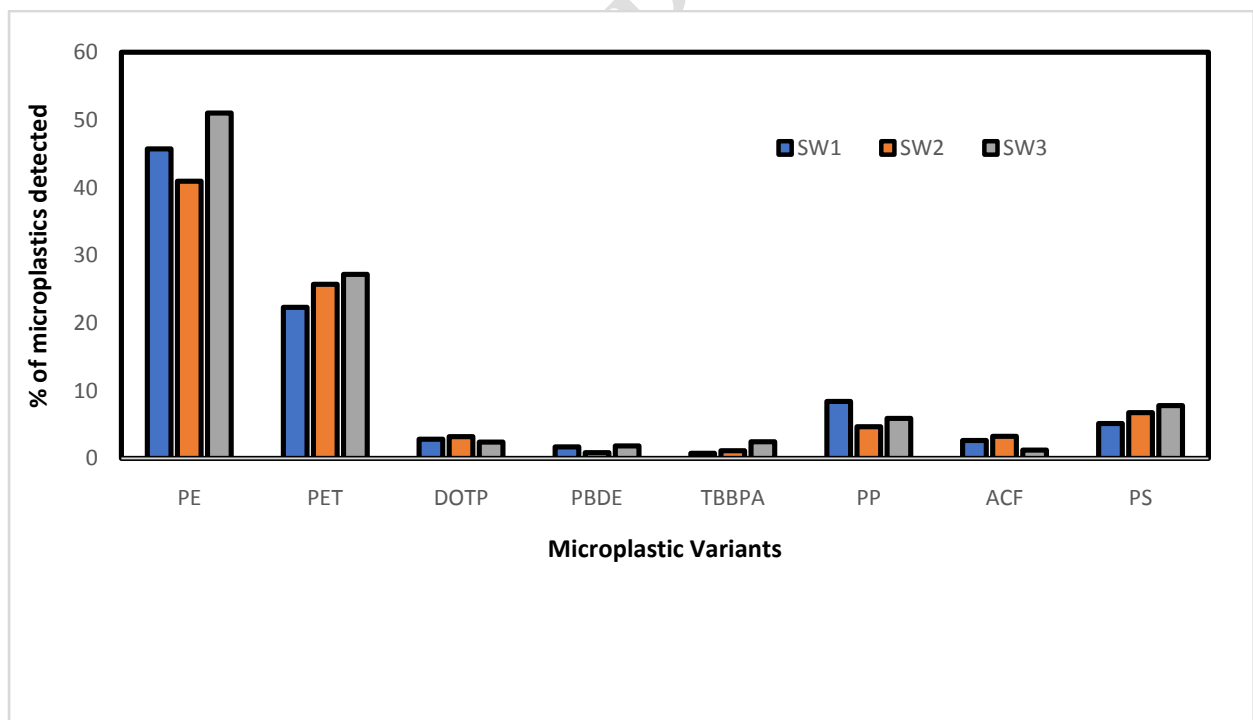


Figure 2: Microplastic concentration (in percentage %) of water samples collected from Imo River

LEGEND:

PE – Polyethylene

PET – Polyethylene Terephthalate

DOTP – Dioctyl Terephthalate

PBDE – Polybrominated Diphenyl Ether

TBBPA – Tetrabromobisphenol A
PP – Polypropylene

ACF – Acrylic Fiber
PS – Polystyrene

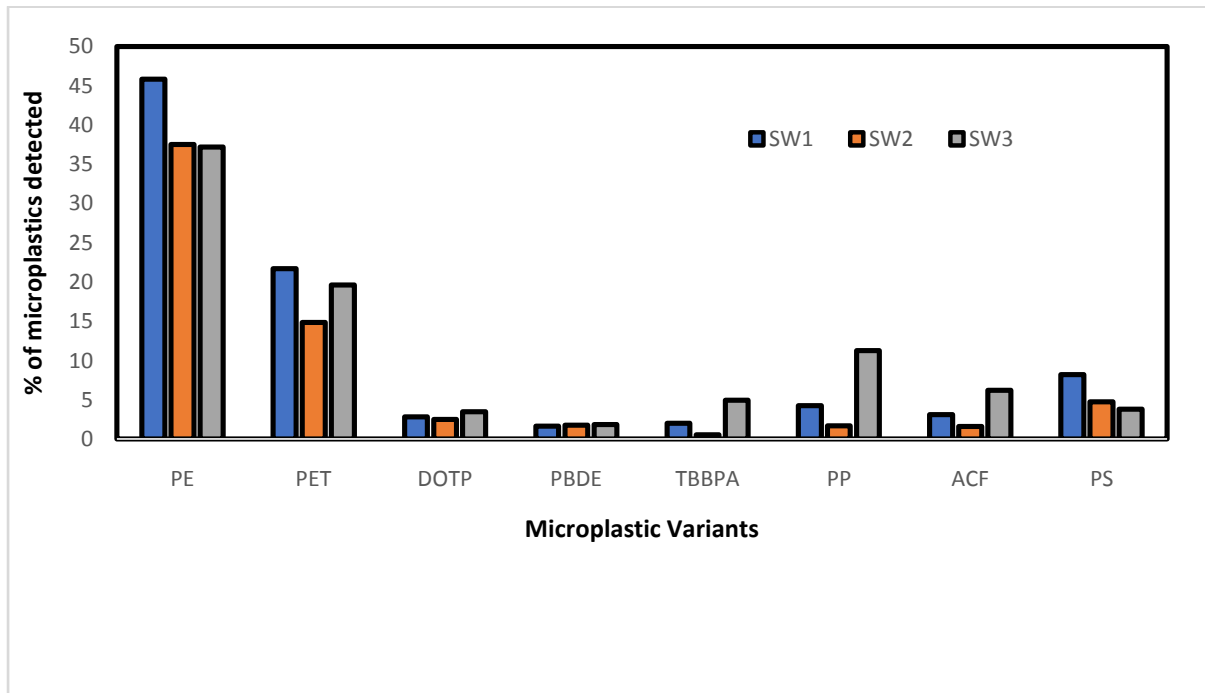


Figure 3: Microplastic concentration (in percentage %) of water samples collected from Ntawogba River

