

## Python Aided Visualizations of the Phthalate Acid Esters (PAEs) Accumulation and Metal Distribution in Coastal Sediments of the South-Western Portions of Nigeria, Gulf of Guinea

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### Abstract

Coastal environment is an important area in ecology as it supports several natural and human activities, hence the need to access their associated risk matrices. Lagos state (in Nigeria) is a mega city and an economic hub in West Africa, this suggests that lots of anthropogenic activities interfering negatively with the ecosystem could be imminent. Some of those are effluence discharge, microplastic pollution, and resulting in phthalate acid esters (PAEs) accumulation in coastal sediments. Microplastics (MPs) and PAEs concentrations at four (4) different regions (Elegushi, Atican, Eleko, and Oniru Beaches) of Lagos coastal sediment have been assessed. Sediment samples were collected during the dry season from the beaches. The MPs content was separated from the sediments by density flotation in a saturated solution of sodium chloride (NaCl). Polymer analysis was conducted using the PerkinElmer Spectrum Two Attenuated Total Reflectance – Fourier Transform Infra-Red Spectrometry (ATR-FTIR). The MPs found in the area were characterized based on plastic and polymer types. The obtained data was visualized using python data manipulation and analysis libraries. The MPs concentrations based on plastic types in the area follows; Oniru>Elegushi>Eleko>Atican corresponding to 51.06%, 35.30%, 6.91%, and 6.73% respectively. Based on MPs distribution on polymer types, the concentration follows the order of; Oniru>Elegushi>Atican>Eleko with respective percentage contributions as 51.06%, 35.30%, 6.91%, and 6.73%. The phthalate esters (PAEs) analyzed in the sediment and extracted include Butyl benzyl phthalate (BBZP), di (ethyl hexyl) phthalate (DEHP), Diethyl phthalate (DEP), Dimethyl phthalate (DMP), Dibutyl phthalate (DnBP), and Di n-octyl phthalate (DnOP). The PAEs with the highest impact of fouling within the study area is DEHP (80.82%) whereas DnOP has the least contribution (0.15%). Relative to the beaches, the contamination resulting from the sum of the six PAEs ( $\Sigma$ 6PAEs) follows; Oniru beach (46.17%), Eleko beach has the least (6.23%) whereas Antican and Elegushi beaches have relatively the same concentration (23.80% and 23.79% respectively). These results imply that the level of soil contamination by PAEs, is dependent on the MPs accumulation in the area. Therefore, rising concentration of MPs and associated PAEs can interfere with the physical and chemical properties of sediments, which by extension will influence the overall biodiversity of the coastal environment and food chain. To mitigate these ecological implications, it is crucial to identify and reduce the sources of microplastic pollution in the area.

**Keywords:** Python, Phthalate Acid Esters, Accumulation, Metal Distribution, Coastal Sediments, Nigeria, Gulf of Guinea

### Introduction

A coastal zone is an area where the land and sea meet (Schlüter et al., 2020). Given that coastal areas are home to 67% of the world's population (Nwilo et al., 2020), and that coastal zones are continually changing as a result of the endless interplay between the ocean and land, therefore, it is crucial to understand sediment dispersion and its composition in coastal settings. Waves and winds constantly erode rock and deposit silt along the shore, the rates of erosion and deposition vary greatly from day to day along such zones (O'Neil, 1985). Storms can also cause the energy hitting the coast to increase, making coastal areas more vulnerable to natural disasters. Understanding the interplay between the land and the oceans is crucial for comprehending the dangers related to coastal zones.

Industrialized cities could be poor in waste management systems (as in the case of commercial cities of Lagos and

Ontisha) impacting environmental resources significantly. Phthalic Acid Esters (PAEs), are a class of organic compounds, also known as dialkyl or alkyl aryl esters of 1,2-benzene-carboxylic acid can lead to fouling of environmental resources. These compounds are routinely added to plastics to increase the flexibility of the materials. Pharmaceuticals, pesticides, health and beauty goods, and children's toys use PAEs as solvents and emulsifiers, which are the most produced and widely used synthetic organic chemicals (Dodson et al., 2012; Abdi et al., 2021; Wang et al., 2023). The discharge of hazardous substances threatens the safety of the soil organisms and influences nutrient availability (Akpa et al., 2023b). Studies have shown that there are always higher concentrations of PAEs in urbanized areas than in remote areas suggesting strong anthropogenic influence as the primary factor triggering PAE contributions (Heo et al., 2020). Therefore, urbanization is one of the leading causes and sources of PAEs, widely recognized as organic pollutants of

primary importance to the environment. Today, PAEs are one of the world's most yielding compounds due to their numerous uses and rising demand with an annual world production of roughly 6 million tonnes (Li *et al.*, 2020). PAEs are biotoxins, their interactions could arise from covalent and/or non-covalent binding (Li *et al.*, 2023), also its relatively unrestricted bonding attribute enhances its mobility and permeation into environmental media (Fromme *et al.*, 2002). Relative to non-covalent connections between phthalate plasticizers and their parent substances, PAEs have the potential to leak considerably into the environment and create environmental contamination, which could result in widespread exposure among the general public (Wang *et al.*, 2015).

Several researches have stressed the ubiquitous nature of PAEs in environment and environmental resources. These include PAEs being present in face mask (Vimalkumar *et al.*, 2022; Xie *et al.*, 2022), PAEs in indoor dust collected from 28 classrooms in Tehran, Iran (Abdi *et al.*, 2021), presence of PAEs in Jeans and school cloths (Gong *et al.*, 2015; Tang *et al.*, 2020), face towel (Rovira and Domingo, 2019; Zhang *et al.*, 2023; Wang *et al.*, 2023), PAEs interaction with soil and water (He *et al.*, 2015; Li *et al.*, 2023; Fred-Ahmadu *et al.*, 2020). These pegged Phthalate Acid Esters (PAEs) as one of the dangers found in high concentrations in human residential areas, and are suspected of causing diseases like asthma and skin-related issues in children (Wormuth *et al.*, 2006). These associated hazards dignify the need to study the accumulation and distribution of PAEs in coastal sediments of Lagos beaches as it can provide insight into the sources of the pollution and the potential impacts on the ecosystem. Phthalate Acid Esters (PAEs) have been shown to accumulate in coastal sediments, and their presence in the environment can have negative impacts on aquatic organisms and human health (Roy *et al.*, 2022). Studies have shown that PAEs can be found in high concentrations in coastal sediments in various parts of the world, and these concentrations are likely the result of a combination of factors, including industrial activities and the discharge of untreated wastewater into the coastal waters (Heo *et al.*, 2019; Arfaeinia *et al.*, 2019; Li *et al.*, 2020).

Currently, studies that evaluated PAEs distributions and destructive effects are few (Heo *et al.*, 2020) in Nigeria and other African countries notwithstanding the availability of several kinds of research on pressing environmental issues, the aspect of PAEs effect on environmental matrices, bio-species, and health risk

impact has been grossly underscored in cemerical cities of many developing countries of Africa. The contaminants arising from PAEs extend short to long-term impacts on human and bio-lives/health not just as environment inputs. The complications regarding the PAEs follow that there is no specific maximum or least permissible limit yet established relative to its PAEs concentration in the environment (Abdel daiem *et al.* 2012; Klavarioti *et al.*, 2009). This together with its ubiquitous nature put them on the page of hard pollutants to control as researchers have defined their presence in the lithosphere, water bodies, atmosphere, diverse particulate matters, and most daily need materials by humanity (Net *et al.*, 2015; Wang *et al.*, 2014; Kong *et al.*, 2013; Yang *et al.*, 2014; Abdi *et al.*, 2021; Li *et al.*, 2023; Wang *et al.*, 2023).

