Chapter One

Introduction

1.1 Background to the Study

The worldwide manufacture of phthalate esters (PAEs) has been estimated to have reached as high as 8 million tons per annum with the continuously increasing demand of plastic-based consumerism particularly in the Asian region which is reaping the benefits of logistics market dominated by plastics[1]. Being the most widely used plasticizers, a lot of phthalates are physically added to the plastic material in large amounts to increase flexibility and strength of plastic. Phthalates are omnipresent within several environmental matrices as they do not require being covalently (i.e. in a chemical sense) bound to plastics to be able to leach into all types of media[2]. With phthalate-containing food packaging, exposure to sunlight and/or high temperatures, and intensive shaking may further promote phthalate leaching. Phthalates in the environment have been determined as emerging contaminants and classified as endocrine-disrupting chemicals as they could cause different toxicities to organisms and endocrine disruptions in biological systems which pose serious health risks[3]. Specifically, during processing and storage, they are able to transfer to the food, beverages, and drinking water in plastic packaging[4].

Production of phthalate esters (PAEs) is by phthalic anhydride and alcohols, which are phthalic acid esters[5]. Phthalates are also odorless, tasteless, and colorless and have liquid forms existing within a high range of temperature (25 °C - 50 °C) and are stable chemically. During the 1930s, plastic polyvinyl chloride (PVC) was added to di(2-ethylhexyl) phthalate (DEHP) to make it plastic (i.e. flexible and elastic). PAEs according to Organization for Economic Cooperation and Development were used on a global scale in multifactorial quantities up to about 5.5 million

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metric tons in a year via diverse resources, such as household stuffs (furnishings, clothing, cosmetics, children's toys, nutritional supplements/food packaging, etc.), building and traffic materials, industrial sectors (paints and varnishes, adhesives, lubricants, waxes, cleaning materials, electronics, inks) or others (e.g. pharmaceuticals, medical Due to this, the PAEs could be detected in multiple environmental matrices such as the atmosphere, lithosphere (soil, sediment) and hydrosphere (surface water, and wastewater, etc.).

Existential exposure of human beings to PAEs may occur via multiple routes that include ingestion, inhalation, skin absorption/contact, and intravenous injection. To illustrate, the human body could be readily available to PAEs through oral exposure (i.e., eating contaminated food, or controlling toys used by children); through the air ambient air mixed with PAEs; on through skin exposure to plastic products (i.e., personal care products, paints, clothes or cosmetics, etc.); and through intravenous exposure in the case of medical equipment[7]. In the meantime, PAEs belong to the type of endocrine disruptive chemicals (EDCs), which may produce significant effects on the respiratory, reproductive, and the endocrine system of human beings. To date, PAE exposure has been associated with numerous health issues such as abnormal effects on the reproductive system, asthma and allergies among others. As an example, numerous studies revealed that reproductive failure due to the functions of testicular cells is associated with PAEs toxicity[8]. In addition, some earlier studies showed that PAEs portray health dangers, making them aggravate hypertension risk, altering the level of thyroid hormone, and even leading to metabolic complications[8,9].

The exposome concept refers to the totality of the environmental exposures impacts on the lifetime health of a person[10]. It is considered to be the human right to have clean water to drink. The past researchers have revealed more than 30 kinds of phthalates and their different variations

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that originates in various sources of contamination, such as tap water bottled water, water purifiers, etc[11]. The presence of phthalates in drinking water sources is therefore a concern since it manifests in large quantities and varieties that make it a crucial part of the daily consumption. Through the exposome concept, it is imperative to document the current evidence along with assessment of existing opinion on health risks of phthalate exposure through drinking water in the entire human life cycle[12]. A number of nations, in addition to the World Health Organization (WHO), have provided standards regarding the quantity of phthalates that is allowed in drinking water. As an illustration, China has established maximum levels of 8, 3 and 300 mg/L of di-(2-ethylhexyl) phthalate (DEHP), di-n-butyl phthalate (DBP), and diethyl phthalate (DEP) respectively[13]. Deviation of 8 mg/L has been set at the maximum limits of DEHP establishment by the WHO whereas that of the same phthalate in the United States is afforded a maximum of 6 mg/L[14,15]. Nevertheless, high phthalates have been identified in some countries where there is no particular limit of phthalates established in drinking water. Research in India report high phthalates between 4.665 to 7553.94 mg/L in raw water sources and between 3.31 and 8633.57 mg/L in the drinking water treatment plants and 0.77 and 1438.20 mg/L in the tap water. In the same token it has been found out that bottled water in Nigeria is likely to contain phthalates with varying concentration as high as 1740-2370 mg/L[17]. Ingestion of phthalates by using drinking water in these areas is very high and surpasses the suggested limits contained in the WHO, which implies a massive summation and lifetime exposure to people. Upon ingestion, phthalates are easily absorbed and are known to be endocrine disruptors which bind to molecular receptors causing hormonal imbalance, and this has been associated with numerous medical problems including reproductive abnormalities, neural disorders, and other chronic illnesses like obesity and hypertension in people of all ages[18,19,20,21].

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It might be observed that the presence of PAEs in the environment in large concentrations is one of the issues of concern across the world[22]. Phthalates are capable of escaping out of landfills and contaminating the ground water by leaching. Under this scenario, the destiny and transport of the PAEs can not only assess the risks of exposure but also realize their tendency in the environment. Moreover, PAEs released during the industrial and domestic wastewater treatment facilities find direct entry into the water or sewage sludge that has severe impact to the ecosystem and human health through food chain[23]. One of the studies under analysis established the presence of phthalates in the surface waters at the level of 22.7 mg L^{-1}, with the top range of 288 mg L^{-1} on the wastewater[24]. Therefore, it is mandatory to eliminate PAEs in wastewater sources through implementation of several potential technologies of treating waste water.

PAEs share some typical features, which are shared among many environmental pollutants, including anthropogenic nature, persistence, and possible ecological hazards[25,26,27,28]. When they are discharged into the environment, the PAEs experience unique transformation and removal mechanisms in the various media. The main pathways of PAEs degradation in the atmosphere are found to be through photo oxidation processes with hydroxyl radicals (OH•) and the major mechanism of the resulting compound removal is through wet and dry deposition. It is remarkable that quite sophisticated bidirectional air-sea exchange patterns are observed with diethylhexyl phthalate (DEHP), which is caused by Henry constant. In the water, little contribution of hydrolysis to the PAE degradation comes into light and photo- degradation and especially through aerobic microbial degradation signifies major methods of disposal of PAEs[30]. Degradation of PAE In sediment settings, microbial activity appears to be the main factor controlling the degradation of PAE, where rates are highly dependent on redox conditions, temperature, and pH30. Equally, the deposition of PAEs in soils is mainly through atmospheric

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deposition and sludge applications and their normal lives depend on the kind of soil and the arrangement of microbes that regulate the degradation process[29,30]. But tracings involving the continued and high release of PAEs in the environment due to plastic wearing and industrial waste waters further complicates the issue of the usage patterns of the environment.

Such compounds are therefore usually found in the drinking water as they either pass through dumping of industrial wastewater and landfill leachate[31]. Close to surface and groundwater contamination by PAEs is as a result of agricultural activities, more so due to the wide usage of plastic mulch films. In another study, it was found that the residue of a plastic film not only led to increased soil PAE concentration, but that the residues had a profound effect on inhibiting microbial activity, diversity and enzyme functioning, which was dependent on the color of residue and the volume of coverage[32]. Although there is already information on these sources and pathways, the effects of urbanization and related land-use changes on contamination by PAE in drinking water sources are not well understood, and this is one of the key gaps requiring exploration.