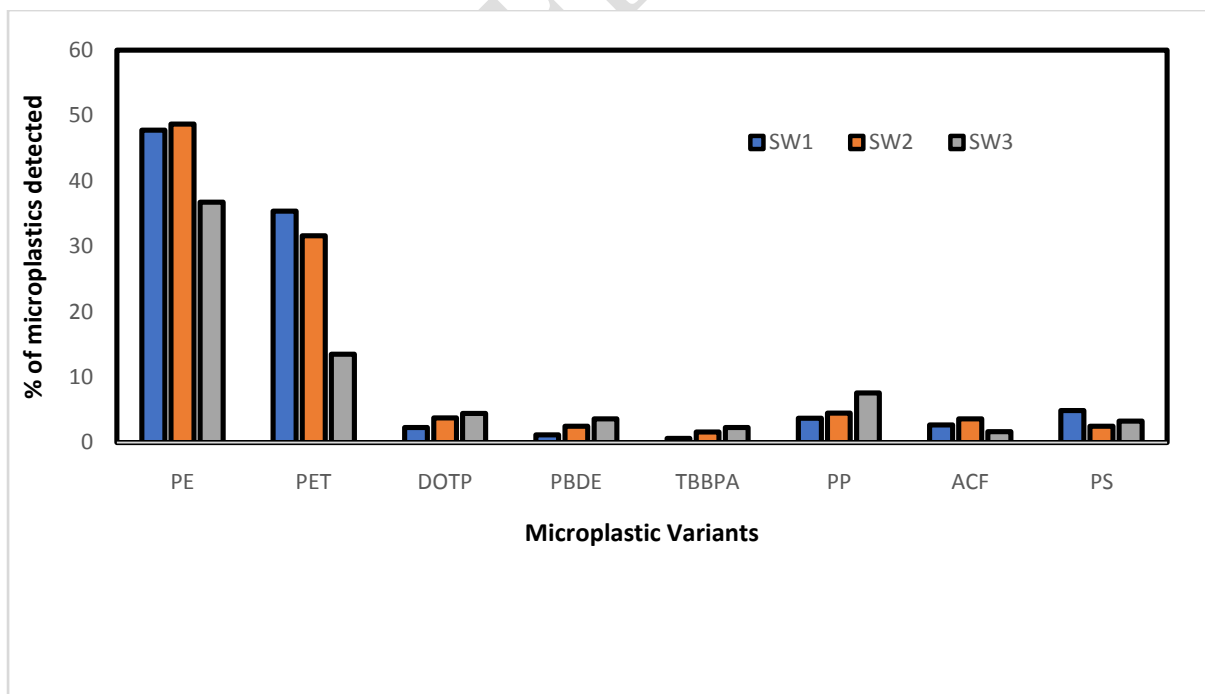


Figure 4: Microplastic concentration (in percentage %) of water samples collected from New Calabar River

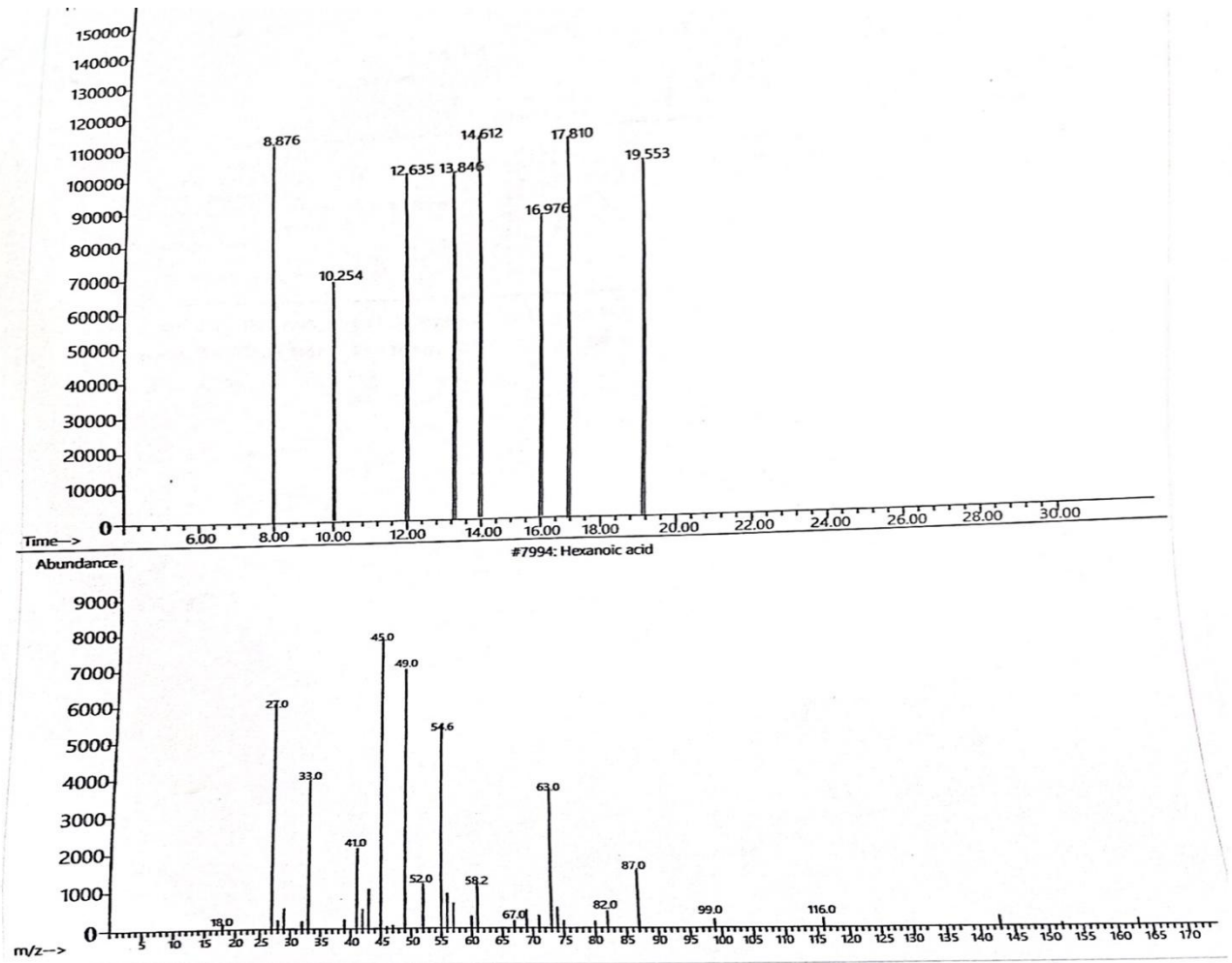


Figure5: GC-MS chromatogram of water samples obtained from New Calabar River (SW1)