Microplastics, on the other hand, are small plastic particles that are smaller than 5mm in size (Fred-Ahmadu *et al.*, 2020; Razeghi *et al.*, 2021). They are also widely found in the coastal environment and are known to have negative effects on marine life and the environment. Microplastic pollution can harm biodiversity and species that are of ecological importance, including mussels, salt-marsh grasses, and corals. The ubiquity of microplastics poses danger to reptiles like sea turtles, mammals, and birds. In 2012, the Convention on Biological Diversity Mammals, Canada reported that 45% of marine mammal species and 21% of seabird species are harmed by feeding on microplastics or getting entangled in them (Rochman, 2013). Plastics are synthetic materials; hence plastic pollution is of anthropogenic origin. Shopping bags of varied sizes and water sachets (50-centiliter plastic bags) constitute the major plastic waste in Nigeria (Dumbili, 2020). According to Yalwaji *et al.* (2022), polyethylene bags made up the greatest stream of waste at the University of Lagos, accounting for 24% of all waste generated there. Plastic made up 9% of the institution's total waste, but just 3% of the total trash. Due to the prevailing poor plastic management in the area, litter around the area comes from various anthropogenic sources and makes its way to the coastlines, marshes, and substrates (Fred-Ahmadu *et al.*, 2020). The sources of plastic pollution come from two broad sources: *municipal/industrial sources and nonpoint sources* (Wormuth, 2006, Tobiszewski *et al.*, 2012).

Nonpoint sources constitute a major contributor to plastic pollution along the Lagos coast. This plastic pollution comes from numerous diffused, convoluted sources. They originate from human activities like

agricultural activities, land development, forestry, transport facilities, atmospheric deposition, and industrial processes (Fred-Ahmadu *et al.*, 2020). The domestic waste sources include urban runoffs, sewer overflow, and open drainage dumping and littering. Some plastics are carried by runoff from streets, agricultural fields, and other land surfaces and are deposited on the coasts where they break down into microplastics and Nano-plastics that constitute pollution. Because there are so many diffuse sources that contribute to nonpoint sources of pollution, it can be challenging to control and reduce (Wormuth, 2006; Tobiszewski, 2012). Agricultural waste such as manure, fertilizer, pesticides, and silage plastics also contribute to this menace along the coast (Benson *et al.*, 2014; Benson and Fred-Ahmadu, 2020).

The indiscriminate disposal of industrial and municipal waste is a major plastics-related pollution source within the commercial city of Lagos and adjoining coastal areas. The study area is an urban environment with numerous companies ranging from pharmaceuticals, distillers, fashion makers, and electronics. The majority of industries in Nigeria do not have effective effluent treatment facilities, therefore they release their effluents into water bodies without proper treatment, frequently into the closest water bodies. The pharmaceutical industry has been characterized as a key source of plastic pollution in developing countries (Balakrishna *et al.* 2017). Ogunbanwo *et al.* (2022) x-rayed the contribution of pharmaceutical facilities to the Nigerian pollution index relying on data from the spatial distribution of pharmaceutical companies within the Lagos coastlines. The result shows that the clustering of pharmaceuticals along the riverine area of Lagos is three orders of magnitude higher than the average in Europe and the United States.

The pressure on the hinterland occasioned by global population explosion, infrastructural development, coastal expansion by compensatory flooding, and melting of ice relative to global warming instigate further environmental/soil pollution, reduces and relatively mount serious pressure on agricultural land constituting severe land tenure problem. Soil pollution attenuates crop yields and accentuates health risks via bio-accumulation and food ingestion (Akpa *et al.*, 2023a, 2023b). Studies have shown that there is a proportionate relationship between food security, soil pollution, and human health (Akpa *et al.*, 2023b; Obasi *et al.*, 2023; Philip *et al.*, 2023; Obiora *et al.*, 2016; Obasi and Akudinobi, 2020). Water is a major carrier of pollutants and also an easy channel of pollution

migration anchoring on its universal solvent characteristics.

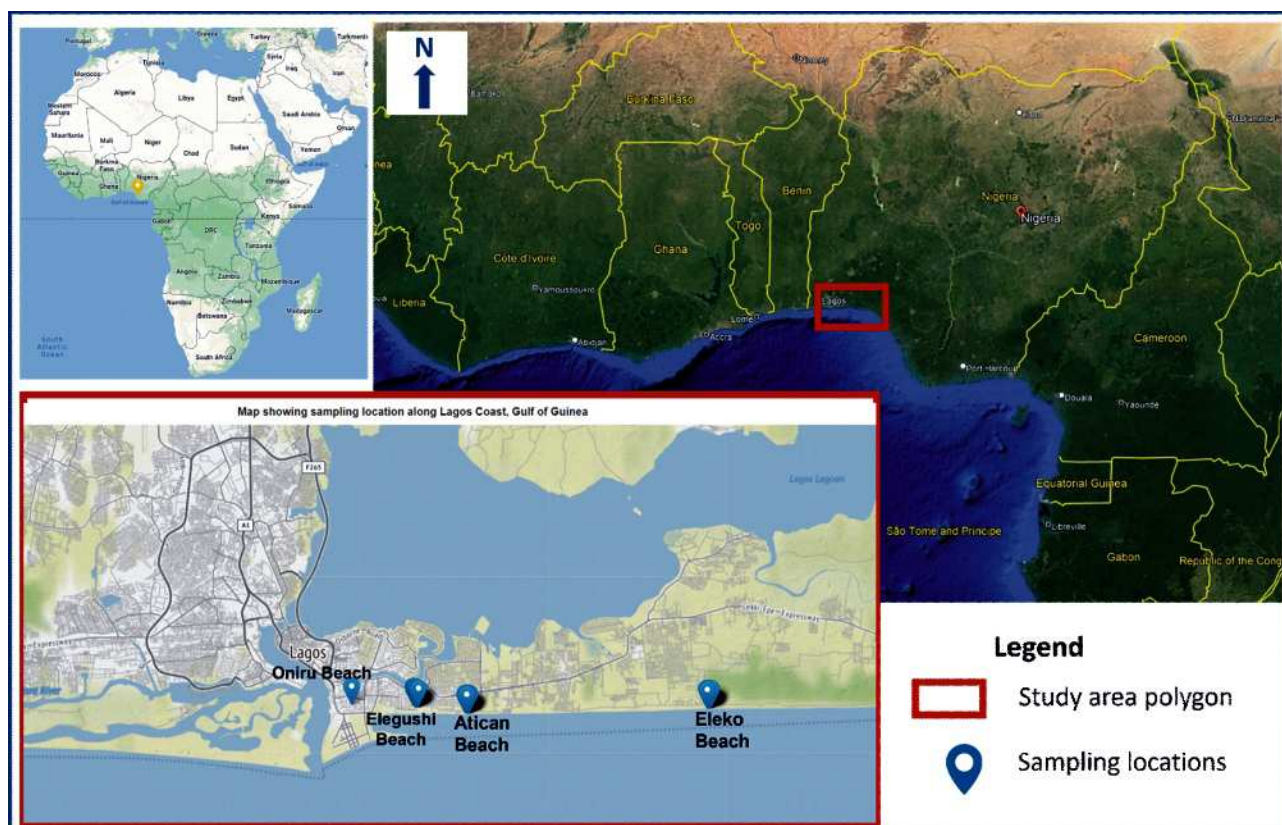
Previous research work in the study area does not link the occurrence of PAEs to health risk, and influence on bioenvironments and its habitants. Ecological and human health risks relative to contact with PAEs are one of the focuses of this research. This search evaluates distributions of the PAEs across the beaches and relates their concentrations to health risks as well as evaluating their contamination characteristics. The mishandling and abuse of PAEs through production processes and waste disposal is an emerging trend in society, favouring their spread in the environment and environmental media.

In the study area, the sampled locations are within the industrial, municipal, and residential hub of Lagos state, and the plastics stem from these sources. This study also utilizes various Pythonic tools such as Pandas, Matplotlib, and Seaborn to visualize the specific sources and distribution of PAE contamination in coastal regions. These tools are powerful and widely used in data visualization research, and their ability to integrate with other tools and libraries makes them an ideal choice for this study. Python's flexibility allows researchers to analyze and visualize data in a variety of ways, which can help to identify patterns and trends in the data that might not be immediately apparent. Additionally, Python's ability to generate high-quality visualizations makes it well-suited for publication and dissemination of research findings. The use of Python also allows for easy updating and sharing of outputs through web-based platforms. This can be especially useful for ongoing research projects, as it allows for the rapid dissemination of new findings and the ability to collaborate with other researchers. Overall, the use of Python in this study helps to effectively manage and reduce PAEs pollutants in the environment and provides a better understanding of their sources and distribution along the Lagos coast. Nevertheless, due to constant access to beaches as a recreational center and uncontrolled waste management, MPs concentration may increase rather than decrease with population growth, it became patient to appraise the PAEs level in the beach sediment and their corresponding health risk in this research.

