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Investigation of Microplastics and Potentially Toxic Elements (PTEs) in Sediments of two Rivers in Southwestern Nigeria

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Abstract

Microplastics (MPs) are emerging and ubiquitous contaminants, known to accumulate in river sediments. In many developing nations, the absence of policies for managing plastic waste puts the inland river ecosystems at risk of excessive abundance of plastics and MPs. However, only limited studies have reported MPs in river environments in these countries. The current study therefore examined the abundance and nature of MPs and potentially toxic elements (PTEs) in the sediments of the Odo-Ona and Ogun Rivers in Southwest Nigeria. MPs were extracted from the sediments using the density separation method and categorized according to their size, colour and shapes. The range of MP abundances found in the Ogun River sediments was 66.6 ± 12.2 to 311 ± 20.8 particles/kg, while that of the Odo-Ona River ranged from 133 ± 50 to 433 ± 100 particles/kg. The MPs polymer analyses revealed the presence of polyethylene (PE), polypropylene (PP) and polyamide (PA) particles in the sediments. PE was most abundant in the two rivers, constituting 72.8 % and 59.7 % of MPs (with 0.5 – 5 mm size), recovered from the Odo-Ona and Ogun Rivers, respectively. High concentrations of Cr and Pb with ranges of 10.3 – 48.3 and 10.1 – 211 mg/kg, respectively, were detected in the sediments and were associated with anthropogenic effects. This study reveals the impact of indiscriminate waste dumping on the water bodies, and calls for strict enforcement of environmental laws in the country.

Keywords: Microplastics; potentially toxic elements (PTEs); sediments; Odo-Ona River; Ogun River; Nigeria

Introduction

Demand for plastics has risen steadily over the past seventy years, owing to their wide applications and usage daily, their durability, flexibility, and cost-effectiveness. Due to the increased global production of plastics as a result of this high demand, there are now more plastic industries in almost every location. Nevertheless, a significant amount of plastic waste is produced and released into the open environment as a result of careless management and disposal of plastic materials (Ding et al. 2019). Particles having a diameter of less than 5 mm are known as microplastics (MPs), which are formed when large plastic trash breaks up due to UV light and other environmental degradation processes. By treating materials improperly throughout the plastic production process, small plastic particles also find their way into the environment (Mai et al. 2020). MPs are categorized as secondary, which comes from the decomposition of big plastic wastes in the environment, or primary, which are first manufactured in tiny sizes, as observed in microbeads and cosmetic items (Du et al. 2021). MPs may also be described in terms of their shapes (as beads, fibres, fragments, films, spheres), colours, sizes, and polymer types (Doyle et al. 2011).

Global MP trends indicate a concerning rise in pollution of river environments. A large compilation of data sets on MPs pollution of freshwater was provided by Cera et al. (2020). MPs have been found in freshwater environments in all continents, except the Antarctica. Lentic waters were also generally more contaminated than lotic waters, and the water phase were less contaminated than the sediments. Polypropylene and polyethylene MPs have been found most frequently (Cera et al. 2020). Awareness of MPs pollution of freshwater environments is also increasing in Africa. The highest MPs contamination of a river in Africa was recently reported by Idowu et al (2024).

MPs are emerging and ubiquitous environmental contaminants and have been studied significantly in wastewater systems (Barkmann-Metaj et al. 2023; Gray et al. 2018) and in marine ecosystems (Andrady 2011; Peekan et al. 2018). Despite being crucial to our understanding of the function rivers play in transporting MPs to the ocean, research on MPs in freshwater ecosystems has been scarce (Van Wijnen et al., 2019). According to Drummond et al. (2022) and Krause et al. (2021), MPs can also linger in river sediments for decades, harming aquatic ecosystems and the food web. Increased MP retention in sediments may be caused by the pH and salinity of the surrounding water, the physical and chemical properties of the sediment particle, and other factors (Liu et al. 2019). Additionally, because of their relatively large surface area, MPs can adsorb additional chemical contaminants such as potential toxic metals (PTEs), OCPs, and polycyclic aromatic hydrocarbons (PAHs), which can increase their toxicity in the environment (Bakir et al. 2014; Idowu et al. 2024). PTEs are released into the environment by a variety of human-initiated processes, including the production, use, and disposal of electronic devices, mining, smelting, burning of wastes, as well as industrial effluents (Idowu 2022). PTEs may impair the nervous system, vitamin D metabolism and reproductive system. They may also cause brain impairments, kidney damage, as well as gastro-intestinal diseases (Wani et al. 2015; Ayejoto and Egbueri 2024). Because MPs can spread through the food chain, they could be dangerous to both humans and animals (Ferreira et al. 2015).

Plastic wastes are inappropriately managed in most African countries when compared with the world's more industrialized nations. Specifically, it has been determined that the top 20 nations in the world for the production of plastic garbage include Nigeria, Egypt, Algeria, Morocco, and South Africa (Jambeck 2018). In terms of population size, Nigeria is the largest African country and a primary consumer of products using plastics for packaging. The country is regarded as the ninth contributor to plastic pollution globally (Dumbili et al. 2020). Yearly, an estimated two and a half million plastic tons of garbage are produced; less than 12% of this gets recycled (Obiezu 2019; Babayemi et al. 2018).

The majority of studies that investigated MPs pollution in aquatic ecosystems in Nigeria have focussed on the Lagos Lagoon, a brackish estuary that borders the Atlantic Ocean (Olarinmoye et al. 2020; Yahaya et al. 2022; Akinhanmi et al. 2023; Dada and Bello 2023). This is partly because Lagos is a densely populated megacity, with plastic wastes management challenges that may impact the MP levels in the Lagoon. There have only been a few studies that report MP levels in freshwater sediments (Oni et al. 2019; Ebere et al. 2019). MPs were studied by Oni and colleagues at Ox-Bow Lake in Yenagoa, South-South Nigeria., while Ebere et al. (2019) determined MPs in five small rivers in South-Eastern, Nigeria. There is thus a great need for investigation of further rivers in different parts of the country.

The current study is focused on two rivers (Ogun and Odo-Ona) in the South-Western part of Nigeria. Ogun and Odo-Ona Rivers are of economic, cultural, and social importance due to their usage for fishing, agriculture, drinking, domestic, and recreational purposes. The rivers are particularly of interest to MPs study because they receive domestic sewage and wastewater from small-scale industries. Thus, the purpose of this study was to ascertain the quantity and properties of MPs found in river sediments. It also sought to ascertain how much PTE was present in the river sediments.

Materials and methods

Overview of the study area in Southwest Nigeria

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Ibadan, the capital of Oyo State, is the third most populous metropolitan area in Nigeria, behind Lagos and Kano cities. The Odo-Ona River in Ibadan, situated in the city's northern region, is one of the two main rivers that drain the city. Through the Apata Ganga in the local government zone of Ibadan Southwest, the river empties into the Oluyole local government territory. It is 55 km long and 81 km wide (Alayande et al. 2012). The river receives wastes mainly from industrial and domestic activities.

The second water body (Ogun River) flows southwards and travels approximately 410 km. Before emptying into the Lagos Lagoon, it passes through the Nigerian states of Ogun at Ifo Local Government Area, Ibarapa, Iseyin, Abeokuta, Owode, and Ikorodu. Being a large river, the Ogun River receives anthropogenic wastes from industrial, agricultural, sewage treatment, and tourism activities. Marsh woodland and swamp form the Southwest region's vegetation cover. The yearly rainfall in the region ranges from 1,220 to 2,500 mm, with rainy and dry seasons in the climate (Adeleye et al. 2020). Agriculture, fishing, and commodity trading are the primary sources of income and socioeconomic activities in the region.