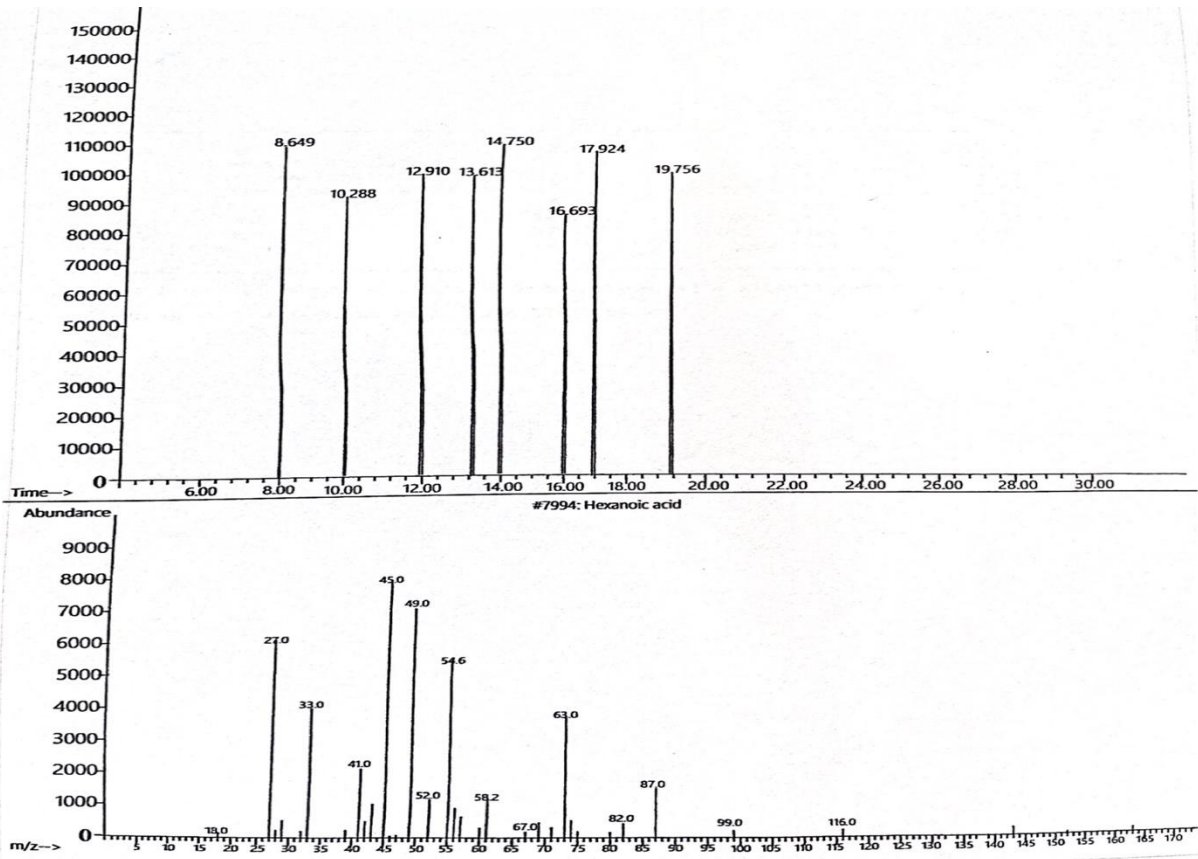


Figure6: GC-MS chromatogram of water samples obtained from Imo River (SW1)

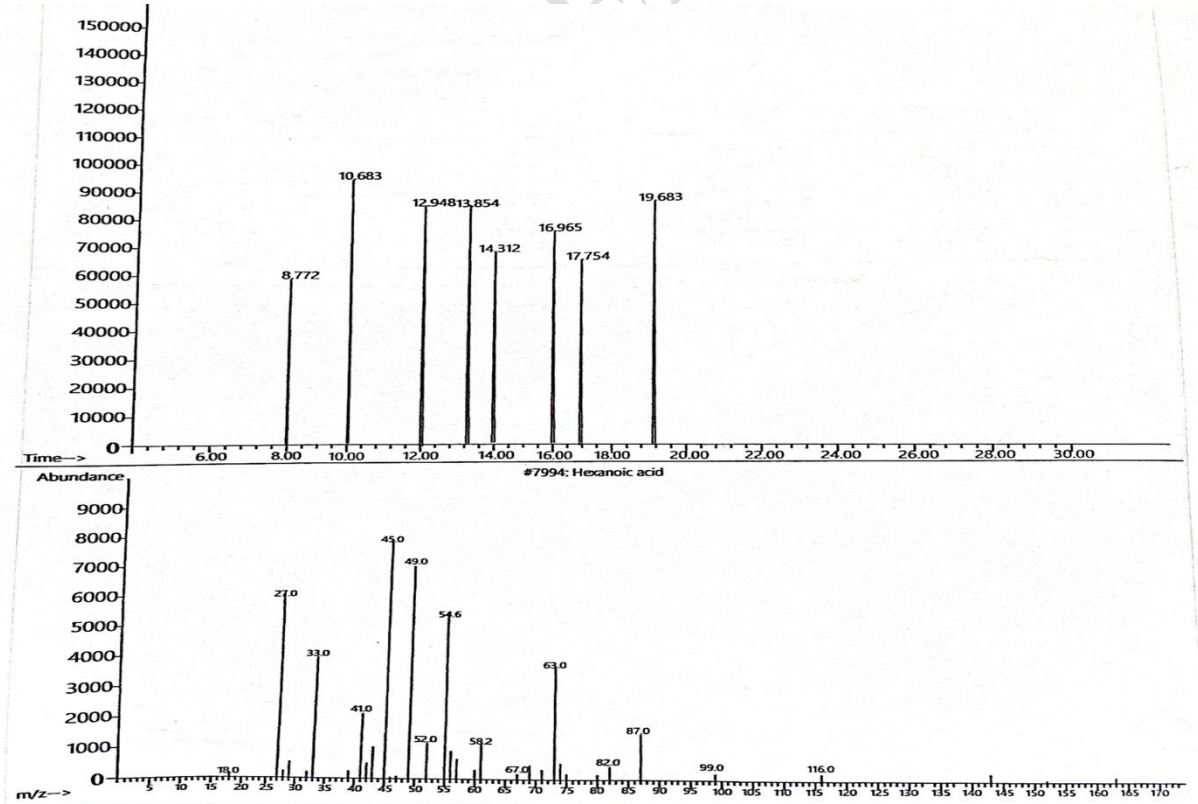


Figure7: GC-MS chromatogram of water samples obtained from Ntawogba River (SW1)