The changes in land use are closely linked to the behavior (distribution) of PAEs. As an example, in Industrial zones, road dust has higher concentrations of PAEs because of industrial production and indisposed wastes[33]. In comparison, PAEs can be adsorbed into sediments in natural segments of the environment, such as mangrove wetlands through the organic carbon in process of reducing the bioavailability of the PAEs and the mobility of the PAEs in the waters[34]. Moreover, the role which influences the land use patterns on PAE distribution, also is exposed to the impact of other factors. As an example, topographical differences may cause varying degrees of PAEs. Areas prone to collect increasing amounts of PAEs are plains, and the terrain is mountainous, which limits the time of waste dumping into rivers[30]. The concentrations may also

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be influenced by season and with the highest concentrations of PAE in the months of the rainy season due to run off and human related activities[35]. Such interactions are pointers to the complex aspects of land use, topography and PAE behavior in the scenario of urbanizing landscapes.

1.2 Statement of the Problem

Phthalate esters (PAEs) are man-made chemicals and used in large quantities as plasticizers in production of polyvinyl chloride (PVC) products, personal care products and food packaging among other consumer goods[2]. These products have a weak chemical bond and thus PAEs easily leach in the environment causing contamination of water bodies, soil and air almost everywhere. Their concentration in ground waters raises serious concern in view of their recalcitrance, bioaccumulation potential and their toxic effects like endocrine disruption, reproductive toxicity and carcinogenicity[36].

Poor waste disposal mechanisms and extensive use of plastic materials in urban and peri-urban centers of developing countries such as Nigeria are some of the factors leading to the rise of PAEs in the environment. Gbagi General Market, located in Ibadan, is a large commercial centre that utilizes a large quantity of the plastic product and packaging material, as well as the possibility of inappropriate disposal of PAE-containing waste. The fact that the market is located near residential areas and uses shallow sources of water (e.g., wells and boreholes) as the source of drinking and domestic water is of concern as it may put people at risk of exposure to PAEs containing water.

Whilst there has been ample data in line with PAE pollution into the water systems globally, there still exists little information as regards their presence, instances in their distribution as well

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as their health risks to the groundwater sources in the immediate vicinity of Nigerian markets. PAE pollution in the surface water and in industrialized areas has also been previously documented, with a smaller level of concern given to market environments that might increase the level of pollution due to its high human traffic and inadequate level of waste disposal systems. Moreover, the absence of regulatory surveillance and community knowledge about the dangers of PAEs in Nigeria points to the necessity of focusing the studies in the territories with the highest exposure such as Gbagi General Market.

The project undertaken will evaluate concentrations, spatial distribution, and possible sources of the PAEs in the groundwater within and outside Gbagi General Market. The results will offer key information to determine contamination rates, the existence of hot tail zones, and the number of risks that could be suffered by the vendors, consumers, and residents using the groundwater nearby. Also, the work will make a contribution to the overall comprehension of PAEs contamination in the urban market context and assist in formulating evidence-based advice regarding waste disposal strategies and water safety policy.

1.3 Justification of the Study

Phthalate esters (PAEs) are commonly used as plasticizers in plastics, and other wide-ranging consumer products such as packaging material, cosmetics, and food containers[3]. They are non-chemically bound to plastics thus easily leach into the environment tainting water sources. A number of PAEs like Dodecanoic acid DEHP and dibutyl phthalate (DBP) can be categorized as endocrine-disrupting chemicals (EDCs) and have been implicated in reproductive disorders, developmental toxicities, and carcinogenesis[35]. It is vital to measure their occurrence in groundwater to remain desirous of safeguarding the health of the population, more so, in places where groundwater is a major source of drinking water.

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The Gbagi General Market is considered as one the biggest offices in Ibadan where plastic materials are greatly used in packaging, storage and even disposal of waste. The possible leakage of PAEs into the groundwater and the inappropriate treatment of plastic wastes render a great threat. As most residents and traders use the wells and boreholes to get drinking water, the study will present important information on the extent of the contamination, and this would facilitate in establishing whether or not the water can be used. Although researchers have carried out researches on PAEs contamination in other areas, there is no sufficient record of their presence and distribution in the groundwater of the state of Ibadan, especially in high-risk locations such as markets. The study will address a valuable research gap, which will create a baseline around which to monitor and take regulatory measures in the future.

The results of the proposed study will update policymakers, environmental authorities/organizations, and public health authorities regarding the necessity of having more stringent rules when it comes to plastic waste management and groundwater protection. It will also assist in carrying out remediation measures in case the levels of contamination surpass the allowable limit dictated by the World Health Organization (WHO) and other organizations. This will create awareness among users of the market, residents, and local authorities about the dangers of not disposing plastics properly by determining PAEs contamination in groundwater. It will stimulate the adherence of optimal waste management as well as the use of alternative plastic product substitutes.

Since PAEs can be harmful to people, this study might be described as both timely and necessary in view of the environmental sustainability of the Gbagi General Market and the need to safeguard the lives of the people. The results will add to scientific knowledge, policy decisions and assist in minimizing exposure to harmful contaminants when using drinking water. This

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justification underlines the importance of the study to deal with a severe environmental health concern and offer practical knowledge to stakeholders.

1.4 Aim and Objectives of the Study

The aim of this study is to assess the presence, concentrations, and spatial distribution of phthalate esters (PAEs) in groundwater samples collected from the Gbagi General Market in Ibadan, Nigeria, and evaluate their potential health risks to consumers.

The specific objectives are to;

1. Identify and quantify the levels of selected phthalate esters (PAEs) in groundwater sources within and around Gbagi General Market using High-performance liquid chromatography (HPLC).
2. Determine the spatial distribution of PAEs in groundwater by analyzing samples from different locations within the market to identify contamination hotspots.
3. Assess potential sources of PAE contamination, including leaching from plastic waste, packaging materials, and other anthropogenic activities in the market.
4. Compare the detected PAE concentrations with permissible limits set by international regulatory bodies (e.g., WHO, USEPA) to evaluate compliance and safety.
5. Estimate potential health risks associated with exposure to PAEs in groundwater by calculating hazard indices for different population groups.
6. Recommend mitigation measures and policy interventions to reduce PAE contamination and protect public health.

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1.5 Research Questions

1. How are the concentrations of different phthalate esters (PAEs) in groundwater samples that have been collected in Gbagi General Market?
2. What are the commonest PAE in study area groundwater?
3. What are the relationships of the identified PAE concentrations to regulatory limits by WHO, NAFDAC or USEPA?
4. What are the potential human health hazards involving exposures to PAEs, due to the drinking water at Gbagi Market?

1.6 Significance of the Study

Phthalates refer to the endocrine disrupting chemicals (EDCs) that cause cancer and reproductive complications as well as developmental problems. Their presence in ground water is also considered as it can assess the possibility of danger to people who are using water in the market and those living around. The research determines the sources of pollution (e.g. plastic wastes, leachates of packed products, industrial effluents) that penetrate into the groundwater and degrade the quality of groundwater. The results can be used in determining mitigation procedures to avert any further contamination. The outcomes could result in harder environmental policies on plastic consumption and garbage administration in markets. It is also able to shape the policies, regarding safe water supply and limits of phthalates exposure in Nigeria.