Sampling of the river sediments

The sampling exercise took place in January 2021. Three replicate samples of the sediment were collected from five locations on each river, designated as (A – E), with successive points separated by an approximate distance of 2 km. The triplicate grab samples from each location were combined into a single bulk composite sample. At the two rivers, the sampling point A was the most upstream, while the point E was the most downstream. On Odo-Ona River, the sampling points are geographically located between latitude 7º 22’ 52.2’’ N and 7º 30’ 10.1’’ N, and between longitude 3º 50’ 46.7’’ E and 3º 59’ 57.8’’ E. Similarly, at Ogun River, the sampled section is between latitude

7º 11' 12.4'' N and 7º 36' 08.3'' N, and between longitude 3º 19' 55.3'' E and 3º 27' 42.5'' E. Fig. 1 shows the study area map of the region. The sampled section of Odo-Ona River was within the Urban area, while that of Ogun River started from an Urban part (point A) and moved towards the rural area (point E). The sampled section, in each case for the Rivers, provided a continuous 10 km stretch of the river that could be conveniently accessed for the sampling. This stretch of the river was divided into five approximately equal distances, and samples were taken from each of the five points.

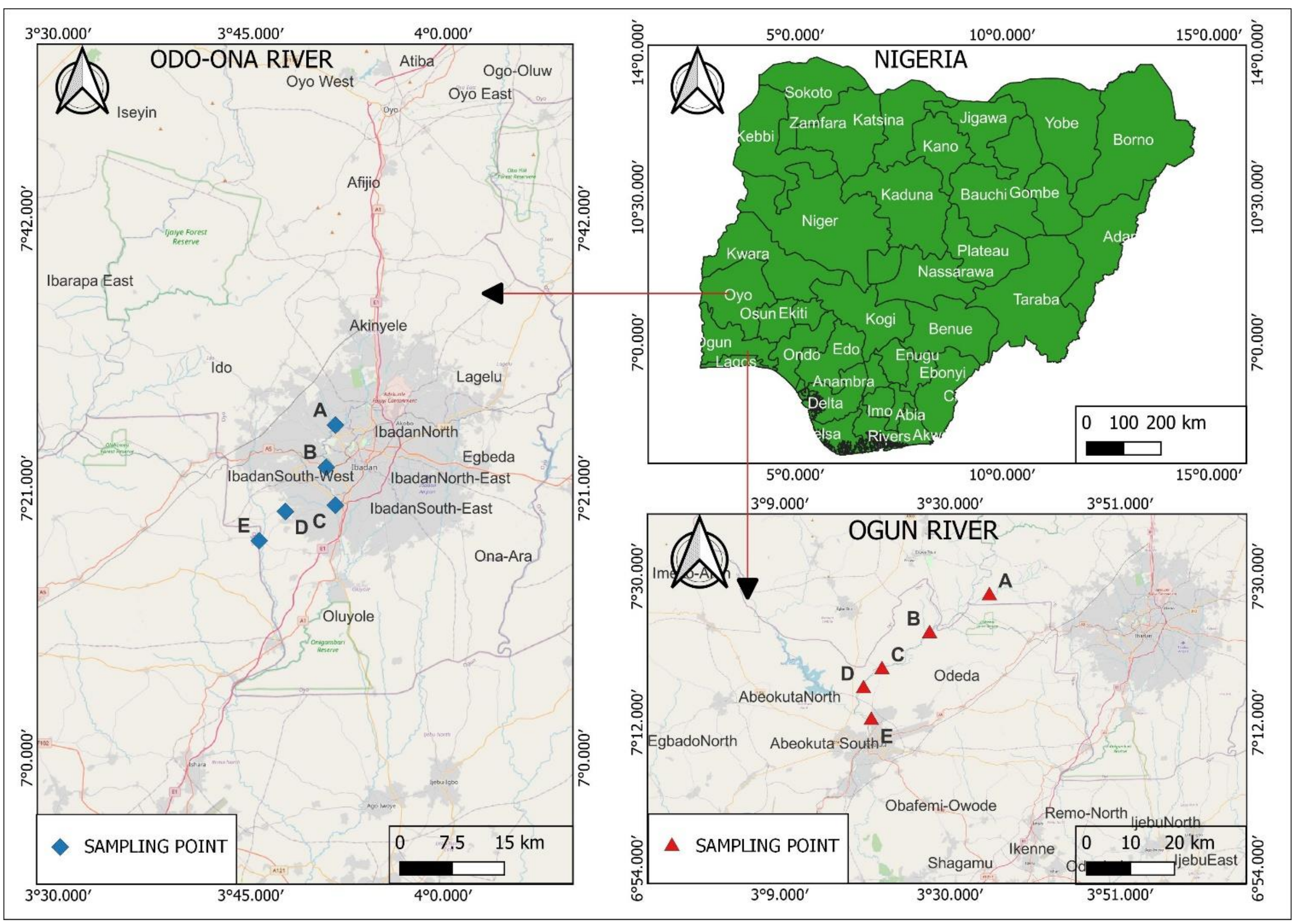

Fig. 1: Study area map showing the Odo-Ona and Ogun Rivers in Southwest Nigeria

Using a hand trowel made of stainless steel, the top 15 cm layer of sediment was sampled. At each river sampling location, the composite sediment sample collected weighed approximately 500 g. To transport the samples to the laboratory, they were kept in aluminium Ziplock foil bags. The samples were subsequently dried for 36 hours at 40 ^{o}C in an oven. Some physicochemical properties of the sediments - pH, conductivity (µS/cm), organic matter content, and texture (% sand, % silt, and % clay) were determined according to standard guidelines (Sarkar et al. 2019). Details of the procedure used for the physicochemical analyses are highlighted in the Supplementary Information (Note 1).

Sample preparation and extraction of MPs

The method of Shokunbi et al. (2024) was used to prepare and extract MPs from the sediments. Following oven drying, a 5 mm mesh size was used to sift each sample, and 50 g was weighed into three separate 1 L glass beakers. Sodium chloride (200 mL) with a density of 1.2 g/cm^3 was added and a clean glass rod was used to swirl the mixture for two minutes. To get rid of any plastic fragments and other particulate matter that might potentially contaminate the samples, the NaCl solution was filtered through a 0.45 µm nitrocellulose filter membrane (Fisher Scientific, UK) prior to use. The liquid layer from the stirred mixture was transferred into another beaker after the sample was allowed to stand for 2 hours. To break down organic materials, 5 mL of 30% hydrogen peroxide (H_2O_2, Fischer Scientific, UK) was added to the recovered liquid layer. The mixture was then kept in a fume chamber for 24 hours to allow complete removal of organic matter and to precipitate any sand particles present. The top clear liquid layer was then carefully filtered through a 0.45 µm membrane under pressure and the MPs were collected on the membrane. A copious

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amount of pre-filtered milli-Q water was used to rinse each beaker and the water was also filtered through the same membrane. The filter was carefully taken out with clean tweezers and placed in a sterile petri dish to dry in a desiccator.

Identification of MPs using microscopic and FTIR analyses

The method described by Shokunbi et al. (2024) was used to identify MPs collected from the sediment samples and to ascertain their sizes, shapes, and colours. A stereomicroscope (Bysameye, China) was used to view and photograph the dried membrane filters at magnifications ranging from 40 to 100X. MPs abundance was recorded as items/kg by multiplying each result by a factor of 20, and shapes were categorized as fibres or fragments. Utilizing ImageJ (version 1.53k) as the imaging software, the MP sizes were measured.