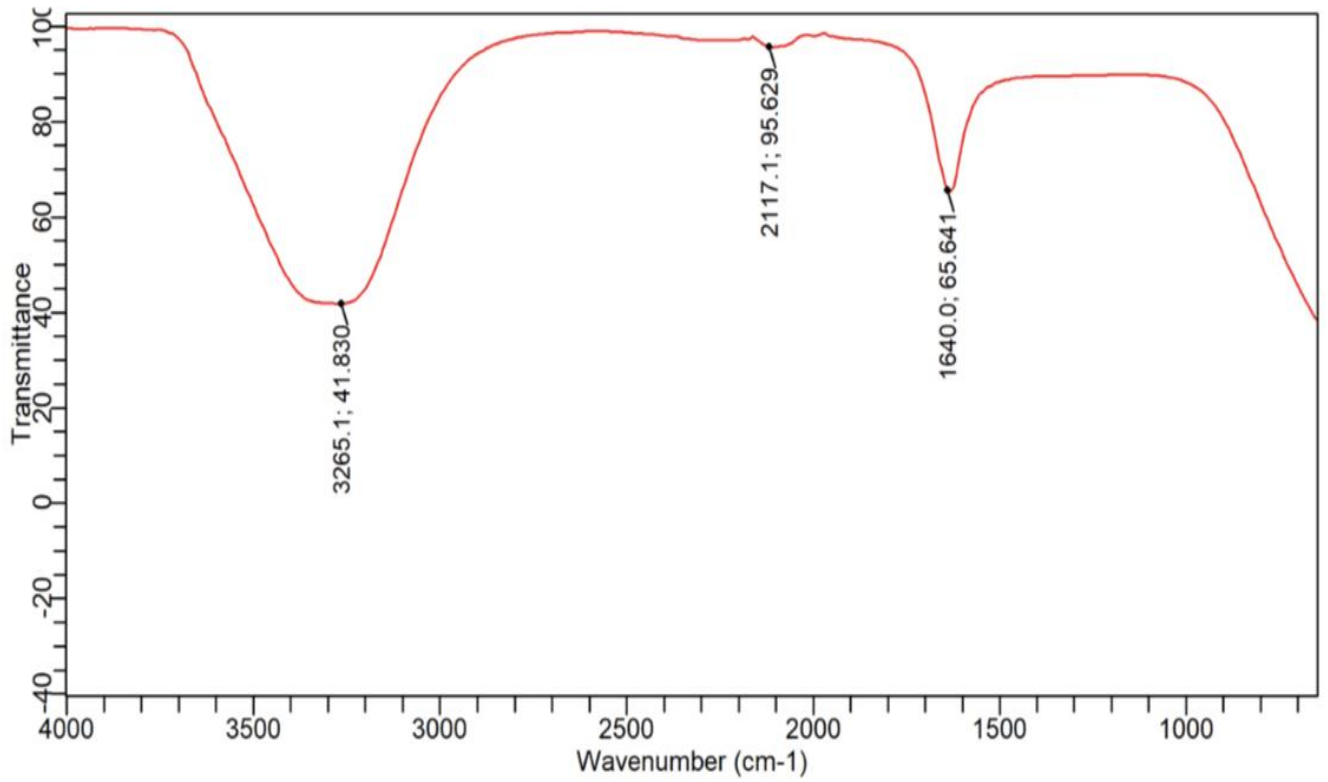


Figure8: FT-IR spectra of microplastics obtained from New Calabar River (SW1)

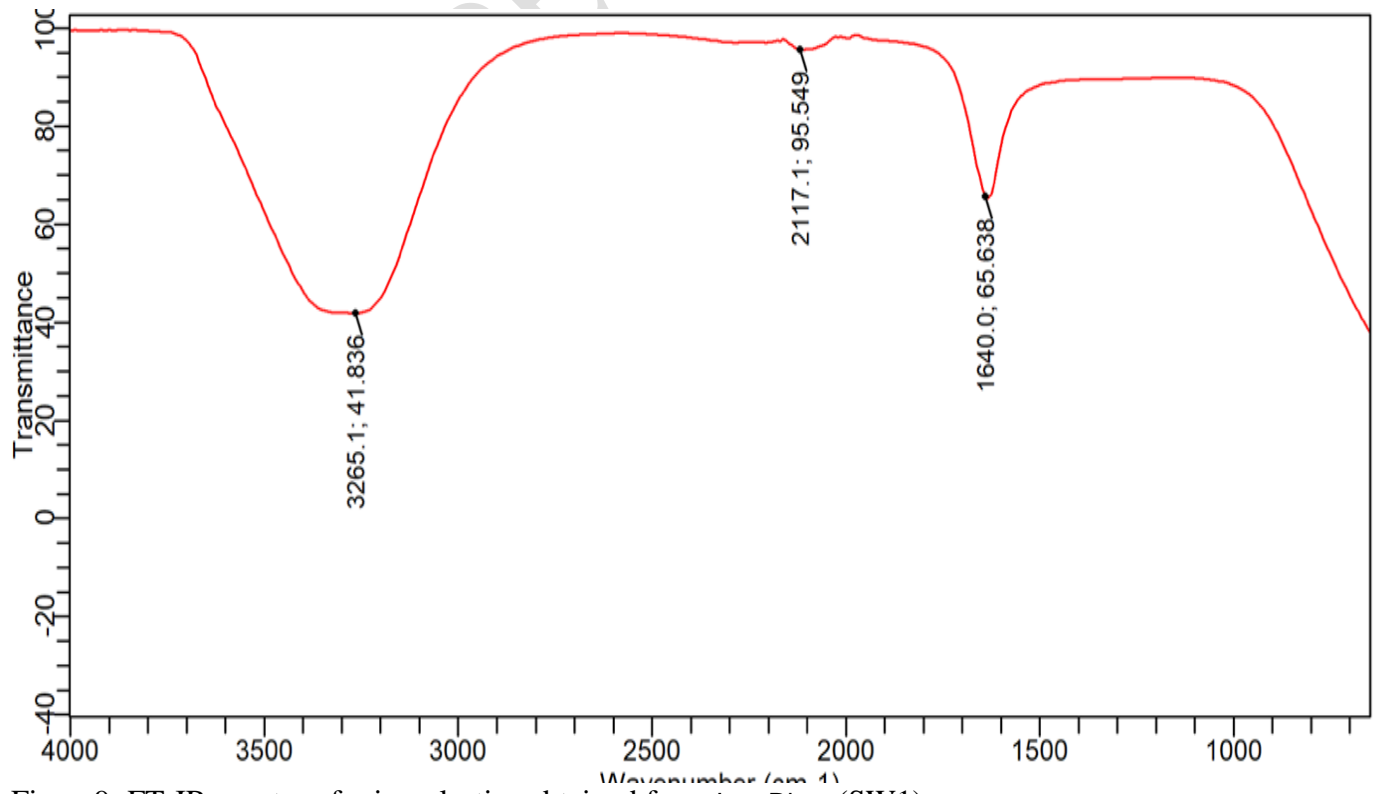


Figure9: FT-IR spectra of microplastics obtained from Imo River (SW1)