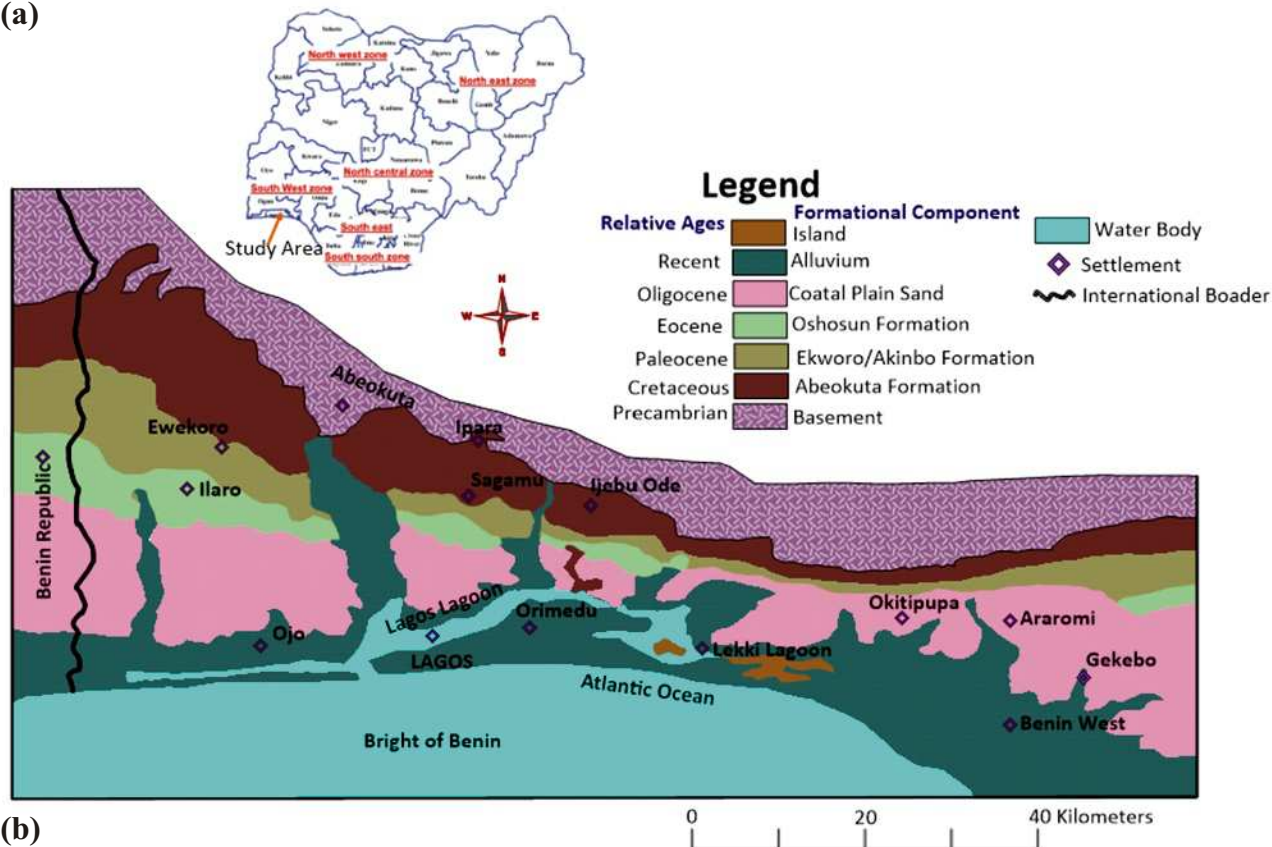
### Geology and Geomorphology of Study Area

Nigeria's coastline consists of barrier islands, sandy beaches, lagoons, estuaries, mud beaches, and creeks of the Niger Delta and has a stretch of about 860 km





(a)



(b)

**Fig. 1:** (a) Location of sampling points (Sourced from google maps, sampling locations plotted using Python-folium library). (b) Geologic Map of the Study area.

(Amosu *et al.*, 2012). It is bounded to the west by the Republic of Benin and east by the Republic of Cameroon. The Southwestern portion of Nigeria comprises six states (Lagos, Oyo, Ogun, Osun, Ondo, and Ekiti). The study was conducted using data collected from beach sediments along the coast of Lagos, Nigeria, with an estimated width of about 180km (Fig. 1a and Fig. 1b). Lagos is a large port city and Nigeria's commercial center. However, the Lagos coast is widely defined as a Barrier-Lagoon complex that comprises lakes, creeks, rivers, and channels. It is characterized by the barrier bar complexes, which are shaped by wave actions resulting in geomorphic features.

These features include:

- I. The lagoon extends approximately 250km and comprises medium to coarse sand grains. The lagoon is described by Zabbey *et al.* (2019) as microtidal waters linked by creek networks surrounded partially by the barrier island.
- II. The transgressive Mahin mud coast, which lies in the west is composed of silt and clay-sized sediments that are usually suspended and deposited due to the red mangrove vegetation dominant in the area.
- III. The arcuate Niger Delta in the east, which spans approximately 450km, and
- IV. The strand coastline is in the easternmost area close to the Nigeria-Cameroon border (Awosika *et al.*, 1993). It is a continuous strip of sand impacted by the Kwa Iboe River, where there is a developed delta and ends at the estuarine Calabar complex (Zabbey *et al.*, 2019).

This barrier-lagoon system is hosted by the Eastern Dahomey Basin, which thins out into the Precambrian basement rocks towards the North and opens out into the Atlantic Ocean towards the South. The study area seats on Dahomy Basin (Benin Basin) constituting sands and shale as the dominating lithologies. The basin extends from Benin Republic into Nigeria (Jones and Hockey, 1964; Nwajide, 2013) having five Formation (Fm) comprising of Abeokuta Fm, Ewekoro Fm, Oshosun Fm, Benin and Ogwashu Fm (coastal plain sand) and Alluvium deposit in their younging order and relative age of Cretaceous, Paleocene, Eocene, Oligocene to Recent respectively. The basal deposit of the Basin constitutes Abeokuta Fm unconformably overlying the Basement Complex. Relative to the Sedimentary package of the Nigerian Sedimentary Basin the Alluvium and the Coastal plain has been characterized as Benin Formation (Jones and Hockey, 1964; Longe *et*

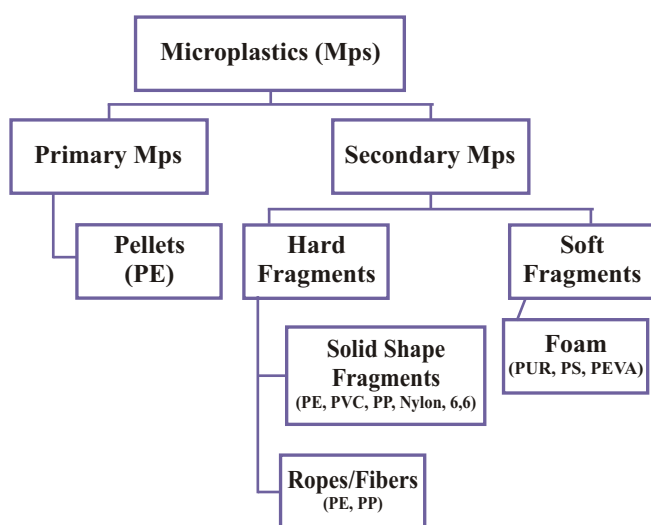
*al.*, 1987; Adegbola *et al.*, 2016), a deposit that results from barrier Beaches (Adeyemi 1972). Topographically Lagos state is low relative to sealevel (Adegbola *et al.*, 2016). An elaborate description of the formational component of the basin and their respective feature has been provided by diverse researchers (Ako *et al.*, 1980; Longe *et al.*, 1987; Omatsola and Adegoke 1981; Okosun, 1990; Nton, 2001; Elueze and Nton, 2004). The Commodore Channel connects the Lagos Lagoon to the Atlantic Ocean directly. Due to this connection, the salinity of the Lagos Lagoon is higher than that of the Lekki Lagoon (Ibe, 1988). The mean annual rainfall on the coast is about 1500mm, with temperatures ranging from 25-36°C daily and peak temperature values in February. Along the coastline, the prevailing wind direction majorly influences sediment transport and deposition by the longshore drift, which is blocked by the coastal defenses and breakwaters of the Eko Atlantic City project (Nwilo *et al.*, 2020).