The polymer composition of MPs was identified by analysing relatively large MP fragments using attenuated total reflectance – Fourier transform infrared (ATR – FTIR) spectroscopy. The IR spectra were recorded in the range 400 – 4000 cm^{-1} with the Nicolet™ iS5 infrared spectrometer (Thermo Fisher Scientific, UK). The spectra measurements involved 16 scans and resolution of 4 cm^{-1}. The OMNIC™ polymer program was used to process the spectra and to compare them with reference spectra in the Hummel & Aldrich polymers database.

Validation of methods used for extraction and enumeration of MPs

An in-house laboratory procedure was used to validate the extraction method for MPs, and their detection and enumeration under the stereomicroscope. One hundred (100) pieces of plastic (comprising 20 pieces from each of LDPE, HDPE, PP, PET and PVC) were mechanically

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generated in the laboratory from large plastic materials. The tiny pieces, consisting of fragments and fibres, were within size range of 200 µm to 4.7 mm. The pieces were then added to 50 g of a dry soil sample that had been previously extracted five times with 200 mL of sodium chloride solution (1.2 g/cm^3), to get rid of all microplastics present in it. The dry soil containing the 100 plastic pieces was then treated as a fresh sample and extracted with sodium chloride solution, exactly as described for the sediment samples. The procedure was performed in triplicate and MPs present on the resulting filters were viewed and counted. Average recovery of the plastic pieces was 95.3 %, indicating that the procedure was adequate for MPs recovery and detection in this study.

Identification of PTEs in the sediments

To determine the concentration of PTEs in sediments, 20 mL of aqua regia (HCl: HNO_3, 3:1) from Fischer Scientific, Loughborough (UK) was added to each digestion tube, containing 1 g of the dried sediment sample. The mixture was left overnight to allow for any strong reactions to subside. The digestion was performed with a MARS microwave digestion system (CEM corporation, Buckingham, UK). Upon cooling the tube, the digested mixture was filtered into a 100 mL volumetric flask. The tube was rinsed twice with 20 mL of deionized water and filtered into the same volumetric flask. The combined filtrate was then made up to the 100 mL mark with the deionized water. Each sediment sample was digested in triplicate.

Using a 7700x inductively coupled plasma-mass spectrometry (ICP-MS, Agilent UK), the digests were analysed for nine PTEs (arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), vanadium (V), and zinc (Zn). Metals such as As, Cd, Cr and Pb were included due to their toxicity at relatively low concentrations, while Cu, Mn, Ni, V and Zn were included because they are associated with industrialization and urbanisation (Wu et al. 2021), consistent with the nature of some of the sampling points in this study. Multielement standards containing Sc-45, Ge-72, In-115, and Bi-209 were used as internal standards to calibrate the instrument. The RF power was set at 1550 W while the argon flow rates were 0.85 L/min for the nebulizer, 5.0 L/min for the plasma, 0.9 L/min for the auxiliary line, and 15 L/min for cooling. The method's accuracy and precision were assessed using standard (LGC 6187) samples from LGC Ltd company. Recoveries ranged from 87 to 123% on average (Supplementary Material, Table S1). Both the reference materials and the sediment samples were analyzed in triplicate.

Quality Control

Contact of the samples with plastic containers was avoided throughout, to prevent contamination with extraneous MPs. A stainless-steel trowel was used for sampling, and to minimize the effects of cross-contamination, it was cleaned with filtered deionized water before and after use at each sampling point. For 24 hours, glassware was submerged in 5% HNO_3 and then thoroughly cleaned with deionized water. All samples and glassware were wrapped in aluminium foil when not in use to prevent contamination by air-borne MPs. The extraction of MPs was performed in a fume cupboard and clean Petri dishes were used to store the filters that held the recovered MPs. To limit airflow into the laboratory during analysis, all windows were closed. Nitrile gloves and a lab coat made entirely of cotton were used during the sample handling and processing. Solutions were filtered through nitrocellulose membranes (pore size 0.45 µm, Fisher Scientific) before they were applied to the samples. Procedural blanks were run in parallel with the actual samples, and MPs were not detected in them.

Risk Assessment of MPs in the sediments

The MPs pollution load index of an entire river (PLI_{river}) was evaluated from the model equations (i – iii), according to the work of Kabir et al. (2021), with CF_i and PLI_i being the contamination factor and pollution load index, respectively, for a single point (*i*) on the river.

$$CF_i = C_i / C_o \quad \text{(i)}$$

$$PLI_i = \sqrt{CF_i} \quad \text{(ii)}$$

$$PLI_{river} = \sqrt[n]{PL_1 \times PL_2 \times PL_3 \times PL_n} \quad \text{(iii)}$$

The variables C_i and C_o denote the number of MP particles at the sampling point *i* and the baseline concentration of MPs in the river, respectively. The baseline MP concentration is taken as the number of MPs found at any sampling point that had the least number of MPs. The variable *n* is the total number of sampling points on a river. Each river is considered polluted if the calculated PLI_{river} value is > 1 (Verma et al. 2022).

Assessment of risks due to PTEs in the River sediments

Geo-accumulation index (I_{geo})

Equation iv was used to compute the geo-accumulation index (Igeo), which is indicative of the level of contamination of the sediments by PTE (Barbieri 2016).

$$I_{geo} = \mathrm{Log}_2 \frac{Cn}{1.5} \times B_n \quad \text{(iv)}$$

Bn is the geochemical background concentration (mg/kg) of each element (13, 0.3, 90, 45, 850, 68, 20, 95, and 60 for As, Cd, Cr, Cu, Pb, Mn, Ni, Vn and Zn, respectively) (Ali et al. 2022). The number 1.5 is the matrix correction factor, and *Cn* is the observed concentration of a PTE in the sediment. The I_{geo} index is classified as follows: $I_{geo} < 0$ (no contamination); $0 \leq I_{geo} < 1$ (uncontaminated to moderately contaminated); $1 \leq I_{geo} < 2$ (moderately contaminated); $2 \leq I_{geo} <$

3 (moderately to strongly contaminated); $3 \leq I_{geo} < 4$ (strongly contaminated) $4 \leq I_{geo} < 5$ (strongly to severely contaminated), and $I_{geo} > 5$ (highly contaminated).

PTE Contamination factor (CF) and Contamination degree (C_d)

Contamination factor (CF) is used to assess the level of contamination from individual PTEs relative to the pre-industrial period (Islam et al. 2023).

$$CF = \frac{C_{element}}{C_{background}} \quad \text{(v)}$$

Where $C_{background}$ is the concentration of PTEs measured at an uncontaminated reference or control site, and $C_{element}$ is the concentration in mg/kg of the observed PTEs at a sample location (Ali et al. 2022; Islam et al. 2023). The geochemical background concentrations used under the geo-accumulation index calculation were also employed here (Ali et al. 2022). $CF < 1$ (implies minimal contamination); $1 \leq CF < 3$ (moderate contamination); $3 \leq CF < 6$ (significant contamination); and $CF \geq 6$ (very high contamination) are the four levels of contamination factor. The total of all the PTEs contamination factors was used to calculate the contamination degree (C_d). Contamination degree values within the range $5 \leq C_d < 10$ (is defined as moderate contamination), $10 \leq C_d < 20$ (is significant contamination), while $C_d \geq 20$ (implies high contamination).

Pollution Load Index (PLI) of PTEs

The pollution load index (PLI) of PTEs in a sediment sample can be determined using equation vi (Abdullah et al. 2015).

$$PLI = (CF_1 \times CF_2 \times CF_3 \ldots CF_n)^{1/n} \quad \text{(vi)}$$

n represents the number of the different PTEs determined in the sediment, and CF is the contamination factor of each metal, as given in equation v. PLI value is categorized into three: no pollution (PLI < 1), baseline level of pollution (PLI = 1), slight pollution (1 < PLI < 2), and severe pollution or degradation of site quality (PLI > 2).