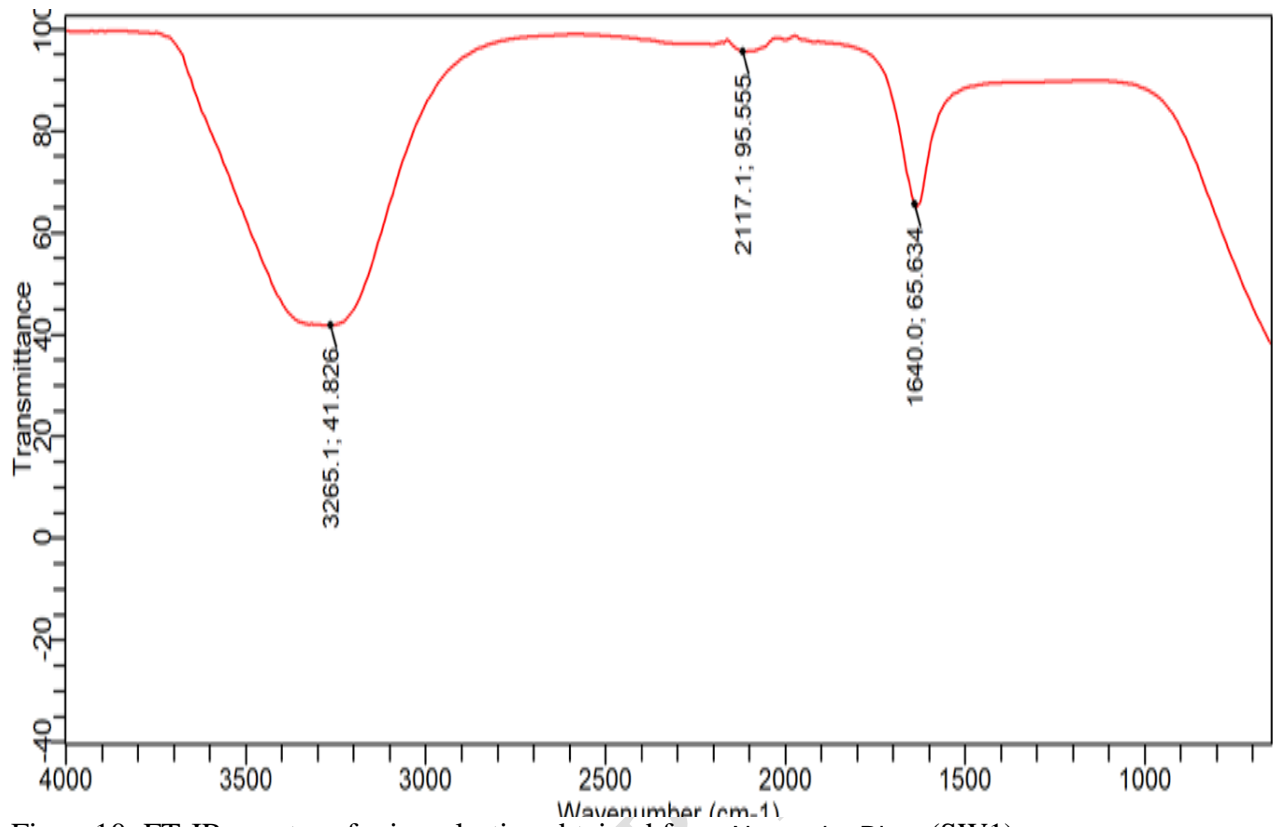
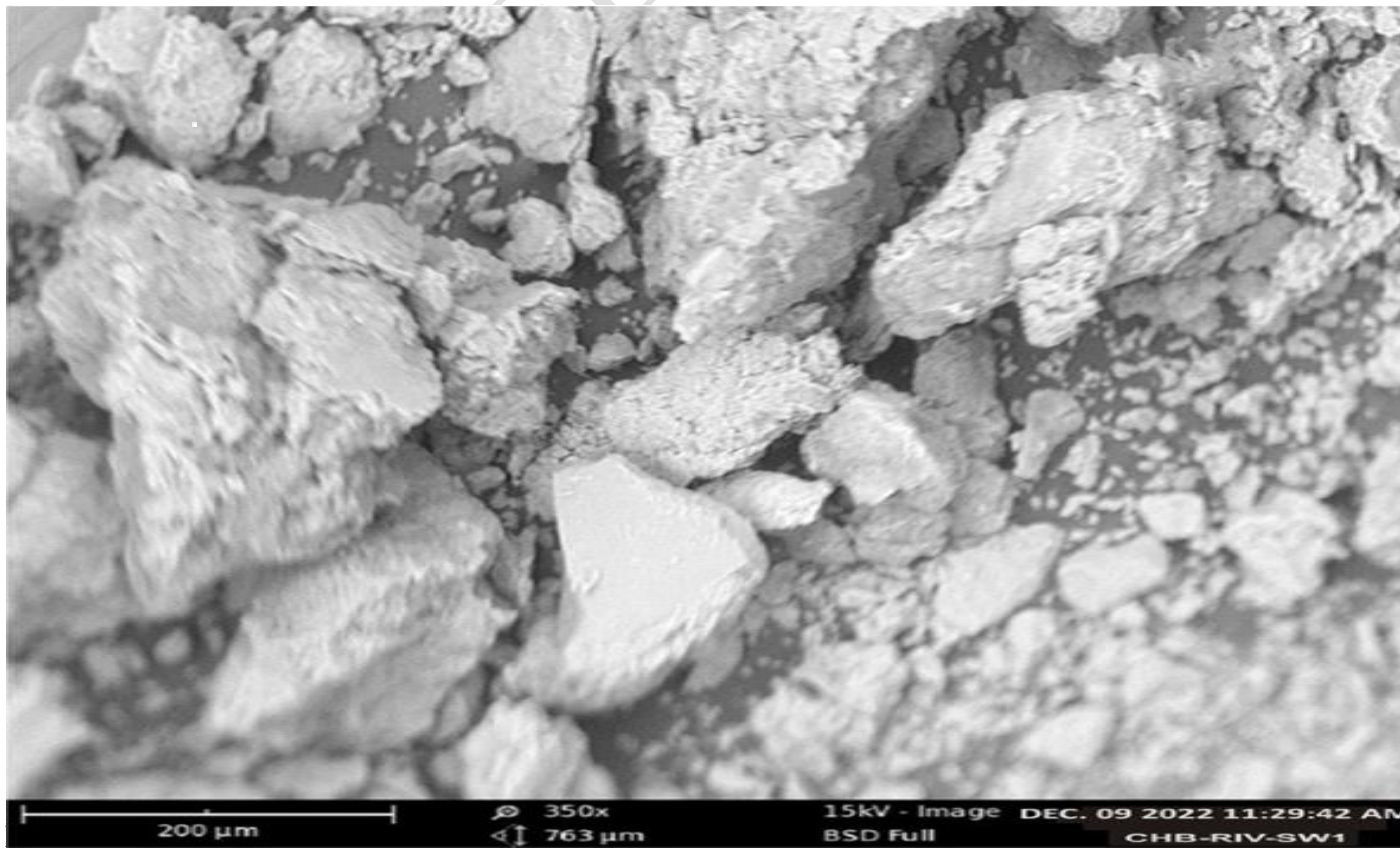