The study also represents the first baseline data on PAE contamination in urban markets of Nigeria and therefore aids in future studies regarding the pollutants of upcoming problems in developing economies in their drive to characterize environmental emergent contaminants. Clean ground water makes agricultural products safer (assuming they are irrigated using ground water)

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and prevents health expenditure due to exposure to the chemicals. The research is vital in ensuring the good quality of water, maintaining the health of the people and ensuring sustainability in the market operations within the city of Ibadan and other cities.

1.7 Scope of the Study

The study aims at evaluating the prevalence and the distribution of the phthalate esters (PAEs) in the ground water sources in and around the Gbagi General Market, Ibadan, Oyo State, Nigeria. The sampling will include the boreholes, hand-dug wells, and other groundwater sources in areas that could likely be heavily-contaminated areas like plastic waste dumps, drainage or business areas. The research will determine and measure ubiquitous PAEs (e.g. DEHP, DBP, BBP, DEP, DMP) in groundwater samples. Determine also the spatial differences in the concentration of PAE at the various sampling sites. The study will also report these scattered comparisons of PAE levels against the ones recognized by international safety standards (e.g. WHO, USEPA).

1.8 Limitation of the Study

The research was narrower on samples of ground water in Gbagi General Market and this could not be the limit of PAE contamination in Ibadan. Seasonal factors (wet vs. dry season) could not be taken into account, which could have an influence at the level of PAE concentration. There were no enough baseline data on PAEs in Nigerian groundwater and comparing research results with those found earlier is challenging.

1.9 Operational Definition of Terms

1. **Phthalate Esters (PAEs):** It is an array of synthetic organic compounds used as plasticizers in commercial and non-commercial items (e.g. packaging, cosmetics, PVC). In the current research, PAEs include certain chemicals (e.g. DBP, DEHP, BBP) that are

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analyzed in groundwater samples with the help of analytical methods (GC-MS, Gas Chromatography-Mass Spectrometry).

2. **Groundwater:** Water found at the depths inside the earth in the soil pores, between cracks of the rock formations.
3. **Contamination:** Ground waters contain PAEs levels above their allowed limit by regulatory authorities (e.g. 0.008 mg/L of DEHP).
4. **Gbagi General Market, Ibadan, Nigeria:** Gbagi is a commercially vibrant area in Ibadan and can be described as one with a large human population, and a high level of plastic waste and risk of chemical contamination of groundwater. In the study, reference will be made to 10-15 sampling points inside and outside the market.

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Chapter Two

Literature Review

2.1 Sources and Pollution Status of Phthalates Esters (PAEs)

The sources of PAEs are mainly in every day consumer products and discarding by burning of solid wastes. Commonly, the interaction between PAEs and plastics is minimal and this is favorable in migration of PAEs in plastic products to the environment[1]. The problem of PAE contamination is also universal and exhibits shifting levels of prevalence in various locations. PAEs can be transferred and leaked into water bodies, hence resulting into pollution of water resources. Wastewater used as industrial and domestic wastewater, waste leachate and agricultural irrigation wastewater have a higher level of PAEs[2]. Globally, PAEs distribution within the aquatic environment represents an extensive concentration range (0.1×10^{-3} - 3.2×10^{3} µ. gL^{-1})[2]. The principal examples of PAEs in water are DMP, DEP, DEHP, BBP, di-n-butyl phthalate (DBP) and dioctyl phthalate (DOP).

Changes in water quality can influence the types of dominant pollutants present; however, most research identifies DEHP as the primary contaminant[3,4]. The general chemical structure of phthalate esters (PEs) is illustrated in Figure 2.1, where R and R′ denote alkyl groups[4]. Commonly used PEs in consumer products include dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIP), di-n-butyl phthalate (DBP), benzylbutyl phthalate (BBP), dicyclohexyl phthalate (DCHP), di-n-hexyl phthalate (DHP), bis(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DOP), diisodecyl phthalate (DiDP), and diisononyl phthalate (DiNP)[5,6]. Seasonal changes can cause notable shifts in PAE concentrations in water, with levels generally being lower in warmer seasons than in colder ones.

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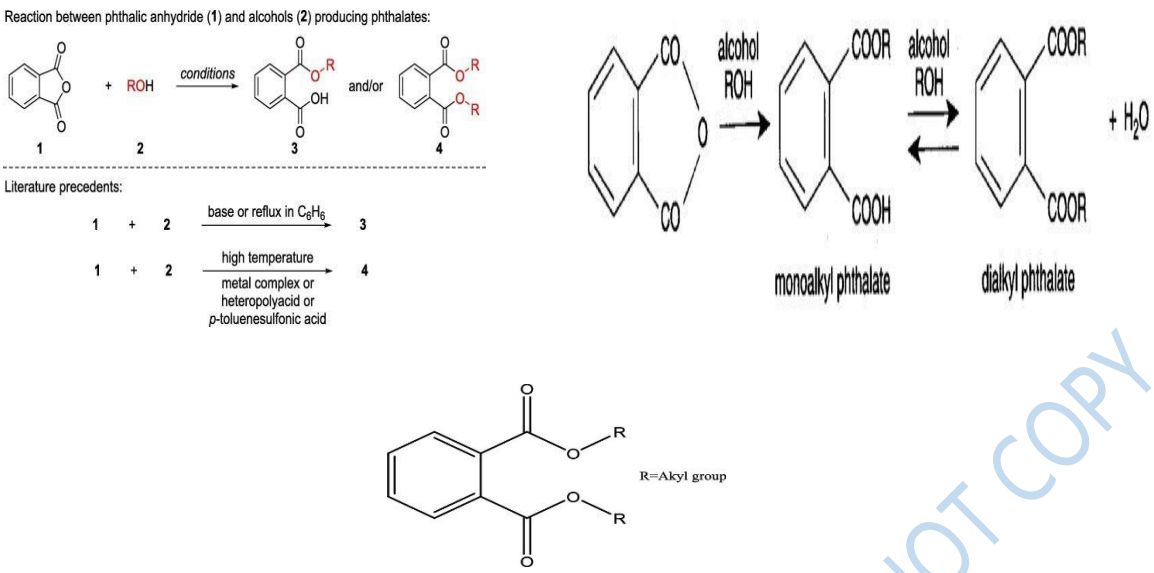


Figure 2.1: General Chemical Structure of Phthalate Ester.

Source[5]

A study on surface water in Jabalpur City, India, revealed marked seasonal differences in PAE concentrations between winter and summer. The highest concentration was recorded in winter at 7553.9 $\mu g \cdot L^{-1}$, compared to a significantly lower level of 410.48 $\mu g \cdot L^{-7}$ in summer[7]. This means winter levels were about 18 times higher than those in summer. The observed seasonal variation is likely influenced by increased photolytic activity and microbial degradation of PAEs during the summer months. Since tap water and drinking water for daily use often originate from natural sources, such as lakes, rivers, reservoirs, and groundwater, these water bodies can act as direct sources of PAE contamination[7,8]. Furthermore, the transfer of PAEs between different media is affected by factors like the chemical nature of the carrier, environmental conditions, materials involved, and interacting substances[9]. The study also noted that tap water PAE concentrations can be influenced by variables such as the distance the water travels, the type of piping materials,

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transit time, and the use of plastic packaging, all of which may contribute to drinking water contamination[7,8].