Potential Ecological Risks of PTEs in the sediments

The possible negative impacts of the PTEs on aquatic life was assessed using the sediment guidelines published by MacDonald et al. (2000). Organisms may be negatively impacted if the concentration of metals is higher than the possible effect concentrations (PEC). The PEC value (in mg/kg) for each of the elements is known - As (33), Cd (4.98), Cr (111), Cu (149), Pb (128), Ni (48.6), and Zn (459). Further assessment of the ecological impacts was performed via the determination of the potential ecological risk factor (E^i_r) and risk index (RI), using the model equations vii and viii, respectively.

$$E^i_r = T^i_r \times CF \quad \text{(vii)}$$

$$RI = \sum E^i_r \quad \text{(viii)}$$

Here, T^i_r is the toxic response coefficient of a single metal (Tr for As = 10; Cd = 30; Cr = 2; Cu = Ni = Pb = 5, and Mn = Zn = 1), and E^i_r is the ecological risk factor for a sampling point *i*. Decena et al. (2018) defined RI as the total of all the risk factors for PTEs in sediments, while CF is the contamination factor. The values of E^i_r are categorized as follows: $E^i_r < 40$ indicates low risk; $40 < E^i_r < 80$ indicates moderate risk; $80 < E^i_r < 160$ indicates significant risk; $160 < E^i_r < 320$ indicates high risk; and $E^i_r \geq 320$ indicates extremely high risk. According to Decena et al. (2018), the RI values are also categorized into four: RI ≥ 600 = very high risk, 300 ≤ RI < 600 = considerable risk, 150 ≤ RI < 300 = moderate risk, and RI < 150 = risk low risk.

Data analysis

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Abundance of MPs was recorded as items/kg, while the concentration of PTEs was recorded in mg/kg sediment dry weight. The mean and standard deviation (SD) values are presented in both cases. Version 26 of IBM's Statistical Package for Social Sciences (SPSS) was used to analyze the data. Correlation analyses were performed to examine the relationship between MPs abundance and the physicochemical characteristics of the sediments. The confidence interval was set at 95% for the various statistical tests, with P-value < 0.05 indicating statistical significance.

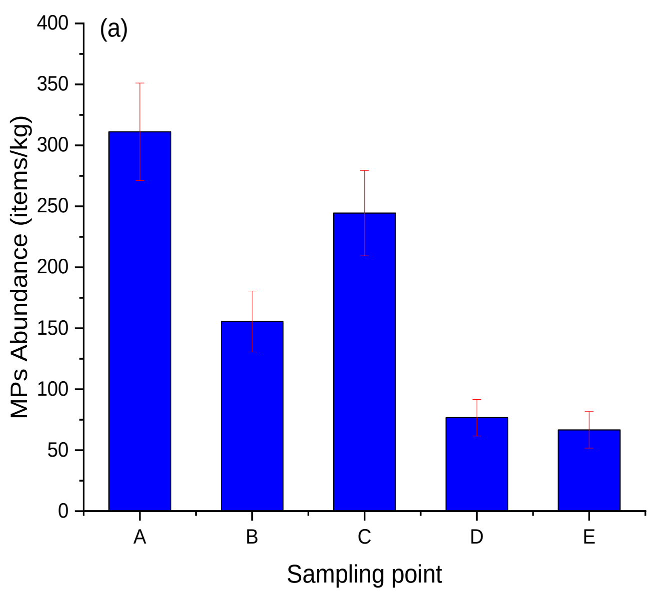
Results and Discussion

Abundance and characteristics of MPs in the river sediments

Abundance of MPs in the sediments of Odo-Ona and Ogun Rivers is presented in Fig. 2. MPs were detected in every sediment sample, with Ogun and Odo-Ona rivers having abundances of 66.7–311 items/kg and 133–433 items/kg, respectively. In the Ogun River sediment, the mean MP abundance was 171 items/kg, with Site A on the River having the highest abundance of MPs (Fig. 2a). This high value could be due to proximity to human activities like farming, fishing, buying and selling of fishes, as well as fisher's cooking and domestic activities. The Ogun River is popular in the region for fishing and agricultural activities. The ongoing intense fishing activities being carried out at the first three sampling points (A, B, and C) may account for the significant concentrations of MPs at these locations. In contrast, the sampling points D and E, which were close to rural settlements, had the lowest abundance values (76.7 and 66.7 items/kg, respectively), likely due to the reduction in human activities.

At the Odo - Ona River in Oyo State, the highest MPs abundance was at point A. This sampling point was very close to automobile repair workshops and local residential houses, where people dumped wastes directly into the river as a means of disposing them of. It is noteworthy that the MPs abundance decreased somewhat consistently with movement from point A to E on the Odo –

Ona River (Fig. 2b), which is also the direction of flow of this river. This finding implies that the area surrounding point A is likely the primary source of plastic pollution in the river. Plastic particles originating from point A may then be carried downstream to other locations, as seen in the levels found at B and C, which are the closest points to point A. This finding underscores the need for regulatory agencies to curb the unwholesome practice of waste dumping into the rivers and waterways. In general, MPs were more abundant in the Odo-Ona River sediments than in the Ogun River sediments, probably due to the dumping of wastes near the former, as observed during the sampling exercise. The most obvious MPs source into the Ogun River was the use of nets for fishing by the local people.



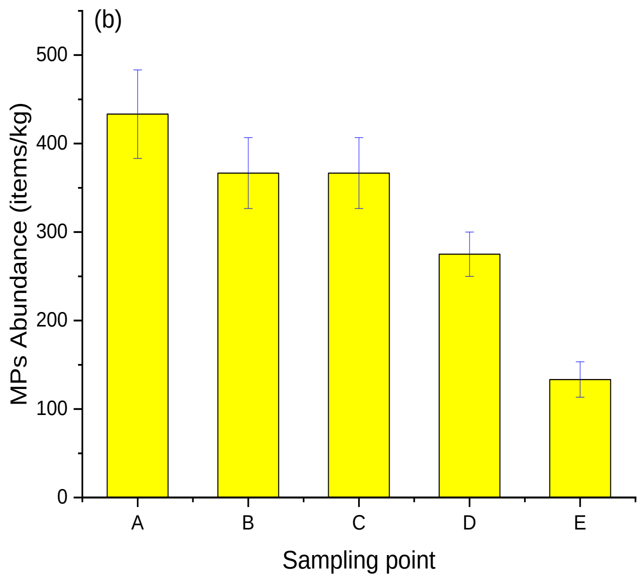


Fig. 2: Microplastics (MPs) abundance in the sediments of the (a) Ogun and (b) Odo-Ona rivers. Data represent mean ± standard deviation (n=3)

The extent of pollution of the rivers by MPs was assessed via the determination of contamination factor (CF) and PLI (Kabir et al. 2021; Verma et al. 2022). The CF values showed that there was moderate MP contamination at the river sampling locations, except points A and C on Ogun River which gave high CF values of 4.60 and 3.66, respectively, and fell within the moderate to severe contamination classification. The PLI values for the rivers were also greater than 1 (Supplementary Material, Fig. S1), implying that they were both polluted with the MPs.