Figure10: FT-IR spectra of microplastics obtained from Ntawogba River (SW1)



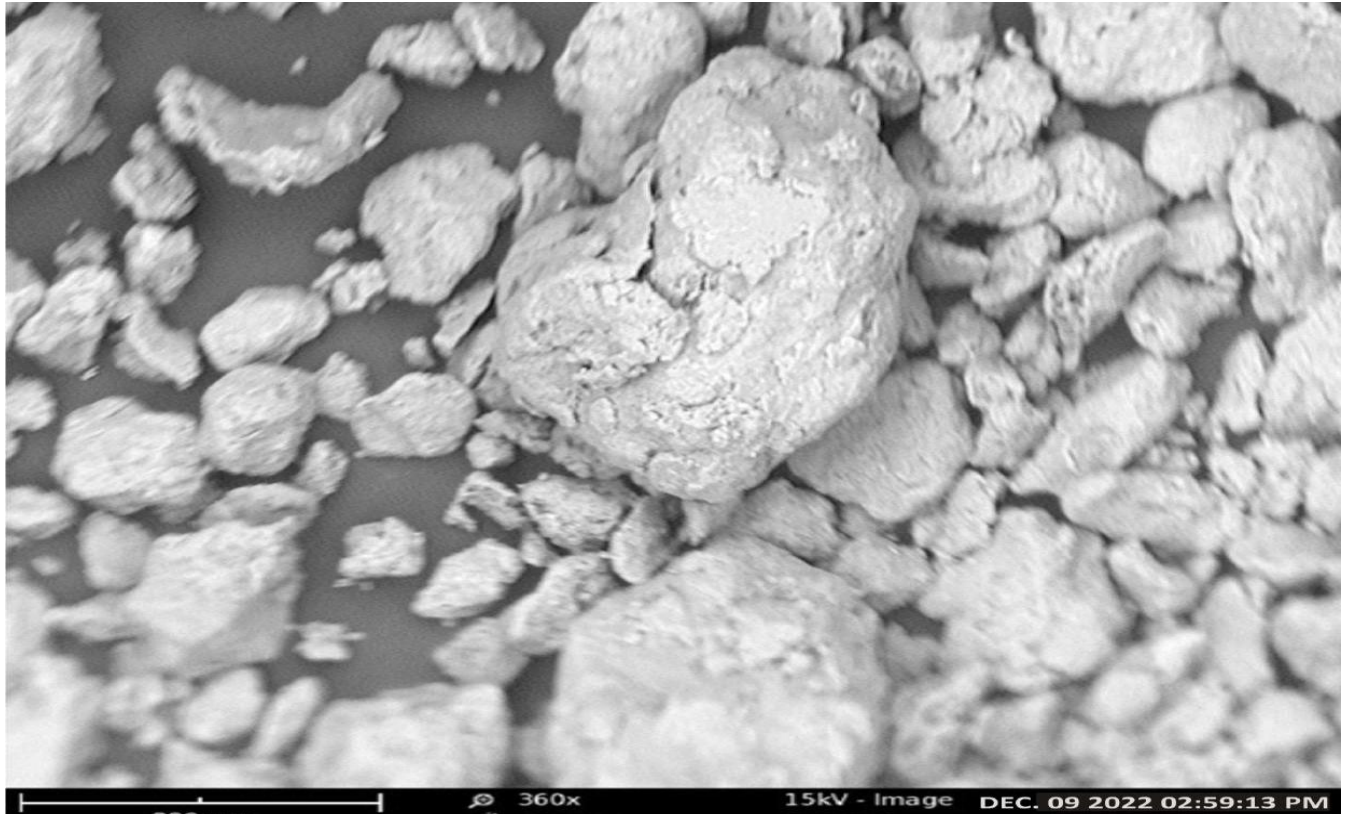


Figure12: SEM micrograph of microplastics obtained from Imo River (SW1)