Daily water treatment is necessary due to the risk of PAE contamination during transportation and distribution. Comparative analyses reveal that PAE concentrations in treated drinking water are greatly reduced[7]. In most water treatment plants, processes are mainly aimed at eliminating bacteria and heavy metals. However, because of their chemical stability, current methods are generally ineffective at removing PAEs[2,10]. Therefore, there is a pressing need to enhance domestic water treatment technologies to reduce human exposure to PAEs through daily water intake. Additionally, the use of PAEs in manufacturing and plastic packaging production should be carefully re-evaluated.

It is important to highlight that soil serves as a major natural reservoir for pollutants, including substantial amounts of PAEs. Due to their high octanol–water partition coefficients, PAEs tend to adsorb strongly onto soil particles, with reported concentrations ranging widely from 1×10^{-3} to 820 $mg \cdot kg^{-1}$ [10], contributing significantly to soil contamination. These compounds can enter soil through surface runoff and atmospheric deposition and are largely linked to agricultural activities. Common sources include agricultural films, fertilizers, sludge used in farming, and wastewater irrigation[11]. Hui et al. reported that sludge organic fertilizers (SOFs) contained relatively high PAE levels among current organic fertilizers, and their application was shown to increase PAE accumulation in soil profiles, thereby elevating human health risks[12]. Variability in PAE concentrations across agricultural soils is well documented[11,13]. For instance, in Lanzhou, China, levels of six PAEs (DMP, DEP, BBP, DBP, DEHP, and DNOP) reached 0.21 $mg \cdot kg^{-1}$, with DNOP as the dominant contaminant, though other studies identify DBP and DEHP as the main PAEs in agricultural soils[11,13]. Such differences are thought to be influenced by varying farming

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practices[11,14,-18]. Notably, PAE levels in greenhouse soils are often significantly higher than in open-field soils likely due to prolonged use of greenhouse coverings and pesticide formulations containing PAEs[11,17,18]. Therefore, effective regulation of agricultural inputs is essential for mitigating PAE-related soil contamination.

Semi-volatile organic molecules known as PAEs can move directly from raw materials into the atmosphere. Research has indicated that the physical and chemical characteristics of chemicals, human variables, and natural conditions can all have an impact on the variation of single PAE pollution. As the temperature rises, PAEs (DEHP, DBP, etc.) will volatilize into the atmosphere with reduced vapor pressure from a variety of environmental media, including soil, water, and plastic products[10]. The concentrations of PAEs in the atmosphere fluctuate widely (4×10^{-3} – 33,851 $ng \cdot m^{-3}$)[10]. Consequently, a significant number of PAEs are present in the atmosphere, with DEHP being the main source[19,20,21]. In Shanghai, China, two people measured the quantities of PAEs in indoor air at 3130 and 2464 $\mu g \cdot g^{-1}$, respectively[21,22]. Numerous individual factors, including the usage of household items and materials for indoor renovation, may be connected to the observed drop in indoor PAE levels. The observed changes in atmospheric PAE levels are also influenced by seasonal variations. There are noticeable variations in atmospheric PAE concentrations between the cooler and warmer seasons in places like Paris, France, Lornea, and Mexico.[23,24]. The observed improvement in source emission rates may be explained by the acceleration of PAE volatilization at higher temperatures, which also lowers the dust–gas partition coefficient (Kd). Consequently, PAE concentration levels in the atmosphere are impacted[10,25,26]. Concerns regarding potential PAE air pollution in industrial regions are also raised by the extensive usage of PAEs in industrial processes. It has been observed that these regions are more polluted than others[19,27,28]. PAEs are intricate compounds found in the

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atmosphere that have the ability to cling to particle matter and travel long distances. Usually, dust, suspended particulate matter, and other solid surfaces are where PAEs are adsorbed. They then move across the environment by undergoing multi-interfacial modification and traveling long distances through the atmosphere.

2.2 Occurrence and Environmental Fate of PAEs

Three processes break down PAEs in the environment: microbial degradation, photo degradation, and hydrolysis[5]. PAEs hydrolyze and biodegrade in the environment very slowly[10, 25]. Nonetheless, a few microbes that could break down PAEs were recovered from various matrices. Achromobacter strains obtained from sewage sludge were used to demonstrate the microbial clearance of PAEs. Likewise, soil-extracted bacteria like Agromyces and Bacillus demonstrated a high breakdown efficiency of PAEs. Additionally, PAE-degraded bacteria were discovered in salty soil or marine water, bioreactors (Pseudoxanthomonas), compost (Providencia), and sediments (Curvibacter)[29,30,31].

Conditions affect the rate of PAE biodegradation, which falls in cold, anaerobic environments that are inhospitable to microorganisms that break down phthalates[21]. The bioavailability of PAEs determines how quickly they biodegrade, and HMW PAEs have lower biodegradation rates and are less bioavailable because of their hydrophobicity[29]. The impact of seasonal variations in temperature, humidity, sun activity, and soil organism activity were highlighted by a PAEs periodic peak seen in the soil during a year-long experiment in the winter and summer[32].

Additionally, phthalates with short side chains, like DMP, DEP, DBP, and BBP, are more biodegradable than PAEs with long side chains, including DEHP, DHP (dihexyl phthalate), and DNOP (di-n-octyl phthalate)[30]. Compared to LMW phthalates, DEHP, the representative of

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HMW phthalate, is more difficult to biodegrade and has a high octanol-water partitioning coefficient (log Kow = 7.5)[10,23]. Important factors in the biodegradation of PAEs include their solubility in water, low log Kow, and weak interactions with soil organic matter. With a log Kow of 2.42, DEP is susceptible to biodegradation[29].

The structure of phthalates affects their vulnerability to deterioration, such as hydrolysis. Compared to PAEs with short side chains, those with long side chains had less hydrolysis[29]. Hydrolysis is impacted by the steric action of phthalates' side ester chains. The phthalates are not hydrolyzed because the side ester chains prevent the hydrolytic enzymes from attaching to them[21].

In a lab setting with pure bacterial cultures and in a variety of settings with their native microflora populations, PAEs can biodegrade[28]. Under aerobic conditions, DEHP is rapidly broken down in the environment. The fungi Penicillium lilacinum, Aspergillus Niger, Aspergillus puniceus, Actinomucor elegans, Phanerochaete chrysosporium, and others can hydrolyze DEHP in aerobic environments, as can many bacteria (e.g., *genomes Rhodococcus, Bacillus, Micrococcus, Enterococcus, Pseudomonas, Acinetobacter, Mycobacterium, Corynebacterium, Brevibacterium, Gordonia,* etc.)[20]. Additionally, there are known fungal species that can break down phthalates in anaerobic, anoxic, and aerobic environments. These fungi can be found in a variety of settings, including soils, sediments, rivers, and marine waters[33]. Some of them, regrettably, are only capable of converting PAEs into phthalate monoesters (PME), which are nonetheless harmful to animals[29]. Finding a single microbe that can fully biodegrade PAEs is challenging. Using different microorganism cultures is the answer[21].