Investigation of MPs characteristics in this study revealed their shapes, colours, and polymer types. The observed shapes across the two rivers were fibres, fragments, and films (Fig. 3). Fibres were dominant at all the sampling points. Fibre MPs are known to emanate from fishing activities and the gradual wear and tear of clothes due to laundry activities (Hernandez et al. 2017). It is noteworthy that both the Odo-Ona and Ogun Rivers are used for the washing of clothes by nearby dwellers. This was witnessed at the Odo-Ona River, with the people discharging the laundry water directly into the river. The lack of centrally managed waste treatment plants in the two river communities also means that laundry wastes from the majority of homes, including those far away from the rivers, are regularly discarded into open drainages, from which they may be carried into the rivers. All the detected fragments and films were irregular in shape, suggesting that they were from secondary sources such as fragmentation of pure water sachet commonly seen in the environment and fishing nets. This indicates that in contrast to other MP shapes like pellets and microbeads, which are the main particles from the plastic processing industries, they originated from the fragmentation of plastic products in the environment (Horton and Dixon 2018). Specifically, the lack of pellet MPs in the sediments is consistent with the area around the two rivers—especially the studied sections—having few plastic production companies. It is known that plastic bag fragmentation produces film MPs (Nor and Obbard 2014). The prevalence of film microplastics in the river sediments is therefore not surprising, given the widespread usage of plastic carrier bags for groceries and shopping in the study area, as well as their careless disposal. National policy needs to be enacted to regulate single-use plastics, with penalties prescribed for unlawful garbage and plastic waste dumping. The inclusion of primary MPs in consumer products (e.g. cosmetics) should also be regulated, in order to reduce the incidence of MPs in the environment.

Using ATR-FTIR, the polymer nature of the MPs was examined. The findings indicated that the three plastic polymer types—polyethylene (PE), polypropylene (PP), and polyamide (PA) were the particles analyzed, all of which had sizes in the range of 0.5 to 5 mm. The IR spectra recorded

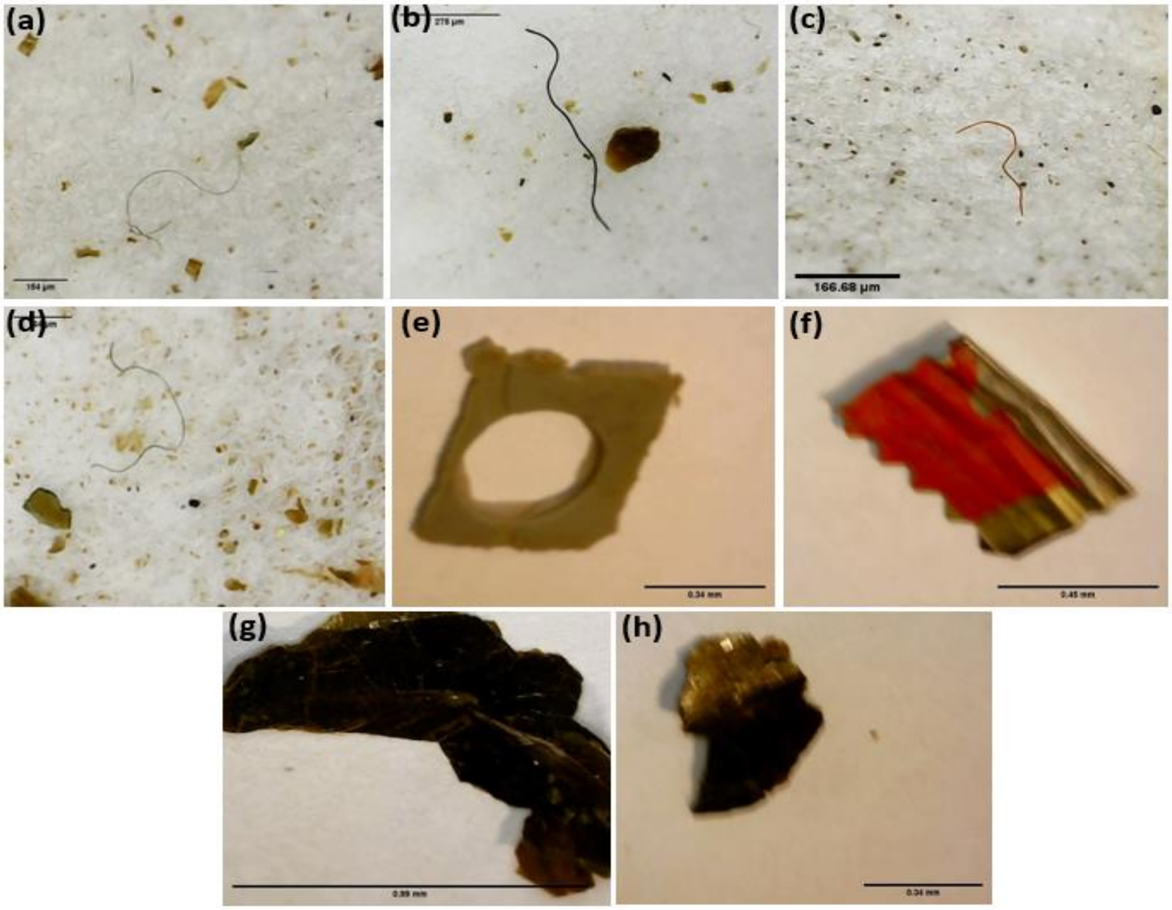


Fig. 3: Images of some microplastics (MPs) detected in the sediment of Ogun and Odo-Ona Rivers: (a –d) fibres; (e – f) fragments; (g – h) films

for these polymers are presented in Supplementary Material, Fig. S2. At the Odo-Ona River, 91 MPs belonging to the PE type were found, while 34 MPs were of the PP type. The numbers of PE, PP, and PA MPs at the Ogun River were 49, 28, and 5, respectively. The prevalence of PE and PP reflects the plastic consumer pattern of the Nigerian populace. This is because PE carrier bags, usually referred to as "polyethene bags", are very popular as single-use carrier bags in the country and are widely disposed of. Similarly, PP plastics are commonly used for food packaging at most fast-food outlets, with people usually discarding the plastics after consuming the products. In

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addition, PP is used in textiles and bottles production, and in some replaceable automotive products (Okolie 2022). The occurrence of the PA polymer in sediments of the Ogun River is also consistent with their use as shopping bags for small grocery items in Nigeria. It is worth noting that, although polyethylene terephthalate (PET) plastic is widely used for packaging carbonated soft drinks and potable water in the country, the polymer was not detected in the river sediments (for the particle size range that could be picked for the FTIR analyses). This may be because PET bottles are the most recycled plastic type in the country. Thus, the awareness of PET bottles and their recycling efforts have significantly reduced the amount of this particular polymer reaching the open environment. Remarkably, some bottling companies have been engaging in the removal of PET bottles from the environment, in compliance with the extended producer responsibility (EPR) policy, introduced by the Nigerian Environmental Standards and Regulatory Enforcement Agency (NESREA) about a decade ago (Allen-Taylor 2022). Also, individuals who engage in informal plastic recycling in the region are known to deal only in PET bottles. Thus, these factors may account for why PET polymer was not detected in the river sediments in this study.

Ecological impact of PE and PP may manifest in the form of apoptosis, genotoxicity, organ damage and mortality that can result from eating or becoming entangled with the floating MPs (Hariharan et al. 2021). PE MPs may also cause a reduction in bacteria and fungi diversity in sediments (Hou et al. 2021). The formation of PE MPs in the environment is accompanied by the release of greenhouse gases, as well as additives and plasticizers, which have endocrine-disrupting effects on organisms in the environment (Iskander et al. 2016).