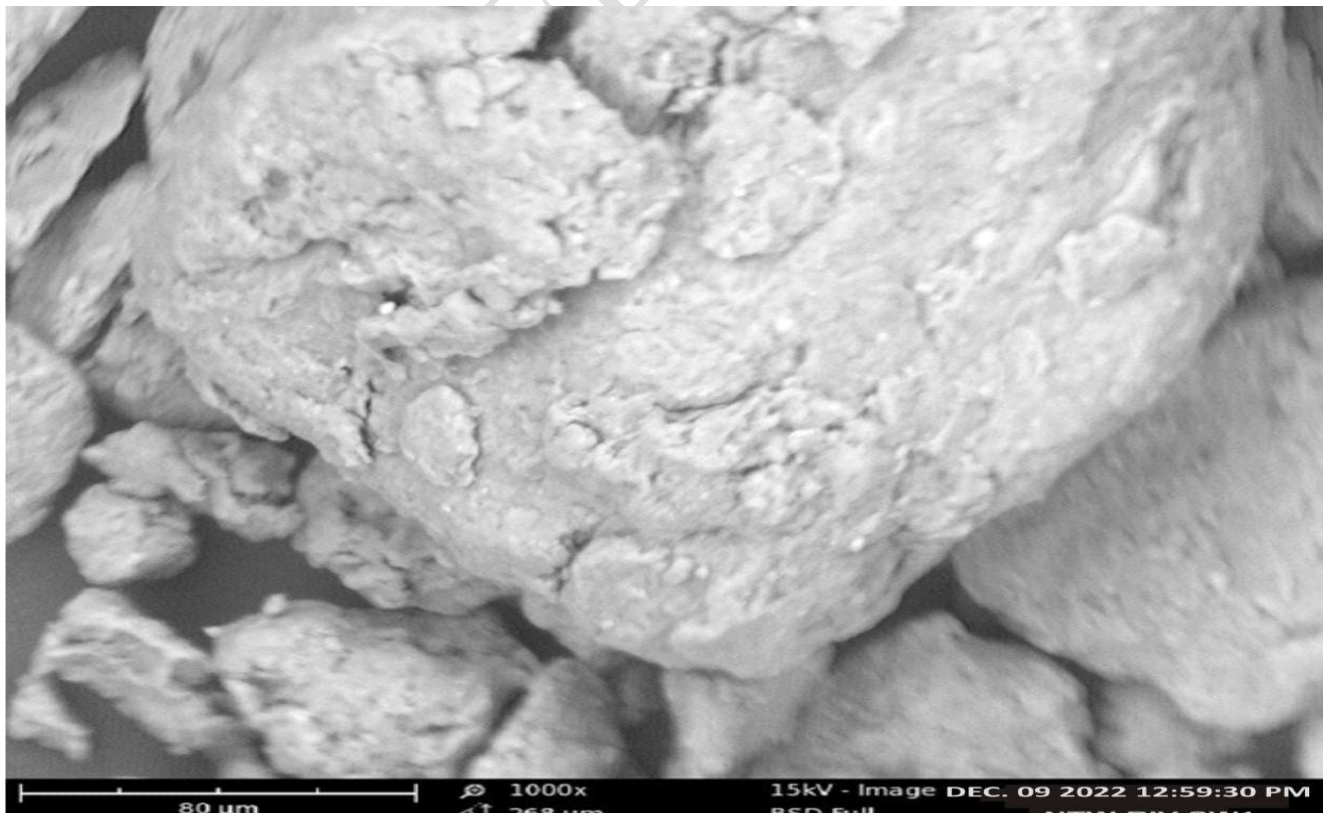


Figure13: SEM micrograph of microplastics obtained from Ntawogba River (SW1)

5. Conclusion

This study evinced a spatial distribution of microplastic pollutants across the three rivers studied utilizing Gas Chromatography-Mass Spectrometry (GC-MS), Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM) methods. Polyethylene (PE) was the predominant microplastic type in the surface water bodies with average abundance of 45.91%, 40.18%, 44.40% across the Imo River, Ntawogba River and New Calabar River respectively. The distribution of microplastic pollutants analyzed indicates improper plastic waste management in the city of Port Harcourt. These plastics degrade into various sizes and are transported by rainwater, wind, and run-off into the waterbodies.

This interdisciplinary study holds substantial significance for understanding the overall health of freshwater ecosystems, the load of microplastics, and possible sources of contamination. Therefore, the results in this study may guide environmental conservation efforts, policy formulation, and freshwater resource management in Rivers State, Nigeria.

6. Life Science Reporting

No life science threat was practiced in this research.

REFERENCES

- Amadi AN, Olasehinde PI, Okosun EA, Yisa J. Assessment of the Water Quality Index of Otamiri and Oramiriukwa Rivers. *Physics International*. 2010;1(2): 116-123.
- Andrade MC, Winemiller KO, Barbosa PS, Fortunati A, Chelazzi D, Cincinelli A, Giarrizzo T. First account of plastic pollution impacting freshwater fishes in the Amazon: Ingestion of plastic debris by piranhas and other serrasalmids with diverse feeding habits. *Environmental Pollution*. 2019;244: 766–773.
- APHA. Standard methods for the examination of water of wastewater. 20th Washington DC, USA. APHA. 2005.
- Atugoda T, Piyumali H, Liyanage S, Mahatantila K, Vithanage, M. Fate and Behavior of Microplastics in Freshwater Systems. *Springer Nature Switzerland AG*. 2021; 42-1.
- Browne MA, Galloway T, Thompson, R. Microplastic – an emerging contaminant of potential concern? *Integrated Environmental Assessment and Management*. 2007; 3(4), 559-561.
- Carson HS, Nerheim, MS, Carroll KA, Eriksen M. The plastic-associated microorganisms of the North. 2013.
- Chikwe OB. *Assessment of Pollution Status of Imo River, Southeastern Nigeria*. 2020. [Unpublished doctoral dissertation]. Nnamdi Azikiwe University.
- Chindah AC, Solomon A, Braide SA, Obunwo CC. Water Quality of streams receiving municipal wastewater in Port Harcourt Niger Delta, Nigeria. *Waste Water – Evaluation and Management*. 2011; 14:283-301.
- Cole M, Lindeque P, Halsband C, Galloway TS. Microplastics as contaminants in the marine environment: a review. *Marine Pollution*. 2011; 62(12):2588–2597. <https://dx.doi.org/10.1016/j.marpolbul.2011.09.025> 14.
- Desforges JPW, Galbraith M, Ross PS. Ingestion of Microplastics by Zooplankton in the Northeast Pacific Ocean. *Archives of Environmental Contamination and Toxicology*. 2015; 69(3):320–330.
- Ding L, Fan Mao R, Guo X, Yang X, Zhang Q, Yang C. Microplastics in surface waters and sediments of the Wei River, in the northwest of China. *Science of Total Environment*. 2019; 667: 427–434.
- Ding J, Zhang S, Razanajatovo RM, Zou H, Zhu W. Accumulation, tissue distribution, and biochemical effects of polystyrene microplastics in the freshwater fish red tilapia (*Oreochromis niloticus*). *Environmental Pollution*. 2018; 238: 1–9.
- Eerkes-Medrano D, Thompson RC, Aldridge DC. Microplastics in freshwater systems: A review of the emerging threats, identification of knowledge gaps and prioritization of research needs. *Water Research*. 2015; 75:63-82. <https://doi.org/10.1016/j.watres.2015.02.012>
- Eriksen M, Lebreton LC, Carson HS, Thiel M, Moore CJ, Borrorro JC, Galgani F, Ryan PG, Reisser J. Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea. *PLoS One*. 2014; 9(12): 111-913. doi:10.1371/journal.pone.0111913.
- Foekema EM, De Groot C, Mergia MT, Van Franeker JA, Murk AJ, Koelmans AA. Plastic in North Sea Fish. *Environmental Science Technology*. 2013; 47(15):8818-8824. <https://www.ncbi.nlm.nih.gov/pubmed/23777286> <http://pubs.acs.org/doi/abs/10.1021/es400931b>
- Gao H, Qi Z, Yu X, An Y, Liu Z, Yang M, Xiong D. Effect of Salinity and Temperature on the Dispersion of Spilled Oil in the presence of Microplastics. *Journal of Marine Science and Engineering*. 2023; 11(791). <https://doi.org/10.3390/jmse11040791>