Microorganisms' metabolic breakdown is the primary pathway for DEHP decomposition[34]. The molecules of PAEs are first "cut" into smaller monoesters, which are then followed by phthalic

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acid (PA). The next stage is the enzymatic breakdown of PA into benzoic acid (BA) via esterase. CO_2 and H_2O are the end products of the cleavage of the BA ring[29,34,36]. PAEs interact weakly with polymers through van der Waals forces or hydrogen bonds[37]. Since PAEs simply leach from polymers under the right temperature, pH, and other conditions, these weak interactions account for their widespread prevalence in the environment[29,36,38,39]. In outdoor products, this process is facilitated by natural elements such as wind, rain, ice, UV radiation, insects, and bacteria41. Phthalates are mostly used in plasticizers[42]. The source of PAEs in the environment is any plastic processing, from manufacture to disposal[42,43,44,45]. All environmental matrices contain PAEs, which are regarded as air, water, wastewater, and soil contaminants (Table 2.1, Figure 2.3)[45]. They can be detected in wildlife fluids and tissues[46]. While DEHP and BBP are more abundant in the dust phase, more volatile PAEs like DEP, DMP, DBP, and DIBP (diisobutyl phthalate) are more common in the gas phase. Because of its association with industrial activity, PAE concentrations are higher in urban areas[47,48]. Additionally, cities have higher levels of PAEs in the air than do rural regions; the same is true for sediment and river pollution[41]. When thinking about the fate of PAEs, the kind of water is particularly important because bio dilution or bioaccumulation may be seen[49]. Fish and algae taken from a freshwater environment (Songhua River, China) had greater overall concentrations of six PAEs than marine water (Bohai Bay, China), with DEHP and DBP predominating[50]. BBP is the primary phthalate molecule detected in indoor air and dust in homes, and PAEs are more prevalent in interior environments where air concentrations are higher than those outside[44,48]. Local activities are linked to the content of different PAEs in different regions of the city[51]. The largest concentration of DMP, which is used in cosmetics, is found in residential areas. High levels of BBP and DEP, PAEs found in auto parts, are found close to major thoroughfares.

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Table 2.1: The Environmental Matrices' PAE Content

Matrix	DBP	DMP	BBP	DEPH	DEP	DnOP	Reference
Yangtze River in Hubei Province	35.65	0.295	-	54.73	0.365	-	[35]
Xuanwu Lake	800.9	173.4	176.6	1299.5	124.0	64.15	[35]
Tigris River, Iraq	ND-0.26	-	-	0.19-1.7	-	-	[52]
Water of pond	0.02	0.03	1.12	5.73	0.07	0.09	[29]
Ponds	790.0	10.0	6.00	2650	7.00	37.0	[29]
Chengyang WWTP (dry sludge)	16.73	16.44	ND	26.0	20.53	ND	[45]
Effluent	1.58-9.450	0.22-1.87	0.16-48.20	2.84-42.4	1.26-7.04	0.54-2.73	[53]
Soil (dry weight)	6.12	ND	0.861	183.0	ND	6.97	[54]
Water [µg/L] lakes in parks in Beijing	0.066	0.081	0.183	0.239	0.009	0.019	[55]
Jarama River (Spain)	0.34 - 1.05	<0.1	<0.19	<0.46	<0.33	-	[56]

ND no detected; (-) no data

Source[45]

The most common of DEHP, DBP, and DNOP is found in most industrial processes that is prevalent in industrial settings[26]. Accordingly, the most commonly observed PAEs in a surface water (seawater and freshwater) are DEHP, DHP, DMEP (di(2-methoxyethyl) phthalate) DMP, DEP, DBP, BBP, DEHP, and DNOP, with DBP and DEHP most common in fresh and marine

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water[28,48]. After comparison of PAEs concentrations in suspended particles with PAEs concentrations in water and sediments we can find that in want particles the highest concentration is present and the lowest concentration in water. This is attributed to the fact that PAEs are hydrophobic and that the high specific surface area of the suspended particles and PAEs in water gets destroyed through hydrolysis[32].

Effluent of WWTPs is regarded as the primary source of PAE to the aquatic environment since compounds of plastic products are restored to wastewater when washed[45]. Plastic and cosmetics industries are the major contributors to the PAEs in industrial wastes. The presence of PAEs in the environment may also come through landfill leachates. The PAEs levels in the sediments are related to the Organic matter (OM) and phosphorus in the sediment material but not the pH[30]. The sludge contains some HMW phthalates (DEHP, DINP and DIDP) that are strongly sorbed since they have a high log Kow (n-octanol/water partition coefficient) compared to DMP which is not present in the sludge because of its better solubility in water[57]. There is a possibility that DEHP can bio accumulate in the soils and the sediments[23]. The pollutants of it soil are DBP and DEHP, which are effects of atmospheric deposition and sewage sludge amendment[48]. Generally, DMP, DEP, DBP, BBP, DEHP, and DNOP, are the most important pollutants. The total amounts of concentrations of these 6 PAEs form 64.8, 72.9 and 66.9 percent of total phthalates in water, sediments and suspended particles[30]. The less anthropogenic activity the less PAEs concentrations there are in sediments and soils. Thus, on the basis of this fact, they can be applied to determine environmental pollution by PAEs in the area of industrial facilities[50].

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2.2.1 Fate and Transport of Phthalates in Water

2.2.1.1 Surface Water

The PAEs enter the marine environment associated with the streams of the mainland including rivers, streams, runoff, etc. The urban road dust is also defined as one of the transport routes PAEs to the surface water (e.g., lakes and ponds). Figure 2.4 shows the concentration of PAEs in water and the highest level was in the groundwater[23].

It was primarily natural (e.g., hydrolysis, photolysis, sediment-water Absorption/desorption, and microbial metabolism) and physical-chemical properties of PAEs that influenced their distribution in surface water. DEP and DBP took place of photolysis half-lives of 2.4 and 12 years in surface water, respectively, and 0.12-1.5 years in DEHP55. Nevertheless, aqueous hydrolysis of PAEs is not a high risk and a big scatter of the half- lives has been reported: half-life of DMP is 3.2 years compared with 2000 years to half- live of DEHP[10]. Thus, predominant causes contributed to the high levels of PAEs in the source of surface water thereby causing severe accumulation in aquatic organisms and the overall negative effects on the human health and environment.

2.2.1.2 Wastewater

Survival of PAEs in both domestic and industrial wastewater treatment plants (WWTPs) has been reviewed in a general way. The range of PAEs levels in domestic wastewater was reported to be 1 0g L-1 to 100 0g L-1 with DEHP being the highest concentration[58]. The level of phthalate was also high as it was equal to 288.95 fg/L in wastewater[59].

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Figure 2.4: Main Pathways for Transport of Phthalates from the Main Polluted Sources to Groundwater

Source [23]

Overall, the PAEs are seldomly mineralized in the WWTPs as they can be extremely hydrophobic that leads to minimal water solubility. Consequently, there is enhanced PAE adsorption on suspended organic matter and PAEs migration to deposited sludge.

Nevertheless, PAEs might be built up and decayed quickly relying on the contribution of microorganisms in various environments including aerobic and anaerobic conditions. Moreover, mass balance study was conducted on degrading of the DEHP in a WWTP which observed the removal percentage to be above 90% out of which about 30% was by biodegradation. In a similar way, it would be seen that the biodegradation of DEHP at WWTP in the trickle filter ranged between 1% to 44%[43]. In such a way, one can argue that this biodegradation can be regarded as one of the primary procedures of the PAEs removal in the wastewater sources. But the biodegradation of PAEs in WWTPs varies upon key aspects, e.g., the design of the reactors, properties of the sludge, etc[36].