## Methods and Materials

The data used in this study was extracted from the Elsevier Data in Brief archive under a creative commons license (<https://doi.org/10.1016/j.dib.2020.105755>) (Benson and Fred-Ahmadu *et al.*, 2020; Fred-Ahmadu *et al.*, 2020). A total of 150 sediment samples were collected from the Atican (A), Elegushi (E), Eleko (K), and Oniru (O) beaches from August to November 2019 (Fig. 1) (Benson and Fred-Ahmadu *et al.*, 2020; Fred-Ahmadu *et al.*, 2020). Sample collection was achieved using devices such as sample bags (cellophane bags) spatulas, shovels, and trowels. The samples collected were from different compartments of the sediments within each of the respective beaches forming a presentative sample that such a beach such a comprehensive picture of MPs and PAEs distribution in the area was properly captured. Preceding the sample analysis separation of the microplastics from the sediments by density flotation in a saturated solution of sodium chloride (NaCl) was undertaken (Further description of this approach have been described by Fred-Ahmadu *et al.*, 2020; Wang *et al.*, 2023; Munier and Bendell, 2018; Han *et al.*, 2019; Madura *et al.* 2015), which enables MPs separation from their matrix owing to the density contrast between the Mps polymer and the solution. This was accomplished through stirring and agitating the mixture using an orbital shaker for 15 minutes, after which it was allowed to settle for an hour. The floating particles were then extracted using a stainless-steel sieve with a 1mm mesh size. A detailed description of the sample extraction, quality control, and assurance procedures

used have been described by reported by Fred-Ahmadu *et al.*, (2020), and Benson and Fred-Ahmadu, (2020). The samples were viewed using a stereomicroscope for the separation of debris, plastics, and organic matter and the selection of the MPs. The characterization of the selected microplastics was done with attenuated saturated total reflectance infra-red spectroscopy (ATR-FTIR). These microplastics (Fig. 2) were also categorized and quantified based on the plastic type (Table 1a) and polymer type (Table 1b) into PE, PP, PS, PUR, EVA, PET, PA, PVC, Latex & others and Pellets, Foam fragments, Fibers and Hard fragments respectively.

The polymer analysis was carried out using the PerkinElmer Spectrum Two Attenuated Total Reflectance – Fourier Transform Infra-Red Spectrometry equipment with a resolution of 8cm-1, 32 sample scans, and a range of 4000-650 cm-1 and afterward matched with the Agilent polymer ATR library based on acceptable criteria. The Fred-Ahmadu *et al.* (2020) validation approach of spectral data of the polymer was adopted. The phthalate esters in the sample extracts were analyzed using Agilent 7890A Gas Chromatography and Agilent 5975 Mass Spectroscopy Detector (GC-MS) which resulted in duplicate results, however, for this study only the first concentration was used in the visualizations for simplicity especially since there are negligible differences between both results. The metals in the sample extracts were analyzed using the Agilent 720-ES Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). Procedures for the GC-MS and ICP-OES analysis are presented in Fred-Ahmadu *et al.* (2020), Benson and Fred-Ahmadu, (2020).



**Fig. 2:** Classification of microplastics and the relationship with the categorization used in this work (Benson *et al.*, 2022)

### *Python for Fast and Informative Visualizations*

Python is a powerful programming language that is widely used for data analysis and visualization due to its flexibility and the fact that it is open-source. There are several libraries available in Python that are designed specifically for creating fast and informative visualizations and dataframes, such as Pandas, Matplotlib, Seaborn, Plotly, Bokeh, Folium, Geopandas (Morra, 2018). This data was processed and stored in a data frame using the Python Pandas library. Prior to loading the data into python, we updated the data into spreadsheets which are optimized for machine readability according to spreadsheet standards for data organization of Broman and Woo, (2018). Standard data cleaning and wrangling were also carried out to optimize the data and remove machine un-readable attributes.

Pandas library in Python was used for data manipulation and analysis. It provides easy-to-use data structures and data analysis tools for handling and manipulating numerical tables and time series data. The main data structures in pandas are the Series and DataFrame. A Series is a one-dimensional labeled array that can hold any data type. ("Create and display a one-dimensional array-like object - GeeksforGeeks") A DataFrame is a two-dimensional table of data with rows and columns, like a spreadsheet or a SQL table. Outside this Pandas provides a variety of functions and methods for cleaning, transforming, and manipulating data, such as:

- Filtering and selecting subsets of data
- Merging and joining multiple data sets
- Grouping and aggregating data
- Handling missing and duplicate data
- Reshaping and pivoting data

Pandas also provides a powerful interface for reading and writing data in different file formats, such as CSV, Excel, JSON, and SQL. It can also be used to read data from various data sources, like APIs, SQL databases, and NoSQL databases. It's commonly used in combination with other libraries such as numpy and matplotlib for data exploration and visualization and with scikit-learn for machine learning.

### **Results and Discussions**

The result revealed that the PAEs concentration is not isotropic in the area, a variation that instigated diversity in types of microplastics discharged across the area originating from different human-related



activities/production processes. The MP entering point, current impact on the beach sediment and water quality, beach visitors, and types of MP also contribute to an increase in PAEs discharge, redistribution of the MPs, and concentration variability in their area and environment. Due to constant access to beaches as a recreational center, MPs' concentration may be on increase rather than decrease. Seasonal variations such as precipitation influence the MPs and PAEs concentration in an environment (Heo *et al.*, 2020; Zhang *et al.*, 2018; Paluselli *et al.*, 2017; Kim *et al.*, 2011).

Generally, the MPs quantification based on plastic types follows the decreasing order of Oniru beach>Elegusgi beach>Eleko beach>Atican beach (Table 1; Fig. 3) corresponding to 51.06%, 35.30%, 6.91% and 6.73 respectively. Pellet is a basic constituent of primary microplastics (PMPs), its relative abundance in the study area follows a decreasing order of Elegushi>Atican>Eleko>Oniru constituting 13.13%, 2.19%, 1.28%, and 0.12% respectively of the total quantified MPs by plastic types (Table 1a). From the Benson *et al.* (2022) MP categorization, foam fragments, fibers, and hard fragments constitute the secondary microplastics (SMPs) class. Hard fragments and foam fragments constitute the highest content of MPs in the study area (Table 1b). The highest quantity of foam fragments was recorded at Elegushi beach, whereas highest quantities of fibers and hard fragments were documented at the Oniru beach axis (Table 1).

**Table 1a:** Microplastics quantification by plastic types.

Sample site	Pellets	Foam fragments	Fibres	Hard fragments	Total
Elegushi	157	522	41	476	1196
Atican	5	158	14	51	228
Oniru	2	395	46	1287	1730
Eleko	3	32	19	180	234

**Table 1b:** Microplastics quantification by polymer type.

Sample sites	PE	PP	PS	PUR	EVA	PET	PA	PVC	Latex	others	Total
Oniru	879	413	322	57	16	2	33	0	3	5	1730
Elegushi	407	208	491	21	10	4	40	3	1	11	1196
Atican	38	22	123	19	9	0	8	2	0	7	228
Eleko	107	56	23	9	0	3	22	6	0	8	234

largely to contaminants quotient of the environment and its media/resources. The PAEs with the highest impact of fouling of the soil within the study area is DEHP (80.82%) whereas DnOP has the least contribution (0.15%). DEHP indicating higher PAEs risk quotient at Lagos beaches corresponds to observation and findings of Colacino *et al.*, (2010) and Wang *et al.*, (2023) on

The characterization of MPs by polymer types (Table 1b), revealed that Oniru beach constitutes polymer with a high contribution of MPs, similar to the result of MPs quantification by plastic type (Table 1a), this corresponds to the levels PAEs found in the area (Table 2). The MPs distribution across the study area based on polymer type follows Oniru>Elegushi>Atican>Eleko (Table 1 and Fig. 3) with respective percentage contributions of 51.06%, 35.30%, 6.91%, and 6.73%. The polymers that constitute the MPs that characterized the presence of PAEs in the study area are PE, PS, PP, PUR, PA, EVA, PVC, PET, latex, and others in the following proportions 42.24%, 28.31%, 20.63%, 3.13%, 3.04%, 1.03%, 0.33%, 0.27%, 0.12% and 0.92% respectively. Based on the plastic type quantification, Elegushi and Oniru areas have the highest microplastic concentration for all the plastic types except for pellets whereas Atican and Eleko areas have higher concentrations of it than in Oniru areas (Table 1). Microplastics characterization of the area on the basis of polymer type designates a similar trend as that of quantification by plastic types (Tables 1 and 2, Fig. 3).