- GESAMP. Sources, fate, and effects of microplastics in the marine environment: part two of a global assessment. (Kershaw, P.J., and Rochman, C.M., eds). (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). *Reports and Studies GESAMP*.2016; 93(220).
- GESAMP.Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection. Sources, Fate, and Effects of Microplastics in the Marine Environment: A Global Assessment. *Reports and Studies GESAMP*. 2015; 90-96. <http://dx.doi.org/10.13140/RG.2.1.3803.7925>
- GESAMP.Guidelines for the Monitoring and Assessment of Plastic Litter in the Ocean KershawPJ, Turra A,Galgani F, eds. IMO/FAO/UNESCO IOC/UNIDO/WMO/IAEA/UN/UNEP/ UNDP/ISA Joint Group of Experts on the *Scientific Aspects of Marine Environmental Protection*. 2015; 99, 130.
- GESAMP (Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). Sources, fate, and effects of microplastics in the marine environment: a global assessment (Kershaw PJ, ed.). (IMO/FAO/UNESCO-IOC/UNIDO/WMO/IAEA/UN/UNEP/UNDP Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection). *Rep. Stud. GESAMP*.2015; 90(96).
- Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. *Science Advances*. 2017; 3(7):1700782.
- Kalagbor IA, Echem OG, Banwo E. Water quality assessment of Ntawogba Stream in Port Harcourt metropolis, Rivers State, Nigeria. *International Journal of Water Resources and Environmental Engineering*,2021;13(1):6-87.
- Kalčíková G, ŽgajnarGotvajn A, Kladnik A, Jemec A. Impact of polyethylene microbeads on the floating freshwater plant duckweed *Lemna minor*. *Environmental Pollution*.(2017).
- Lenaker P, Corsi SR, Mason SA. Spatial Distribution of Microplastics in Surficial Benthic Sediment of Lake Michigan and Lake Erie. *Environ. Sci. Technol*.202155(1):373-384.<https://doi.org/10.1021/acs.est.0c06087>
- Liang L, Ting L, Yao Z, Chunhui C, Zhengwei F,Yuanxiang J.Interaction between microplastics and microorganism as well as gut microbiota: A consideration on environmental animal and human health. *Science of the Total Environment*. 2019; 667: 94–100.
- Makhdoumi P, Naghshbandi M, Ghaderzadeh K, Mirzabeigi M, Yazdanbakhsh A, Hossini H. Micro-plastic occurrence in bottled vinegar: Qualification, quantification and human risk exposure. *Process Safety and Environmental Protection*.2021;152: 404-413. <https://doi.org/10.1016/j.psep.2021.06.022>
- Nartey VK, Hayford EK, Ametsi SK. Assessment of the Impact of Solid Water Dumpsites on some Surface Water Systems in the Accra Metropolitan Area, Ghana. *Journal of water Resource and Protection*. 2012; 4(08):605-661.
- Ogunfowokan AO, Okoh EH, Adenuga AA, Asubiojo OI. Assessment of the impact of point source Pollution from a University Sewage Treatment Oxidation Pond on the Receiving Stream a Preliminary Study. *Journal of Applied Sciences*. 2005; 6(1):36-43.
- PlasticsEurope. Plastics – the Facts 2016. (Available at www.plasticseurope.org). Accessed 1 November 2016.
- Reisser J, Shaw J, Hallegraeff G, Proietti M, Barnes DK, Thums M, Wilcox C, Hardesty BD, Pattiaratchi C. Millimeter-sized marine plastics: a new pelagic habitat for microorganisms and invertebrates. *PLoS One* 9. 2014. e100289.

- Rodrigues MO, Abrantes N, Gonçalves FJM, Nogueira H, Marques JC, Gonçalves AMM. Spatial and temporal distribution of microplastics in water and sediments of a freshwater system (Antuã River, Portugal). *Science of Total Environment*. 2018; 633:1549–1559.
- Rochman CM, Manzano C, Hentschel BT, Simonich SLM, Hoh V. Polystyrene plastic: a source and sink for polycyclic aromatic hydrocarbons in the marine environment. *Environmental Science Technology*. 2013; 47(13976). <https://doi.org/10.1021/es403605f>.
- Rødland ES, Okoffo ED, Rauert C, Heier LS, Lind OC, Reid M, Thomas KV, Meland S. Road De-Icing Salt: Assessment of a Potential New Source and Pathway of Microplastics Particles from Roads. *Science of Total Environment*. 2020; 738:139-352.
- Schirrinzi GF, Pérez-Pomeda I, Sanchís J, Rossini C, Farré M, Barceló D. Cytotoxic effects of commonly used nanomaterials and microplastics on cerebral and epithelial human cells. *Environmental Resources*. 2017; 159.
- Stanley HO, Immanuel OM, Nwagboso A. Water Quality Assessment of the New Calabar River. *Journal of Applied Life Sciences International*. 2017; 15(2): 1-5.
- Uche A, Sikoki F, Nzeako SO. Endoparasitaemia of *Chrysichthys nigrodigitatus* in a Tidal Freshwater Body in the Niger Delta, Nigeria. *International Journal of Scientific Research in Environmental Sciences*. 2014; 2(7):250-260. <http://dx.doi.org/10.12983/ijres-2014-p0250-0260>
- UNEP. Marine plastic debris and microplastics – Global lessons and research to inspire action and guide policy change. United Nations Environment Programme, Nairobi. 2016.
- UNEP (United Nations Environment Programme). Biodegradable Plastics and Marine Litter. Misconceptions, concerns and impacts on marine environments. United Nations Environment Programme (UNEP), Nairobi. 2015.
- Van A, Rochman CM, Flores EM, Hill KL, Vargas E, Vargas SA, Hoh E. Persistent organic pollutants in plastic marine debris found on beaches in San Diego, California. *Chemosphere*. 2012; 86: 258-263. <https://doi.org/10.1016/j.chemosphere.2011.09.039>
- Van Cauwenberghe L, Devriese L, Galgani F, Robbins J, Janssen CR. Microplastics in sediments: A review of techniques, occurrence, and effects. *Marine Environmental Resources*. 2015; 111:5–17.
- Wang W, Ndungu AW, Li Z, Wang J. Microplastics pollution in inland freshwaters of China: A case study in urban surface waters of Wuhan, China. *Journal of Science Total Environment*. 2016; 575:1369-1374.
- Wang F, Wong CS, Chen D, Lu XW, Wang F, Zeng EY. Interaction of toxic chemicals with microplastics: a critical review. *Water Resources*. 2018; 139: 208–209.
- Wagner M, Scherer C, Alvarez-Muñoz D, Brennholt N, Bourrain X, Buchinger S, *et al.* Microplastics in freshwater ecosystems: what we know and what we need to know. *Environmental Sciences Europe*. 2014; 26(12).
- Yuan W, Liu X, Wang W, Di M, Wang J. Microplastic abundance, distribution and composition in water, sediments, and wild fish from Poyang Lake, China. *Ecotoxicological Environmental Safety*. 2019; 170:180–187.
- Zhang C, Chen XH, Wang JT, Tan LJ. Toxic effects of microplastic on marine microalgae *Skeletonema costatum*: interactions between microplastic and algae. *Environmental Pollution*. 2017; 220:1282–1288.