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2.2.1.3 Landfill Leachate

The problem of the PAEs contamination of the landfill's leachate has been investigated in the European Union multiple countries. Due to their release sources that are numerous, it is quite easy to determine that high concentration of PAEs is able to be found in land fillers leachate. There is a risk that landfill PAEs may reach the groundwater with their leachates leading to potential threat of environment. Exposure to PAEs depends on many factors such as the kind of the landfill, character of the landfill and circumstances of the environment. In one of them, some common PAEs leachates that were identified on old landfills comprised DEHP (1.3 - 73.9 61 µg L^{-1}) and DMP (0.6 - 4.72 61 µg L^{-1})[61]. Moreover, highly leachates of landfill were also indicated in the literature review results (1275 µg L^{-1}) [4].

Increased levels of PAEs may be attributed to industrial activity-related sources, house hold products, etc., which may be contributed to the high abundance and prevalence of these species. In the meantime, plastic pollution, and PAEs as a result of the practice of disposing and treating municipal solid waste by landfilling method is potentially a major threat to human and environmental health. The deposition has the potential to transfer the pollutants to the water bodies after a process of surface runoff, and leachates through depth flows, and surface water (e.g., rivers, lakes, streams and runoffs) and promote the transfer to the ground water sources[54].

2.3 Overview of PAEs Concentrations in Raw Water Sources and Drinking Water

Regional and worldwide statistics show that PAE concentrations vary greatly among different water matrices, frequently surpassing health recommendations and underscoring the shortcomings of traditional water treatment.

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2.3.1 Tap Water System

Traditional drinking water treatment plants (DWTPs) are not set up to treat the new pollutants such as phthalates and only get rid of suspended solids, bacteria, and natural organic matter[62]. As a result, the treated water that is distributed by DWTPs usually has residues of the phthalates used in them. Moreover, secondary contamination of drinking water with phthalates in a drinking water supply network can occur due to use of plastic pipes (e.g. polyvinyl chloride (PVC) and polyethylene (PE)). This further poses a higher risk of human exposure to phthalates through tap water. Phthalates in the raw water sources have a great variance based on geographical location. According to the given global dataset (n = 20), a study documents the highest aggregate levels of six major types of phthalates (e.g. DEP, DBP, dimethyl phthalate (DMP), benzyl butyl phthalate (BBP), DEHP, and di-n-octyl phthalate (DNOP)) range between 3927.89 to 7553.94 mg/L (Table 2.2)[3].

By contrast, aggregate concentrations are much lower reported in China; seven measured phthalates have been reported to range between 0 and 0.005 mg/L, including the six common phthalates measured in the earlier study[63]. This lower measurement might be because of the nationwide water treatment plant upgrading program focused on the elimination of the new contaminants like phthalates in the complex loop of the water exchange between the environment and customers such as the installation of new treatment processes like ozonation, granular activated carbon, and sand filtration[64]. In wastewater treatment plants (WWTPs), activated carbon, advanced oxidation process (AOPs), membrane filtration, membrane bioreactor, coagulation, and integration of various processes are being used to eliminate the contaminants/phthalates[65].

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Other significantly high limits of presence are also being reported with DEP being in Mexico with a figure of 7.600 mg/L, DBP in Russia with 25.50 mg/L, and DEHP with an astounding 8351.85 mg/L in India[71]. DEHP and DBP are among the phthalates that are usually highly abundant. The occurrence of phthalates in raw water sources can be associated with a number of factors such as releases of untreated urban and industrial wastewaters, insufficient managing of the solid wastes, and utilization of raw wastewaters in agriculture irrigation that all sum up in the emphasis on the presence of regional differences in the level of phthalates[71]. Moreover, the striking seasonal change in concentrations may be the result of the disparity of degradation rate of phthalates in natural water bodies that is affected by various factors including but not limited to the light intensity, temperature, and the presence and activity of microbial populations in natural water bodies[63].

Table 2.2: Phthalates Concentration at Different Stages in the Drinking Water Supply System

Source	Total PAEs	Minimum	Maximum	Mean	Median	Reference
Bottled water	5	0.41	3.09	-	-	[66]
Bottled water	8	1.15	2.47	-	-	[67]
Bottled water	6	4.68	7.54	-	-	[68]
Bottled water	1	1.15	3.04	-	-	[43]
Tap water	6	0.072	0.153	-	-	[69]
Tap water	15	0.27	76.36	-	3.92	[35]
Tap water	6	0.53	2.4	-	-	[66]
Tap water	22	0	0.447	-	-	[70]
Surface water	6	4.665	410.48	-	-	[7]
Surface water	16	0.437	20.5	1.93	-	[30]
Surface	1	0.3	0.82	1.7	-	[62]

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water						
Surface water	9	0.1245	0.8365	-	-	[71]

Source: Field Survey, 2025

The phthalates may be introduced into the tap water in upstream raw water supplies (via high concentrations), through the midstream (poor removal rates in the treating plants), and downstream contamination (leached by domestic water transport systems and household water purifier), or some combination of these[50]. The highest phthalates concentrations reported in tap water were 1438.200 mg/L in India and the minimum concentrations of phthalates measured were 0.153 mg/L in the United States[54]. Though the data on the particular phthalate levels in DWTPs influent and effluent water is wanting, there is evidence that on average phthalates removal rates in DWTPs are usually too low[70].

Namely, the removal rate of DEHP is 8.2 - 33.4 percent in Korean plants[64]. Use inside plastic water piping Systems There were also concerns over phthalates leaching out of plastic water-supply pipes and elements of filter systems used in municipal water supply systems. In chemical migration investigations, a maximum of 16 phthalate types was found to leach out of seven water-supply materials and up to three times more in distribution systems than in the water leaving the treatment plants[62]. Additional testing involved assessing the total amounts of 22 varieties of phthalates in tap-water, with a range varying between none detected (N.D.) and 0.447 mg/L and the concentrations augmented after the corpus operandi purification procedure in water vending machines of between 0.025 and 1.100 mg/L. In the meantime, the results of treatment through water boiling machines recorded the levels of phthalates between N.D. and 0.841 mg/L[65].

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2.3.2 Bottled Water

The bottled water is a convenient form of water that is largely favored by consumers because of its perceived quality assurance. But behind this healthful wrapping is a possible health hazard because the phthalates in plastic bottles are able to leach out into the water. Indicatively, the greatest concentration of phthalates recorded in bottled water was between 4.68 and 7.54 mg/L whereas the lowest level was 1.15 and 2.48 mg/L (Table 2.2)[67,68]. It was also noted by research that levels of phthalates would depend on storage conditions. Waters bought in PET bottles were analyzed directly after the buying, and phthalates could not be detected, but their levels raised significantly after 180 and 365 days of storage[72]. In particular, short-chain phthalates, including DEP, are more likely to leach, but might break down with time, as opposed to being accumulated by long-chain such as DEHP[72]. Further, ineffective handling of lemon including exposure to direct sunlight, high temperatures, and shaking may enhance the leaching process, and hence have significant health implications on consumers[66]. PAE leaching can also occur in bottled water, where values can range from 1.15 to 7.54 µg/L. Remarkably, values ranging from 1740 to 2370 µg/L have been found in several areas, including Nigeria. This leaching process is known to be made worse by storage circumstances such as length of time, exposure to sunlight, and high temperatures.