The phthalate esters (PAEs) analyzed in the sediment extracts include Butyl benzyl phthalate (BBZP), di (ethyl hexyl) phthalate (DEHP), Diethyl phthalate (DEP), Dimethyl phthalate (DMP), Dibutyl phthalate (DnBP), and Di n-octyl phthalate (DnOP) (Table 2 and Fig. 4). The highest and lowest concentrations of DMP, DEP, DnBP, BBZP, DEHP, DnOP was found at Atican Beach and Elegushi Beach, Oniru Beach and Eleko Beach, Oniru Beach and Eleko Beach, Atican Beach and Elegushi Beach, Oniru Beach and Eleko, Elegushi Beach and Eleko Beach respectively (Table 2; Fig. 4) for corresponding values.

The identification of the above PAEs across the beaches infers their ubiquity in the environment contributing

phthalates associated with dietary intake and review of health risk induced by PAEs in biological macromolecules respectively, where DEHP was also documented to have highest concentration. Relative to the study beaches, the highest contamination of the six PAEs ( $\Sigma 6$ PAEs) was recorded at Oniru beach (46.17%), Eleko beach has the least (6.23%) whereas Atican and

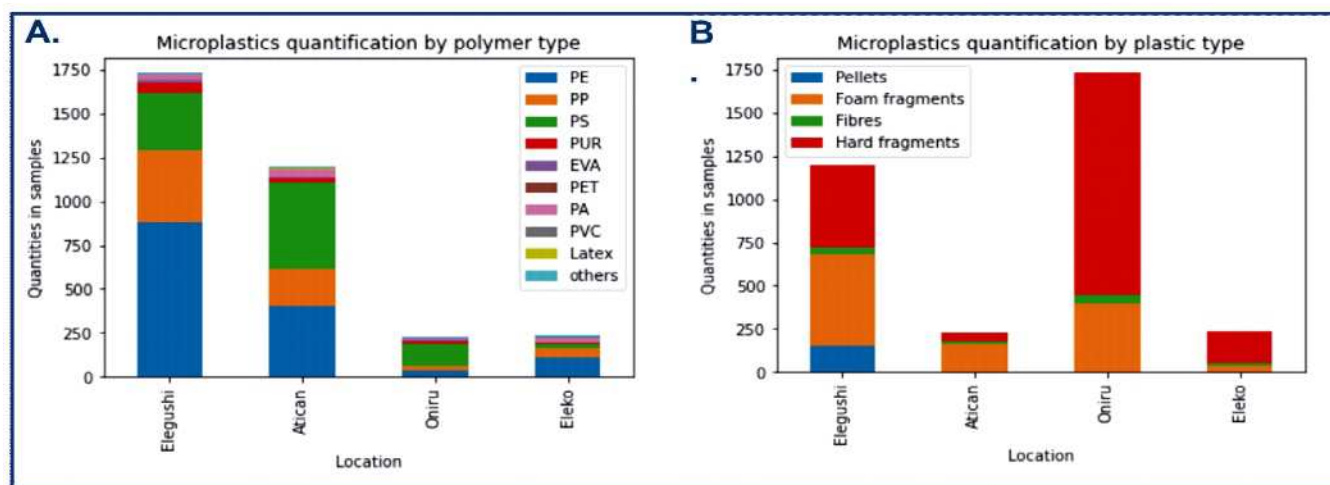


Fig. 3: Microplastics quantifications by polymer and plastic types

Elegushi beaches have relatively the same concentration (23.80% and 23.79% respectively). These concentrations across the beaches are the resultant of effluent discharge around Oniru area and environs, also

Table 2: The average distributions PAEs across the study area

Sample Locations	DMP	DEP	DnBP	BBZP	DEHP	DnOP
Atican Beach	15.215	0.045	2.815	6.27	36.45	0.04
Elegushi Beach	0.045	0.095	9.545	0.1	50.865	0.16
Eleko Beach	0.005	0.005	2.955	0.025	12.97	0.01
Oniru Beach	0.07	0.105	11.23	0.145	106.31	0.16

their abundance in the sediment is impacted by water and current interactions on the coastal sediments. Different PAEs have diverse physiochemical properties which describe their ubiquitous nature. They have been found to have various high levels of solubility in water (DMP (4200mg/l), DEP (1100mg/l), DnBP(11.2mg/l), BBZP(2.7mg/l)) (Hadjmohammadi *et al.*, 2010). This high solubility is characterized by their abundance in water resources, stream sediments, soil samples, air, and food chain as it has been documented by various researchers across the globe (Dargnat *et al.*, 2008; Prieto *et al.*, 2007; Heo *et al.*, 2019; Iordache *et al.*, 2022; Li *et*

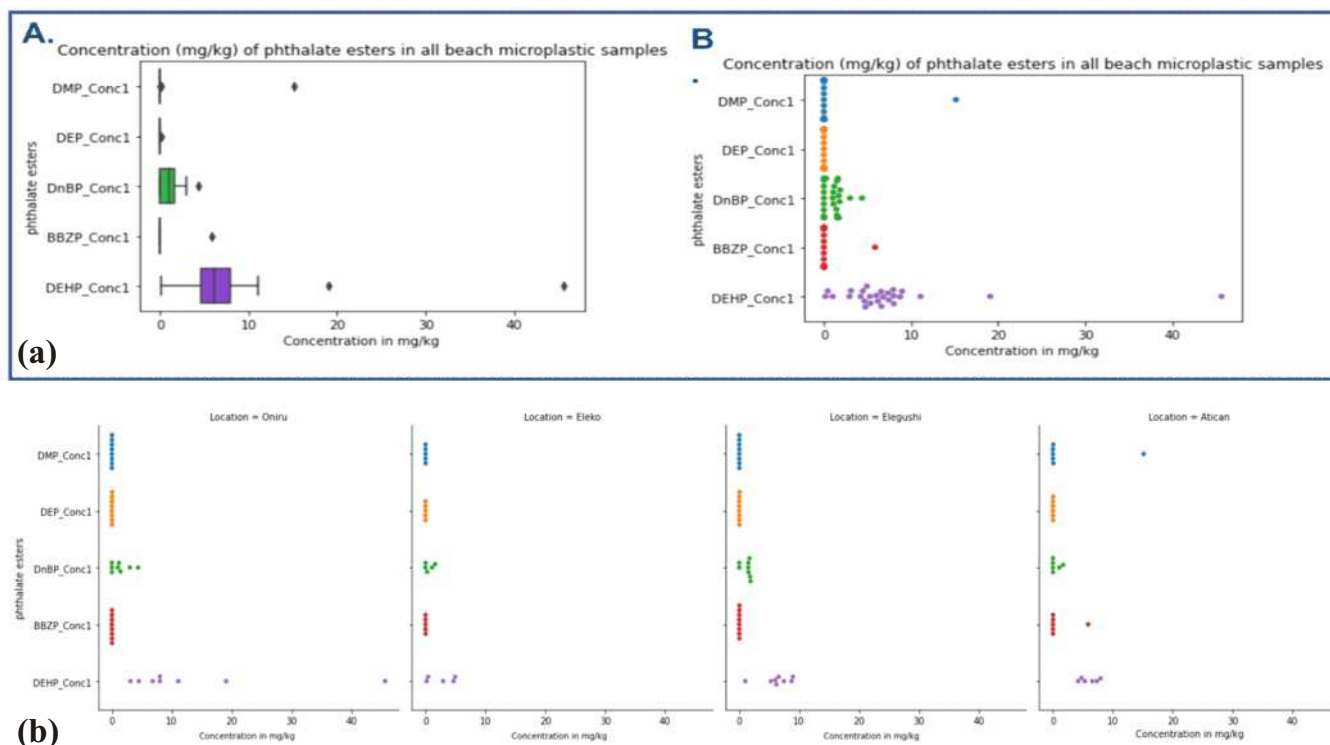


Fig. 4: (a) Concentration Phthalate esters across the Beach. (b) Concentration Phthalate Esters in Oniru, Elko, Elegushi and Atican Beach respectively.