The colours of MPs can reveal information about their origins, ages in the environment, and possible impacts on aquatic system organisms (Verlis et al. 2013). Colours of MPs found in the

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two rivers were black, blue, brown, red and white. In addition, some yellow MPs were found in the Odo – Ona River. Interestingly, black-coloured MPs occurred most frequently in the two rivers, constituting 46 % and 54.9 % of MPs recovered from the sediments of the Odo-Ona River and Ogun River, respectively (Supplementary Material, Table S3). The dominance of black MPs is in agreement with the prevalence of PE plastic polymers in the sediments. This is because the widely used carrier bags, responsible for the PE polymer fragments in the sediments, are normally produced in black colour. Fishes have a high tendency to ingest brown, white or yellow-coloured MPs from water, due to the resemblance of such MPs to zooplankton (Boerger et al. 2010). The presence of MPs with these colours in the rivers indicates potential hazards to fishes and other organisms that feed on coloured planktonic prey.

Table 1 summarises an attempt to compare the concentrations and forms of MPs in the current study with those from other freshwater investigations. Levels in the previous studies were higher than those reported in the current study in some cases, but lower in others. For example, MPs abundance in Wei River, China (360 -1320 items/kg) (Ding et al. 2019), and Vaal River, South Africa (at an average of 463.28 ± 284) (Saad et al. 2022) were both higher than the abundance in both Ogun and Odo-Ona Rivers. In contrast, much lower levels were found by Mutlu et al. (2024) in the sediment of Coruh River Basin, Turkiye (289 MPs/kg), Akdogan et al. (2023) in the sediment

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Table 1. Abundance of microplastics (MPs) in the sediments of Ogun and Odo-Ona Rivers compared with MPs abundance in other freshwater sediments

Study area	**Freshwater**	**Size (mm)**	**Abundance (items/kg)**	**Polymer shape**	**Polymer type**	**Reference**
Ogun River, Nigeria	River	< 5	66.7 ± 12.2 – 311 ± 20.8	Fibre, Fragment, Film	PP, PE, PA	This study
Odo-Ona River, Nigeria	River	< 5	133 ± 30 – 433 ± 100	Fibre, Fragment, Film	PP, PE	This study
River Kelvin, UK	River	< 5	50 – 244	Fibre, fragment	PP, PE	Shokunbi et al. 2024
South-west Rivers, Nigeria	River	< 1	64.1 – 114 (Dry season) 28.5 – 71.9 (Wet season)	Fibre, fragment, film, pellet, granules, foam	PP, PE	Ololade et al. 2024
Vaal River, SA	River	0.02 – 0.5	463 ± 284	Fragment	PP, PE, PEVA	Saad et al. 2022
Qinghai-Tibet, Tibet	River	0.02 - 5	41.5 ± 22.3	Fibre, fragments, spheres, foams, films	PP, PE, PS, PET, PA, PVC	Feng et al. 2021
Taihu Lake, China	Lake	> 0.02	460 – 1390	Fragment, pellet	PVC, PE	Zhang et al. 2021
Ox-bow Lake, Nigeria	Lake	0.02 – 5	347 – 4030 & 507 – 7590	Fibre	PET, PVC	Oni et al. 2020
Lake Ziway, Ethiopia	Lake	0.15 – 5	0.05 – 36.2	Fragment, fibre	PET, PP, PE	Merga et al. 2020
Auckland, New Zealand	River	0.06 – 0.5	80	Fragment, fibre	PE, PP, EVA	Dikarewa and Simon 2019
Wei River, China	River	< 0.5	360 – 1320	Fibre	PVC, PS, PE	Ding et al. 2019

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Bloukrans River, SA	River	-	6.3 ± 4.3 & 160 ± 139	-	-	Nel et al. 2019

Table 2. Pearson correlation coefficients between microplastics (MPs) abundance and physicochemical parameters of sediment of Ogun and Odo-Ona Rivers

	MPs	Ph	Cond	OM	AN	AP	%Sand	%Silt	%Clay
Ogun									
MP	1.000								
pH	0.752	1.000							
Cond	-0.667	0.962**	1.000						
OM	-0.801	-0.952*	0.946*	1.000					
AN	0.915*	-0.764	0.705	0.883*	1.000				
AP	0.913*	-0.544	0.657	0.727	0.576	1.000			
%Sand	0.872	0.921	-0.976	0.962**	-0.738	-0.804	1.000		
%Silt	-0.869	-0.835	0.880	0.922*	-0.721	0.912*	0.959**	1.000	
%Clay	-0.663	-0.860	0.920	0.800	0.587	0.392	-0.310	0.639	1.000
Odo-Ona									
	MPs	pH	Cond	OM	AN	AP	%Sand	%Silt	%Clay
MP	1.000								
pH	-0.96**	1.000							
Cond	-0.688	0.711	1.000						
OM	0.325	-0.101	0.310	1.000					
AN	0.320	-0.101	0.325	1.000**	1.000				
AP	0.676	-0.619	-0.106	0.630	0.644	1.000			
%Sand	-0.812	0.913*	0.484	-0.664	-0.876	-0.746	1.000		
%Silt	0.860	-0.808	-0.276	0.598	0.606	0.941*	-0.834	1.000	
%Clay	0.860	-0.808	-0.276	0.598	0.606	0.941*	-0.834	1.000**	1.000

Note: AP – Available phosphorus, AN – Available nitrogen, Cond – conductivity, MPs - Microplastics, OM – Organic matter

* Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed).

of Ergene River, Turkey (97 – 207 items/kg), Merga et al. (2020) in the sediments of Lake Ziway, Ethiopia (average abundance of 33.2 items/kg) and by Dikarewa and Simon (2019) in the sediments of Auckland

River, New Zealand (with a mean abundance of 80 items/kg). The results of this investigation are in line with some studies that have reported high amounts of fibrous MPs in the sediments of freshwater bodies (Nayeri et al. 2023; Neelavannan et al. 2022; Xia et al. 2021). Table 1 highlights a few more research that in the previous five years have found a significant presence of fibrous MPs in freshwater sediments.

Some physicochemical properties of the sediments were determined to examine if any relationship existed between them and MPs abundance in the sediments. The soil particle size distribution, represented in terms of %sand, %silt, and %clay in the sediments, and physicochemical parameters (pH, electrical conductivity (EC), organic matter (OM) content, available nitrogen (AN), available phosphorus (AP)), were determined (Supplementary Material, Table S3). Based on the Pearson's correlation analyses performed, there was no relationship between the abundance of MPs and any of EC and OM. However, strong and positive correlations were observed between MPs abundance and AN ($r = 0.915$, $p < 0.01$); AP ($r = 0.913$, $p < 0.01$), and the percentage of sand ($r = 0.872$, $p < 0.01$) in the Ogun River sediments (Table 2). The observed correlation between MPs abundance and the plant nutrients (AN and AP) at the Ogun River, may be due to the fact that some cultivated lands are adjacent to the stretch of the Ogun River sampled. It is likely that water run-off from these agricultural fields carry inputs like fertilizers with them into the river. It has already been established that agricultural fertilizers do contain significant amounts of MPs (Moeck et al. 2023; Cusworth et al. 2024). This explanation is also consistent with the fact that the particular correlations of MPs with AN and AP were not observed for the Odo-Ona River, which lacked farmlands in its vicinity. Positive correlation of MPs abundance with sand content implies that more sandy areas of the river sediment retained more MPs, compared with sections of the sediment that were less sandy. Additionally, a high but negative correlation ($r = -0.960$, $p < 0.05$) was found between MPs abundance and the pH of the Odo-Ona River sediments (Table 2). Mutshekwa et al. (2023) previously observed a similar inverse association between MPs abundance and pH from a study of the sediments of two freshwater lakes in South Africa. However, the reason for this is not yet understood.