2.3.3 Surface Water

The concentrations of PAE (median: 1405.33 ng/L) in surface water, especially in China, were much higher than those of other organic micropollutants. The two most common congeners were found to be dibutyl phthalate (DBP) at 638.5 ng/L and di-isobutyl phthalate (DiBP) at 581.0 ng/L. China is the largest producer and consumer of PAE in the world, as seen by these levels, which are higher than those in rivers in Madrid, Spain (696 ng/L) and Marseille Bay (191 ng/L)[71].

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Because of the widespread use of plastic mulch film in agriculture, the Haihe, Liaohe, and Songhua River basins in northern China have greater concentrations of PAEs in their surface water. In contrast, research on PAEs in agricultural soils revealed that southern and eastern China had higher levels, which were associated with industrialization and socioeconomic growth. Instead of being a direct contradiction, this apparent disparity in geographical patterns between soil and surface water suggests that various environmental matrices are impacted by different dominating routes and sinks[71]. Agricultural runoff from the extensive use of plastic mulch in the north seems to be the main input for surface water, which raises river concentrations. In the more developed southern and eastern regions, industrial and urban inputs may be the main cause of soil deposition, along with direct accumulation from plastic mulch leftovers. This demonstrates how complicated and frequently matrix-specific the sources of contamination are. Understanding groundwater contamination at Gbagi Market will necessitate taking into account the direct discharge of urban and industrial waste from market operations[71].

2.4 Health and Ecological Risk Profile of PAEs

2.4.1 Bioaccumulation and the "Exposome" Concept

It is known that phthalate esters are endocrine disruptors that easily move from their origins into soil and other environmental systems, where they can bioaccumulate in crops and then into the human food chain7. They also represent a serious hazard to larger ecosystems because of their ability to accumulate in species through the food chain.

The "phthalates drinking water exposome," which characterizes the ongoing, lifetime exposure to PAEs mostly through drinking water, is an essential idea for comprehending human exposure[71]. The human body gradually accumulates PAEs and their metabolites as a result of this continuous exposure. By identifying phthalate metabolites in biological samples like blood, urine, and

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amniotic fluid from people of all ages, biomonitoring studies offer strong proof of this pervasive exposure. For example, a person who drinks three liters of water a day on average may consume roughly 24 μg of DEHP each day, which the body would then circulate for two days before excreting. Over time, this persistent consumption and the ensuing bioaccumulation lead to the emergence of numerous chronic illnesses[73].

The idea of the "exposome" completely reinterprets the paradigm of risk assessment by concentrating on cumulative, lifetime exposures rather than acute, single-source exposures. This viewpoint is especially relevant to groundwater, which frequently provides communities with a reliable, long-term source of drinking water[70]. This implies that, if found in groundwater, even apparently modest quantities of PAEs may lead to substantial bioaccumulation over the course of a person's lifetime. Thus, assessing not just the immediate toxicity but also the possibility of long-term health impacts from ongoing, low-level exposure is necessary to comprehend the long-term public health implications of groundwater contamination[33].

A growing number of epidemiological and toxicological studies have connected exposure to phthalates to a wide range of harmful health consequences, such as neurological conditions, obesity, cardiotoxicity, endocrine and reproductive dysregulation, and even some types of cancer[72]. Because of their possible negative effects on human health, phthalates exposed through drinking water have thus become a major public health concern that affects people of all ages[44]. For vulnerable groups, especially pregnant women, the presence of phthalates in drinking water presents unique hazards because exposure may impair fetal development[22]. Similar to exposure to DBP, intrauterine exposure to DEHP can shorten gestational length and possibly result in fetal loss[42]. Studies have shown significant correlations between phthalate exposure and obesity in children and adolescents, with metabolites detected in samples from obese participants[72].

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Furthermore, exposure to phthalates has been connected to negative impacts on brain development, affecting regions like the limbic system, basal ganglia, and cerebral cortex, which may result in cognitive and behavioral issues. DEHP exposure at levels of 5 mg/kg and 1500 mg/kg caused cortical plate hypoplasia in mice, according to studies. Furthermore, exposure to phthalates has been connected to negative impacts on brain development, affecting regions like the limbic system, basal ganglia, and cerebral cortex, which may result in cognitive and behavioral issues. DEHP exposure at levels of 5 mg/kg and 1500 mg/kg caused cortical plate hypoplasia in mice, according to studies[72].

Male fertility has been adversely affected by phthalate exposure in adult males, particularly from immunosuppressive medications, which has been linked to lower libido and sperm production as well as deleterious effects on spermatogenesis. According to some research, phthalates may also impair the reproductive health of women by interfering with hormone receptors, which could result in issues like early ovarian failure and an increased risk of reproductive cancer. The detrimental effects of phthalates on female mice have been shown in numerous animal experiments[74]. The steroidogenesis process, which transforms cholesterol into steroid hormones, is impacted by phthalates, which have been demonstrated to suppress the biosynthesis of aldosterone and testosterone by increasing corticosterone levels. Cardiovascular disease is a major cause of morbidity and mortality among the elderly. According to the study, DEHP exposure can lower heart rate variability, a known sign of cardiovascular disease, in treated mice by about 17%. Furthermore, exposure to phthalates is linked to enhanced vascular resistance and vasoconstriction, two important variables in the development of cardiovascular illnesses[74].

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2.4.2 Reported Adverse Health Effects Across Age Groups

Studies in epidemiology and toxicology have increasingly connected exposure to PAE to a wide range of detrimental health effects in different human groups.

2.4.2.1 Endocrine and Reproductive Deregulation

The well-known endocrine disruptors known as PAEs have the ability to change hormone levels. Male fertility is adversely affected by exposure in adult males, which is linked to lower libido and sperm production as well as deleterious effects on spermatogenesis. PAEs may cause hormone receptor disruption in females, which could result in consequences such early ovarian failure and an increased risk of reproductive cancer[73,74]. Moreover, decreased gestational length and possible fetal loss have been associated with intrauterine exposure to DEHP and DBP.

2.4.2.2 Neurological Disorders

Exposure to phthalates has been linked to detrimental effects on brain development, affecting important regions such the limbic system, basal ganglia, and cerebral cortex. Cognitive and behavioral issues might result from such deficiencies. Research on mice has shown that exposure to DEHP particularly caused cortical plate hypoplasia[74].

2.4.2.3 Other Chronic Diseases

Phthalate exposure and childhood and teenage obesity have been found to be significantly correlated, with metabolites often found in samples from obese subjects. By increasing corticosterone levels, PAEs can impede the production of aldosterone and testosterone, influencing the steroidogenesis process. They are also associated with hypertension and cardiovascular disease. For example, exposure to DEHP is linked to increased vasoconstriction and raised vascular resistance, two important factors in cardiovascular illnesses, and can decrease

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heart rate variability, a known sign of cardiovascular dysfunction. Furthermore, exposure to PAE has been connected to specific cancer types[74].