*al.*, 2023; Abdi *et al.*, 2021). The result obtained implies that the level of soil contamination by PAEs, is dependent on the MPs accumulation following the corresponding high PAEs concentration delineated in the key areas characterized by poor waste management practices (See Tables 1 and 2; Figs. 3 and 4). This is a pointer to anthropogenic influences and locality/regional diversities in economic growth, urbanization activities, farm practices, industrial products and byproducts, climatic conditions, soil type, and prevalent water current (mostly in coastal regions), as the results obtained here differ from those of similar studies in many other locations of the world (Hu *et al.*, 2003; Peijnenburg and Struijs 2006; Sun *et al.*, 2016; Heo *et al.*, 2019; Algül and Beyhan 2020; Tao *et al.*, 2020; Wei *et al.*, 2020; Zhou *et al.*, 2021; Xing *et al.*, 2022). Hence the abundance of MPs and PAEs distributions in an environment is as result of urbanization and industrial revolution, agricultural cultivation practice, and to lesser extent environmental resource interaction, therefore characterization of PAEs pollution might be dependent on anthropogenic and environmentally sensitive and this could facilitate the noticeable regional concentration differences in PAEs pollutant (Wang *et al.*, 2015; Net *et al.*, 2015; Mo *et al.*, 2008; Li *et al.*, 2016; Hadjmohammadi *et al.* 2010; Baloyi *et al.*, 2021; Xing *et al.*, 2022). The relative concentrations of PAEs in difference environmental assessment apparatus/matrices (water, soils, etc.) are inclined to the physicochemical interactions among the matrices and PAEs. The behaviour of these matrices is influenced by certain natural phenomena such as ocean currents, rainfalls, humidity, and to a lesser extent temperature which also affect the concentrations of the PAEs in water and sediments (Xing *et al.*, 2022). It is on record that the longer the contact time (aging) of plastic film in an environment, the higher the resultant PAEs contaminant concentration to be envisaged in such an affected environment. Also, gas(s) evaporations and leaching water vapours from soils and vegetables increase PAEs concentration quotient in any concerned environment (Hadjmohammadi *et al.*, 2011; Li *et al.*, 2016).

Therefore, the high levels of MPs in the study area mostly the SMPs suggest remarkable anthropogenic (for which Lagos is known as a commercial hub in sub-Saharan Africa) influence at the high levels of PAEs possibly occasioned by interactions of these MPs with environmental resources (water, air, soils) and contact access to the beaches. Abdi *et al.* (2021) observed no strong correlation between PAEs contents and temperature, which they attributed to PAEs having higher vapour pressure. Basically, higher-weight

molecular PAEs (DEHP, DiNP, BBP) correlated strongly with each other suggesting similar sources such as those from PVCs polymers, toys, plastics, and food processing materials as reliable sources (Wittassek *et al.*, 2011; North *et al.*, 2014; Bu *et al.* 2016; Wang *et al.*, 2019; Abdi *et al.*, 2021). The ubiquitous nature of these microplastics and their easy approach to interaction with environmental resources create an unsafe environment for humanity and other living organisms in the coastal areas. The most vulnerable body parts easily exposed to MPs contact include the skin, hand, hair, face, and Silvia (Abbasi and Turner 2021). There are about ways of microplastics treatment by either of the following ways biologically, chemical treatment, sorption, ingestion, and/or filtration. These approaches tend to reduce MPs concentration in an environment (Othman *et al.* 2021; Hamidian *et al.* 2021; Razeghi *et al.*, 2021).

### **Health Risk Associated with PAEs in the Environment**

These high concentrations of the PAEs in the study area raise concerns regarding the safety of the biota, food chain quality assurance (resulting from uptake and bioaccumulation in plants and human sensitive parts and tissues), and by extension human safety and environmental protection sanity. Several studies across the globe have reported diverse concentrations of PAEs in various coastal regions (Ma *et al.*, 2003; Hu *et al.*, 2003; Yang *et al.*, 2013; Zhou *et al.*, 2021; Xing *et al.*, 2022; Akpa *et al.*, 2023a, 2023b), using water and soil sample (indispensable assets of live support) as evaluating parameter which implies that PAEs contamination in an area is a combination of natural and anthropogenic activities and contacts with it is relatively unavoidable in human daily engagements (Wang *et al.*, 2021; Obasi *et al.*, 2023), results of such studies are presented in Table 3. Wang *et al.* (2021) revealed that farming practices engender the release and accumulation of PAEs in soils and plant tissues compounding the risk quotient facing humanity, identifying the PAEs (DMP, DEP, DIBP, DBP, and DEHP) in maize tissue. It has been stressed that PAEs being highly fat-soluble makes them a vicious threat to human health following their ubiquitous nature, present in soil, air, food chain and water, such that interaction within human body fluid, skin absorption and/or ingestion (food and water) are easy pathways of exposure to various health hazards (Kimber *et al.*, 2010; Li *et al.*, 2014; Gao *et al.*, 2019; Wang *et al.*, 2021; Xing *et al.*, 2022; Obasi *et al.*, 2023).

One of the significant health effects of PAEs is the disruption of the endocrine system which influences

**Table 3:** The concentrations of phthalate esters (PAEs) in study and different environments of the world (µg/L).

Matrix	Sample Code	DMP	DEP	DnBP	BBZP	DEHP	DnOP	Reference
Nigeria (Lagos coast)	Atican Beach	BDL-15.215	BDL-0.045	BDL-2.815	0.01-6.27	4.04-36.45	BDL-0.04	
	Elcusha Beach	BDL-0.045	0.00-0.095	0.00-9.545	BDL-0.1	1.01-50.865	BDL-0.16	
	Eleko Beach	BDL-0.005	BDL-0.005	0.00-2.955	BDL-0.025	0.17-12.97	BDL-0.01	
	Onuiru Beach	0.00-0.07	BDL-0.105	BDL-11.23	0.01-0.145	3.11-106.31	0.00-0.16	
River	France		0.01-0.71	0.07-0.32		0.16-0.31		Dargnat <i>et al.</i> , (2009)
	Spain		0.05-0.28			0.12-4.98		Sánchez-Avila <i>et al.</i> , (2012)
	China	1.45	0.01-0.71	0.02-7.19		0.02-28.4		Zhang <i>et al.</i> , (2012); Shi <i>et al.</i> , (2012)
	Iran	0.87	0.67					Hadjmohammadi <i>et al.</i> , (2011)
	Nigeria	Nd-0.85	0.08-0.35	0.19-1.42	-	0.02-0.82	-	Adeniyi <i>et al.</i> (2011)
Rainwater	France	0.07-0.11	0.14-0.25	0.10-0.16		0.36-0.85		Dargnat <i>et al.</i> (2009)
Estuary	Spain	0.21-0.28	0.07	1.25-1.26		0.22		Prieto <i>et al.</i> , (2007)
	Canada			0.18-3.00		0.01-0.95		Keil <i>et al.</i> , (2011)
Seawater	Iran	0.49	0.52					Hadjmohammadi <i>et al.</i> , (2011)
	Spain	0.25	0.02-0.48	0.25-0.40		0.03-0.62		Sánchez-Avila <i>et al.</i> , (2012); Prieto <i>et al.</i> , (2007)
	South Korea	0.02-0.10	0.02-0.15	0.04-0.36		0.03-0.30		Heo <i>et al.</i> , (2019)
Soil of coastal Area	South China	0.003-0.319	0.004-0.364	0.073-1.109	ND-0.024	0.129-2.628	ND-0.054	Xing <i>et al.</i> , (2022)

growth and developmental changes mostly in male reproductive organs (Chen *et al.*, 2011; Yang *et al.*, 2014; Abdi *et al.*, 2021; Li *et al.*, 2023; Zhang *et al.*, 2023; Wang *et al.*, 2023). The efficacy of PAEs binding to hormone receptors amplifies their health hazard quotient and could result in neurological disorders and attenuation of human immune strength (Hlisnikova *et al.*, 2021; Chang *et al.*, 2021; Zhang *et al.*, 2019, 2023). DEHP could instigate reproductive system disorders/problems mostly in women, reduction in sperm quality in men and low conception in women, early menopause, low child weight at birth, and premature (preterm) birth (Chang *et al.*, 2021; Wang *et al.*, 2023; Zhang *et al.*, 2023). DEP when in contact with skin strongly irritates and can result in oral and nasal mucosa (Mikula *et al.*, 2005).