PTEs in the sediments of Ogun and Odo-Ona Rivers

Table 3 presents the concentrations of PTEs found in the sediment samples. PTE concentrations varied between sampling locations in both rivers, with Odo-Ona River sediments typically containing higher amounts of PTEs than Ogun River sediments. Among the PTEs examined, Mn was the most prevalent in the sediments at every sampling point in the two rivers. The range of concentrations was from 173 to 1110 mg/kg in Ogun River and 549 to 963 mg/kg in Odo-Ona river (Table 3). Mn is a crucial micronutrient that both plants and animals need. Water bodies may contain Mn due to both anthropogenic activity and the breakdown of geologic minerals (Shil and Singh 2019). The National Environmental Standards and Regulations Enforcement Agency of Nigeria's suggested limit of 200 mg/kg for manganese is far greater than the amounts of manganese found in this study. When compared to other elements examined, a prior study that evaluated the pollution caused by heavy metals in sediments from Ologe Lagoon, Agbara, Lagos, Nigeria, likewise revealed a high concentration of Mn (70.5 - 840 mg/kg) in the sediment (Adeyemi et al. 2019). Large amounts of Mn disturb the functions of synapses and impair the central nervous system because Mn ions penetrate the blood-brain barrier. High concentration of Mn in an aquatic environment causes disturbances in the sodium balance, reduces the absorption of calcium and phosphorus, disturbs the metabolism of carbohydrates, and impairs the immunological functions in fishes (Lall and Kaushik, 2021).

Another reason to be concerned would be the amounts of Cr and Pb in the sediments. Cr ranged from 10.3 to 46.1 mg/kg in Ogun River sediments and from 20.9 to 48.3 mg/kg in the Odo-Ona River sediments.

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The Cr concentrations at some of the sampling points are above the maximum limit set for Cr (20 mg/kg) in soil/sediments by NESREA (2020) and are higher than the TEL value (37.3 mg/kg) and USEPA

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Table 3. Potentially toxic elements (PTEs) concentration (mg/kg) in Ogun and Odo-Ona River sediments

	As	**Cd**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**V**	**Zn**
Ogun									
A	1.48 ± 0.0	ND	10.3 ± 1.2	3.33 ± 0.5	173 ± 21.2	ND	ND	12.5 ± 1.0	2.65 ± 0.7
B	1.21 ± 0.1	0.71 ± 0.0	12.5 ± 1.3	6.80 ± 0.5	194 ±13.0	ND	1.10 ± 0.2	13.5 ± 0.3	8.25 ± 1.1
C	1.40 ± 0.1	ND	14.1 ± 0.9	5.99 ± 0.4	254 ± 7.21	7.11 ± 0.1	2.03± 0.1	17.6 ± 0.9	10.0 ± 0.5
D	1.33 ± 0.3	0.19 ± 0.0	46.1 ± 0.2	23.6 ± 1.2	1665 ± 220	12.1 ± 0.1	10.1 ± 0.6	68.9 ± 0.5	42.6 ± 0.9
E	1.93 ± 0.1	0.15 ± 0.0	36.7 ± 2.2	16.8 ± 0.6	1110 ± 71	2.86 ± 0.1	7.36 ± 0.9	44.9 ± 3.9	37.6 ± 4.2
Odo-Ona									
A	1.64 ± 0.2	ND	20.9 ± 1.1	7.01 ± 0.2	549 ± 38	0.00 ± 0.0	5.10 ± 0.7	24.7 ± 3.0	17.6 ± 0.8
B	2.22 ± 0.3	ND	53.8 ± 1.3	11.5 ± 1.4	751 ± 8.9	2.56 ± 0.8	11.4 ± 0.7	41.6 ± 1.9	24.8 ± 2.1
C	2.86 ± 0.1	ND	15.6 ± 0.2	4.71 ± 0.4	200 ± 1.8	ND	2.14 ± 0.1	13.9 ± 0.4	10.0 ± 0.5
D	2.09 ± 0.4	ND	34.5 ± 1.2	19.5 ± 0.3	686 ± 37	0.30 ± 0.0	211 ± 60.0	36.3 ± 9.4	36.3 ± 9.4
E	2.82 ± 0.4	ND	48.3 ± 1.6	16.5 ± 1.2	649 ± 31	37.2 ± 1.5	6.00 ± 0.0	42.3 ± 1.5	40.3 ± 0.7

Values represent mean ± standard deviation (SD), n = 3; ND – not detected.

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Table 4. Comparison of potentially toxic elements (PTEs) (mg/kg) in sediments of Ogun and Odo-Ona Rivers with PTEs in other river sediments and some reference values

Location	As	Cd	Cr	Cu	Mn	Ni	Pb	V	Zn	References
Ogun River, Nigeria	1.47	0.35	23.9	11.3	679	7.36	5.15	31.5	20.2	This study
Odo-Ona River, Nigeria	2.12	0.3	36.7	14.7	719	8.97	48.1	35.4	28.5	This study
River Kelvin, UK	10.4	0.275	33.4	27.6	1410	17.3	63.9	56.1	127	Shokunbi et al. 2024
Astore River Bain, Pakistan	-	0.66	24.3	13.2	16,650	23.6	22.6	-	36.6	Ali and Muhammad 2023
Kunhar River, Pakistan	-	2.1	17.4	14.9	-	46.5	127	-	-	Muhammad et al. 2022
Haihe River, China	-	0.2	-	45	-	64	15	-	-	Zhang et al. 2021
Hooghly River, India	4.0	0.2	31.8	16.7	-	15.5	3.1	-	46.9	Mondal et al. 2020
Brisbane River, Australia	-	-	-	50	-	25	47	-	196	He et al. 2023

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World Rivers	36.3	1.55	130	75.9	1679	74.5	61.1	129	208	Viers et al. 2009
Background										
NESREA	-	5	20	100	200	140	35	-	300	NESREA 2022
TEL	5.9	0.6	37.3	35.7	-	18	35	-	123	MacDonald et al. 2000
PEL	17	3.53	90	197	-	36	91.3	-	31.5	MacDonald et al. 2000
LEL	6	0.6	26	16	-	16	31	-	120	MacDonald et al. 2000
SEL	33	10	110	110	-	75	250	-	820	MacDonald et al. 2000
USEPA	9.8	0.99	43.4	31.6	460	22.7	35.8	-	121	USEPA 1999

Note: NESREA: National Environmental Standards and Regulations Enforcement Agency; USEPA: United States Environmental Protection Agency; TEL: threshold effects level; PEL: probable effects level; LEL: lowest effect level; SEL: severe effect level; – means Not Determined permissible limits in sediments (43.4 mg/kg). According to Ayedun et al. (2019), chromium is typically emitted during the electroplating of materials, the steel manufacturing process, tanning leather, and the textile industries. The high values obtained could be due to the presence of textile industries and automobile workshops, which could be the source of electroplated metals in the river. Pb occurred at a maximum of 10.1 mg/kg in Ogun River sediments, whereas the concentration was up to 211 mg/kg in the Odo-Ona River sediments. The Pb levels in the Odo-Ona River were above the NESREA and USEPA recommended thresholds of 35 mg/kg and 35.8 mg/kg, respectively. Pb is toxic to living organisms, including man, and its toxicity is exerted even in small amounts. Pb interferes with the neurological and reproductive systems' ability to operate normally. In addition, it results in anaemia, hypertension, and kidney impairment (WHO 2011). A study of PTEs in River Abesan and Owo, also in the Southwestern part of Nigeria, reported similarly high concentrations of Pb, which range from 84.2 to 204 mg/kg in the river sediments (Akoteyon 2022). The current study's Pb contents were often greater than the TEL limit (35 mg/kg) and, in some cases, higher than the PEL (91.3 mg/kg), showing that the river is Pb-polluted. PTE concentrations were found in sediments from the Ogun River in the general order Mn > Cr > Zn > Cu > Ni > Pb > As > Cd, but in the Odo-Ona River, the order was Mn > Pb > Cr > V > Zn > Cu > Ni > As > Cd.