Following the danger associated with the intake of DBP, its use has been banned in the manufacturing of toys by USA and EU authorities whereas Taiwan characterizes it as a type 4 level harmful chemical substance (Yang *et al.*, 2014). Apart from PAEs other plasticizers and organic materials are used in some food firms, rain-wears, roofing systems, and the environment, various medical products utilize them expanding their possible contact scope and the chance of their bioaccumulation in tissues (Titow, 1990; Wickson, 1993; Abdel daiem, *et al.*, 2021; Akpa *et al.*, 2023b). IARC (2000) noted that the phthalate content of finished plastic products by weight ranges from 10 to 60% globally. The individual's contact time and exposure to products made with phthalates might be relative to school, home, and

workplace engagements which can accentuate carcinogenic risk of the affected individual (Abdi *et al.*, 2021; Fan *et al.*, 2017; Tan *et al.*, 2013). The appraisal of carcinogenic and non-carcinogenic risk from dust obtained from the twenty-one class portrays a significant risk (Abdi *et al.*, 2021). Significant exposure to PAEs can result in atopic and neurodevelopmental disorders mostly at tender age (Bekö *et al.* 2013; Cho *et al.* 2010; Engel *et al.* 2010). Lingered interactions of PAEs in the body culminate in nerve injuries, whereas interactions with genetic materials can result in genotoxicity and carcinogenicity (Li *et al.*, 2023); and immunotoxicity (Zhang *et al.*, 2022).

Plastics discharged into marine environments could persist for up to fifty years with a significant pollution quotient (Razeghi *et al.*, 2021). The risk associated with PAEs increases with the degree of exposure and reference (Kim *et al.* 2011; Langer *et al.* 2014; Zhang *et al.* 2013; Wang *et al.*, 2014), and can even result in death (Ogonowski *et al.* 2016). These exposures could constitute indoor and outdoor environmental pollution in connection to product usage and indoor and outdoor activities like combustion and cleaning (Abdul-Wahab *et al.* 2015). Human exposure to PAEs has a significant impact on reproduction and growth (Guo and Kannan, 2011; Abdi *et al.*, 2021; Boberg *et al.* 2008). The PAEs risk is more in adults due to the preeminent rate of ingestion and breathing relative to body weight (Selevan *et al.* 2000; Sobhanardakani 2018; Abdi *et al.*, 2021). Children are more susceptible to PAEs exposure through food ingestion, skin absorption, and inhalation

(Abdi *et al.*, 2021). PAEs are also used as plasticizers in textile industries which amplifies human exposure to it (Wang *et al.*, 2023; Zhang *et al.*, 2023). Human exposure to PAEs daily is unavoidable as it appears to be found in all environmental media (Li *et al.*, 2023). These warrant the United States Environmental Protection Agency ban DBP, DMP, DOP, and DEHP while DiBP was integrated into the list by twenty-eight EU countries later (EU 2018).

Since these study beaches and coastal regions are tourist and aggressive agricultural centers the levels of the PAEs concentrations in the Lagos coast are worrisome due to their efficacy of upsetting human body/organs physiological and biochemical mechanisms accentuating various health risks such as; hormone sensitizers, type 2 diabetes, impact on reproduction, carcinogenic, asthma, insulin resistance amongst other health threats (Jugan *et al.*, 2010; Kimber *et al.*, 2010; Casals-Casas *et al.*, 2011; Maqbool *et al.*, 2016; Benjamin *et al.*, 2017; Wei *et al.*, 2020; Xing *et al.*, 2022). These health hazards are similar to those that could result from ingestion of food materials fouled by heavy metals resulting from mining activities (Obasi *et al.*, 2023; Akpa *et al.*, 2023b; Chukwu and Obiora, 2023).

The ingestion and interaction of humans and aquatic organisms on MPs usually steered alteration and imbalance in the physiochemical and biochemical functionality of affected organisms and accentuating bioaccumulations of toxins in their sensitive organs and tissues (Browne *et al.*, 2008; Lusher *et al.*, 2013; Van Cauwenberghe *et al.*, 2015; Nobre *et al.*, 2015; Lu *et al.*, 2016; Steer *et al.*, 2017; Wang *et al.*, 2021; Obasi *et al.*, 2023; Akpa *et al.*, 2023b). The highest concentration found around Elegushi and Oniru areas results from the effluent discharge of industrial waste in the area.

### ***Metal Concentration Distribution Across the Beaches***

The metals analyzed include Ag, Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Si, Sr, Ti, Tl, V and Zn, which were split into two groups based on their relative abundance for better visualization (Table 4 and Fig. 5). The results of the metals sampled across the four beaches are summarized and they are basically below their respective baseline specified concentration across the study area (Table 4). Their concentration in the sediment were as follows Na>Zn>Mg>Ca>Si>Sr>K>Mn>Al>Ba>Pb>B>Cu>Mo>Ti>Tl whereas Se and Ag have the highest concentration of 0.1 mg/kg across the coast. The lowest and highest levels of each of the sampled metals across

the beaches can be deduced from Table 4. The compound concentration of these metals across the beaches follows Elegushi>Oniru>Atican>Eleko with their corresponding percentage abundance of 30.77%, 26.92%, 23.08%, and 19.23 respectively. Generally, the metal's average concentrations were relatively consistent (Table 4, Fig. 5a&b), this depicts relative similarity in the source of contamination, distribution pattern, and prevailing environmental conditions. The narrow variations in metal concentration could have resulted from discharge influence, particulate transportation, minerals, and organic carbon transport arising from wave current and water turbulence. This metal concentration in the sediment sampled might have been characterized by the degree of their remobilization from water to sediments and vice versa. This might follow the precipitation and resuspension of these metals possibly induced by flooding and receding water (Skeaff *et al.* 2002; Iordache *et al.*, 2022). Also, the pH of the water can influence the release of the metals from sediments to water such that persistent beach water regeneration can prevent the accretion of these metals in the beach sediments explaining their low concentration in the study area (Awadallah *et al.* 1993, 1996), which has no consistent trend of variation (Table 4 and Fig. 5). The pH variability have influence on bioavailability/biodiversity and metals mobility in sediment (Akpa *et al.*, 2023b; Adebisi *et al.*, 2020; Smith, 1994).

However, those metals that tend to be embodied rapidly into the sediment have higher concentrations (for example Na, Zn, Ca, Mg, etc. see Table) than other metals. Their enrichment is always straddled by the interplay of variety in geochemical, physiochemical, biogeochemical, and biological factors dominating the environment (Awadallah *et al.*, 1996; Obasi and Akudinobi, 2020; Algül and Beyhan, 2020; Iordache *et al.*, 2022; Obasi *et al.*, 2023), for instance Zn has great tendency of accumulating in biota (Algül and Beyhan, 2020). Therefore contamination quotient in environment and environmental resources could only be achievable when evidential sources of fouling are mitigated/properly managed. Relative analysis of risk factors incurable through the food chain and human interaction with the environmental resource/media requires background knowledge regarding the metal accumulation in these resources/media.

### **Conclusion**

Plastic pollutants that have been underestimated and regarded as aesthetic waste have become a global concern. The coastal environment of Nigeria is



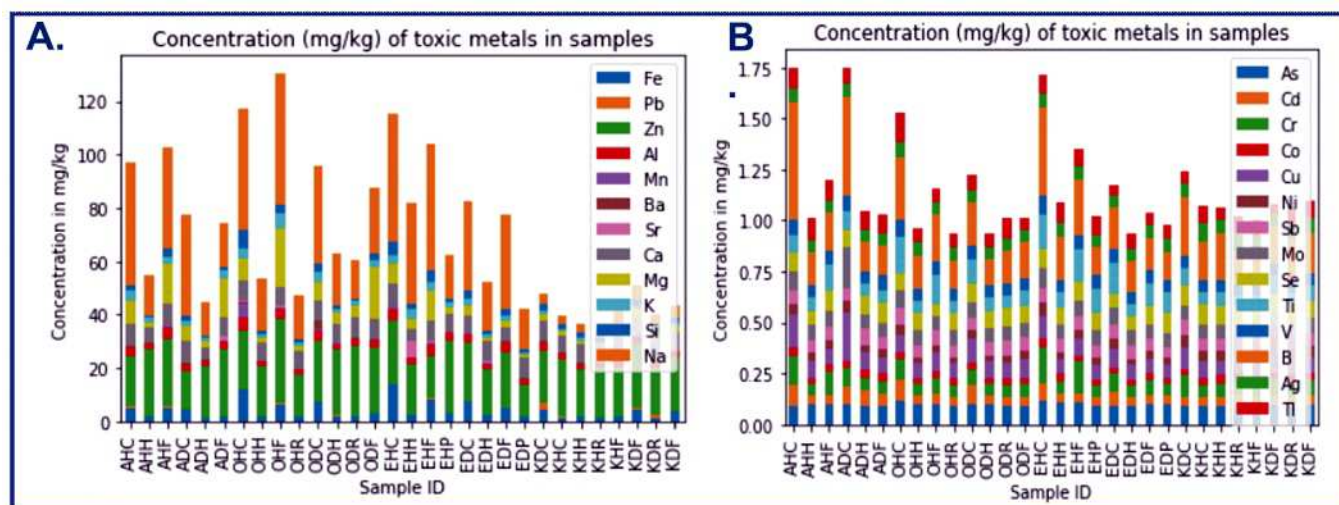


Fig. 5a: Concentration of toxic metals in the samples

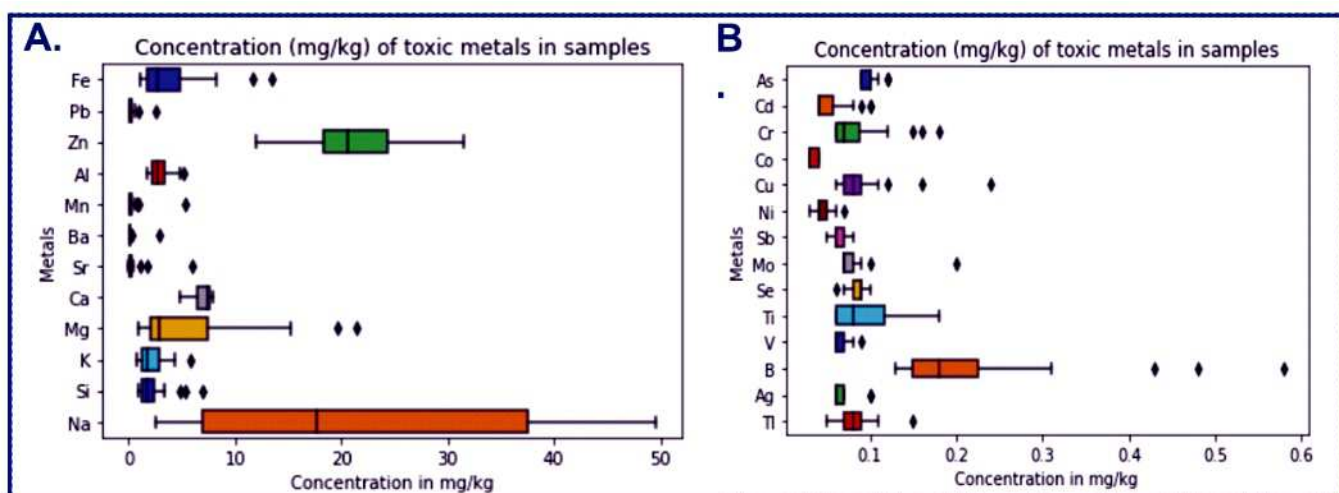


Fig. 5b: Metal concentration quotient in the analyzed samples

Table 4: Average concentration of metals in the analyzed sediment sample across the study Beaches.

Sample Locations	As	Cd	Cr	Co	Cu	Fe	Pb	Ni	Zn	Al	Mn	Sb	Ba
Atican Beach	0.095	0.067	0.092	0.035	0.12	3.127	0.205	0.045	21.443	2.85	0.2	0.067	0.19
Oniru Beach	0.099	0.055	0.071	0.033	0.085	4.484	0.15	0.038	23.286	2.97	0.916	0.066	0.479
Eleko Beach	0.094	0.04	0.075	0.036	0.085	2.28	0.634	0.051	19.7845	2.65	0.1075	0.0613	0.156
Elegushi Beach	0.101	0.049	0.094	0.033	0.078	5.479	0.236	0.0425	19.703	3.101	0.293	0.065	0.155
AV.	0.097	0.052	0.082	0.034	0.09	3.889	0.313	0.044	21.028	2.896	0.391	0.065	0.249
MIN.	0.09	0.04	0.06	0.03	0.06	1.04	0.08	0.03	12.05	1.68	0.05	0.05	0.11
MAX.	0.12	0.1	0.18	0.04	0.24	13.49	2.51	0.07	31.47	5.17	5.28	0.08	2.84
WHO 2011					25		17						
	0.01	0.003	0.05	N/A	2	0.3	0.01	0.02	3	0.2	0.4		0.7
Sample Locations	Mo	Se	Sr	Ti	V	B	Ca	Mg	K	Si	Ag	Na	T
Atican Beach	0.098	0.088	0.435	0.082	0.067	0.283	6.787	8.182	2.477	1.745	0.0633	27.593	0.097
Oniru Beach	0.074	0.084	0.294	0.095	0.065	0.188	7.326	8.525	2.646	2.408	0.0625	28.493	0.0825
Eleko Beach	0.07	0.091	0.064	0.07	0.06	0.199	7.085	1.924	1.194	1.829	0.074	4.121	0.0725
Elegushi Beach	0.076	0.085	0.889	0.119	0.068	0.21	6.638	4.345	2.366	2.583	0.066	31.489	0.0775
AV.	0.078	0.087	0.419	0.092	0.065	0.216	6.970	5.581	2.150	2.167	0.067	22.613	0.0813
MIN.	0.07	0.06	0.02	0.06	0.06	0.13	4.81	0.92	0.84	0.86	0.06	2.56	0.05
MAX.	0.2	0.1	5.96	0.18	0.09	0.58	7.99	21.48	5.78	6.93	0.1	49.51	0.15
WHO 2011	1.5												
		0.04					75	20			0.1	200	

underexplored and understanding of the ecological implications of microplastic pollution in the zones remains shallow. The presence of these chemicals in the analyzed sediment extracts suggests that they have been transported to the coastal area through various pathways such as stormwater runoff, sewage discharge, and atmospheric deposition. This highlights the need to engage in a multi-disciplinary study approach to controlling and reducing nonpoint source pollution, including measures such as better waste management practices, stricter regulations, and public awareness campaigns.

The result of this research in correlation with previous work within and across the study area, established that the current microplastic pollution trends in Nigerian coastlines are on the rise and suggest significant negative ecological and economic implications and corresponding health risks due to human contact and access to these beaches as recreational centers. The level of microplastics and affiliate PAEs quantified in the area has detrimental effects on human and marine organisms, including ingestion, entanglement, physical and chemical interference with growth, reproduction, and bioaccumulation in sensitive organs and tissues, hence human health hazards and coastal organism survival is proportionate to the quantity of untreated effluent discharge and associated harm. The abundance of microplastics in the area is composite with the contamination quotient of the PAEs and they act as

vectors for the transfer of pollutants and pathogens to marine organisms, increasing the risk of disease and mortality of the inhabitants by accumulating in the food chain, leading to a potential impact on human health through the consumption of contaminated seafoods. Additionally, the rising concentration of microplastics and associated PAEs prove to interfere with the physical and chemical properties of sediments, influencing the overall biodiversity of the coastal environment, such that they can cause changes in sediment structure, stability, and erosion patterns, leading to habitat alteration and loss, which in turn affects the biodiversity of the ecosystem. Conclusively, Poor waste management and the discharge of hazardous substances into the environment and environmental media is a vicious threat to the safety of the organisms, plants, humanity, and the ecosystem.

To mitigate these ecological implications, it is crucial to identify and reduce the sources of microplastic pollution, through stricter regulations, better waste management practices, and public awareness campaigns. Additionally, continuous monitoring and research on the distribution, fate, and ecological impact of microplastics in the Nigerian coastlines is necessary to better understand the full extent of the problem and to develop effective management strategies. Integration of water and coastal sediment sampling at diverse compartments might yield better results regarding MPs and PAEs distribution and their effect on the ecosystem.

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