Additionally, the PTE levels in the sediments were contrasted with those from other recent research on freshwater sediments (Table 4). In comparison to the River Kelvin in the United Kingdom (Shokunbi et al., 2024), the Astore River in Pakistan (Ali and Muhammad, 2023), and the Haihe River in China (Zhang et al., 2021), the mean concentrations of Pb and Cr in the current study are greater. As, Cd, Cu, Mn, Ni, V, and Zn, on the other hand, were lower than those found in another research (Table 4). The high concentration of the PTEs, particularly in the Odo-Ona River sediments, could be due to the impact of direct waste dumping, as observed during the sampling exercise. Domestic wastes discharge and anthropogenic activities, such as the location of automobile repair workshops near the river, could have also contributed to the higher concentrations of the PTEs in the Odo-Ona River, compared to the Ogun River.

The sediment samples were moderately to highly polluted with Pb, Cu, Ni, and Zn, according to USEPA sediment Quality Guidelines (SQGs). The established sediment quality parameters, which include the lowest effect level (LEL), portable effect level (PEL), severe effect level (SEL), and threshold effect level (TEL), were generally compared with the PTEs found in the sediments of the Ogun and Odo-Ona Rivers. In comparison to LEL, PEL, SEL, and TEL, the levels of As, Cd, Cu, Ni, and Zn were lower. Conversely, Table 4 shows that Pb concentrations in the Ogun River exceeded both LEL and TEL, while Cr concentrations in the same river above LEL. Roadside dust, which may contain Pb emitted from vehicle exhausts, and urban runoff may have contributed to the comparatively high Pb concentration in certain sediment samples (Shikazono et al. 2011).

PTEs pollution indices and evaluation of ecological risks

The level of PTE contamination of the sediments was evaluated using some indices, including I*geo*, CF, PLI, and C_d. The I*geo* assesses the quality of the sediments and the concentrations of heavy metals (HMs) that have accumulated in river sediment as a result of human activity (Islam et al., 2023). For every element found in the two rivers—As, Cd, Cr, Cu, Mn, Ni, V, and Zn—the I*geo* value was less than zero., suggesting that the sediments were uncontaminated with these elements. However, Pb gave an I*geo* value > 2 at one of the locations on Odo-Ona River (Supplementary Material, Fig. S3), indicating that the sediment was moderately polluted with Pb at this particular location (point D). The significantly high I*geo* value of Pb at point D also implies that the Pb concentrations could not have emanated from a geogenic/lithogenic source alone, but that anthropogenic activities in the area would have contributed to the levels observed. The most probable source would be the automobile repairs workshops which operate close to the sampling point D and discharge materials, possibly including car lead-acid battery wastes, into the Odo-Ona River.

Consistent with the I*geo* index, the CF values determined for the PTEs also showed that the Pb levels at the sampling point D on Odo-Ona River gave the highest at 10.6 (Supplementary Material, Table S4), confirming that the river was contaminated with Pb at this location. Highest CF value of 2.37 obtained for Cd in the sediments at point B on Ogun River, as well as the CF values of 1.96 and 1.15 obtained for Mn and V, respectively, at point D on the river suggest that the sediments were slightly contaminated with these elements at the locations. CF values of 1.13 and 1.0 were also obtained for Mn and Cd at locations C and D, respectively, on Odo-Ona River, indicating that the sediments were contaminated with Mn and Cd at these locations. In contrast, in both rivers, CF values below 1 were obtained for As, Cu, Cr, Ni and Zn, suggesting that the sediments were not contaminated by these elements. The degree of contamination (C_d) was greater than 8 in the Odo-Ona River, which implies moderate to considerable contamination. In Ogun River, two sampling points could be categorized as unpolluted ($C_d < 1.5$), while the rest of the sampling points exhibited a low to moderate degree of contamination. In Odo-Ona River, the sediment samples were from a low degree to a high degree of contamination. The pollution load index (PLI) values for both the Odo-Ona and Ogun Rivers were all less than 1 (Supplementary Material, Table S4). To mitigate PTEs pollution in the environment, best management practices in industries and regulations on the treatment and release of wastewater should be implemented. Indiscriminate disposal and burning of metal-bearing wastes should also be curbed in the region.

The potential ecological risk index (PERI) and the ecological risk factor (Er) were calculated in order to comprehend the ecological importance of the PTE levels found in the sediments. A low potential ecological risk of PTEs in river environments was shown by PERI values (Supplementary Material,

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Table S4), which were below 120 for all sampling stations in the rivers. Additionally, all of the ecological risk factors (Er) for As, Cu, Cr, Mn, Ni, V, and Zn were found to be lower than the guideline's lowest suggested values, indicating a low risk to the river ecology. However, the E_r values obtained for Pb (E_r = 52.8) in the Odo-Ona River and Cd (E_r = 71.1) in the Ogun River suggest that these metals pose a moderate risk to the ecosystem. Put together, the ecological risk assessments imply that the PTEs concentrations currently constitute little concern. However, because human activities can significantly raise PTE concentrations and pose a high ecological risk to river creatures, it is crucial to regularly monitor the catchments of the rivers.

Conclusions

In this study, MPs and PTEs have been investigated in the sediments of the Odo-Ona and Ogun Rivers in southwest Nigeria. Every sample of sediments from the two rivers had MPs. Maximum abundance recorded for a single sampling point was 433 particles/kg for the Odo-Ona River and 311 particles/kg for the Ogun River. The majority of the plastic particles were fragments, fibres, and films, suggesting that they came from secondary sources, which were the decomposition of plastic products that had been discarded into the environment. The unwholesome practice of indiscriminate wastes dumping into rivers was found to be a major factor responsible for the MP levels observed, especially at the Odo-Ona River in Oyo State. As, Cd, Cr, Cu, Mn, Ni, Pb, V, and Zn are the nine (9) PTEs that were identified in the samples; Mn, Pb, and Cr were found in high amounts. The level of PTE pollution in the sediments was assessed by computing various pollution indices. The geo-accumulation index (Igeo) and the contamination factor (CF) both indicated that one of the locations in the Odo-Ona River was polluted with Pb, while some sites on both rivers were contaminated with Mn and Cd. Reduction in the levels of both MPs and PTEs in the river sediments may be achieved by raising public awareness on appropriate disposal of wastes, and promoting the values waste reduction, items

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reuse, as well as recycling. The recent ban on single-use plastics pronounced by the state governments should also be enforced firmly. Future investigations should examine MPs in fish species and other biota in these rivers, as well the impact of seasonal changes on the MPs and PTE levels.

Declarations

Ethical Responsibilities of Authors

All authors have read, understood, and have complied as applicable with the statement on 'Ethical Responsibilities of Authors' as found in the instructions for Authors

Funding

This study was funded by the Petroleum Technology Development Fund (PTDF) of Nigeria and the Commonwealth Scholarship Commission (CSC) in the United Kingdom.

Acknowledgements

The Petroleum Technology Development Fund (PTDF) of Nigeria is acknowledged by the authors for providing OSS with a PhD fellowship. The split-site PhD scholarship that the Commonwealth Scholarship Commission in the United Kingdom offered to OSS to perform part of the research at the Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, Scotland, is also acknowledged by the authors.

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Supplementary information

Supplementary information can be found in the online version at https://doi.org/....................

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