2.4.2.4 Specific Vulnerabilities

Pregnant women are particularly at risk when drinking water contains PAEs because exposure may impair fetal development[73]. Compared to adults, this group has Hazard Quotients (HQs) that are 1.5–2.3 times higher. This discrepancy is explained by physiological vulnerabilities including blood-brain barrier permeability and immature hepatic detoxification mechanisms, as well as behavioral factors like frequent hand-to-mouth contact that increases soil ingestion rates. Obesity and problems with brain development associated with exposure to PAE are also more common in children and adolescents[21]. Because PAE exposure affects steroidogenesis, heart rate variability, vasoconstriction, and vascular resistance, it has been connected to cardiovascular disease, a major source of morbidity and mortality among the aged. For a place like Gbagi Market, a highly extensive risk assessment is required due to the distinct vulnerabilities of various age groups and the detailed listing of negative health impacts. This implies that rather than depending just on a general "adult" risk assessment, a risk assessment must take into account the demographic profile of the exposed population (such as the presence of children, market workers, or residents) and modify public health warnings appropriately. This strategy guarantees that the population's most vulnerable groups are sufficiently safeguarded.

2.5 Ecological Impacts and Toxicity Characteristics

Soil ecosystems are at serious risk from PAEs. Their leaching into soils is facilitated by their physical embedding in the polymer matrix of agricultural films, a process that is accelerated by photo oxidative degradation and mechanical film breakage. Increased rainfall might intensify

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PAE mobilization into soil matrix by aggravating the hydrolytic breakdown of plastic polymers and the consequent leaching of plasticizer additives.

2.5.1 Chronic vs. Acute Toxicity

A significant observation derived from toxicity evaluations indicates that the chronic toxicity value (ChV) associated with phthalate esters (PAEs) is markedly lower than the acute toxicity metrics (LC50 and EC50), frequently by a factor ranging from 2 to 15 (e.g., for Dimethyl Phthalate (DMP)[33]. This finding suggests that cumulative chronic toxicity poses substantially greater risks and longer-lasting effects compared to acute toxicity. The assertion that chronic toxicity is more detrimental than acute toxicity represents a vital consideration in the realm of environmental management. It entails that regulatory frameworks and monitoring initiatives ought to prioritize assessments of long-term exposure and cumulative impacts, rather than exclusively concentrating on immediate, high-concentration occurrences that may be overlooked by traditional acute testing[73]. Environmental laws and groundwater monitoring for PAEs must concentrate on preventing long-term exposure and accumulation, rather than only mitigating acute pollution occurrences, since groundwater contamination usually reflects a chronic exposure pathway. The precise ecological and health problems linked to the most frequently found and high-risk PAE congeners are compiled in Table 2.3. All phthalates are categorized as extremely dangerous pollutants under the Globally Harmonized System of Classification and Labelling of Chemicals, which states that a substance's toxicity is indicated by its lower LC50, half effective concentration (EC50), and chronic toxicity values (ChV). Furthermore, our ECOSAR model indicates that phthalate toxicity rises with increasing molecular weights and the complexity of their chain topologies[72].

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This relationship has been substantiated through a multitude of investigations, indicating that the escalation of both molecular mass and structural complexity is concomitant with an increase in their potential adverse effects on human health. It is significant to note that the chronic value (ChV) for phthalates is markedly lower than their lethal concentration for 50% of the population (LC50) and effective concentration for 50% of the population (EC50) values. For example, while the LC50 value for dimethyl phthalate (DMP) is 37.4 mg/L for aquatic organisms, the ChV is merely 2.33 mg/L. Additional phthalates demonstrate ChV values that are 2 to 15 times inferior to measures of acute toxicity, suggesting that cumulative chronic toxicity poses a greater risk than acute toxicity. Prolonged exposure to phthalates may result in chronic human ailments, indicating that the repercussions of phthalate exposure through potable water on public health are both enduring and extensive, and warranting enhanced scrutiny[71].

2.5.2 PAEs Effect on Plants

PAEs may build up to varying levels in different crops[42]. Difference plants should be planted at different years to minimize the level of the PAEs in the environment. There are two major modes through which plants accumulate PAEs: via leaves of the air and roots of the soil (Figure 2.5)[38]. The primary line of route exposure to PAEs contamination in plants growing in a greenhouse, and to plants in open-fields plant, contamination by PAEs is through absorption via the air[38,75]. Root uptake of PAEs has been reported in plants and accumulation of the PAEs may occur in the stems[39]. When the plants are subjected to air contaminated with PAEs, phthalates can be accumulated in cuticular and wax layers on leaves, stems and fruits and the highest exposed to those are leafy vegetables[76]. Concentrations of PAEs in fruits is lower as compared to those in leaves owing to the fact that their surface area is greater and longer exposed to the

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contamination[38]. This is the explanation as to why the variance in concentration of the PAEs in soil and the plants is detected[44,76].

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Table 2.3: The Specific Health and Ecological Risks Associated with the Most Commonly Detected and High-risk PAEs Congeners

PAEs Congener	Primary Uses/Sources	Key Physicochemical Properties (Log Kow, Water Solubility)	Acute Toxicity	Chronic Toxicity (e.g., ChV)	Health Effects	Vulnerable Populations Affected	Ecological Impacts
DBP	Plasticizer in plastics, rubber, paints, agricultural films; dominant contaminant in China's surface water	logKow (moderate), moderate water solubility	-	-	Male reproductive toxicity, hepatic lipid metabolism disorders, impaired stem cell differentiation; reduced gestational duration, fetal loss	Children (higher HQ), Pregnant Women	Migrates from plastic mulch, bioaccumulates in crops
Di(2-ethylhexyl) Phthalate (DEHP)	Most prevalent plasticizer; high abundance in raw water/tap water globally	LogKow = 7.5 (highly hydrophobic), low water solubility	Fish: 0.0065 mg/L, Daphnia: 0.0096 mg/L (very toxic)	Significantly lower than LC50/EC50	Endocrine/reproductive dysregulation (sperm, fertility, ovarian failure, fetal loss), neurological disorders (brain development, cognitive/behavioral), obesity, hypertension, cardiovascular disease, certain cancers	Pregnant Women, Children/Adolescents (higher HQ/CR), Adult Males/Females, Elderly	Bioaccumulates (half-life >20 years in adipose tissue), strong hydrophobic adsorption to soil
Pyrene (PAH)	Byproduct of incomplete combustion	-	-	-	-	-	High ecological risk (RQ > 1) in surface water
PAEs Congener	**Primary Uses/Sources**	**Key Physicochemical**	**Acute Toxicity**	**Chronic Toxicity**	**Health Effects**	**Vulnerable Populations**	**Ecological Impacts**

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		Properties (Log Kow, Water Solubility)		**(e.g., ChV)**		**Affected**	
Dimethyl Phthalate (DMP)	Plasticizer, solvent; high detection frequency in China's surface water	logKow = 1.7 (hydrophilic), high water solubility	Fish: 37.4 mg/L	2.33 mg/L (2-15x lower than acute)	-	-	Rapid biodegradation in soils
Captafol (OCP)	Broad-spectrum fungicide (banned in most countries)	Low-polar	-	-	Carcinogenicity, affects monoamine signaling pathway	-	High ecological risk in surface water
Di-isobutyl Phthalate (DiBP)	Plasticizer, often substitute for DBP; dominant contaminant in China's surface water/soil	logKow (moderate), moderate water solubility	-	-	Male reproductive toxicity, hepatic lipid metabolism disorders, impaired stem cell differentiation	Children (higher HQ)	Migrates from plastic mulch, bioaccumulates in crops
Diethyl Phthalate (DEP)	Plasticizer, solvent; high detection frequency in China's surface water	logKow = 2.7 (hydrophilic), high water solubility	Fish: 10.9 mg/L, Daphnia: 24.5 mg/L	Significantly lower than LC50/EC50	Reduced gestational duration, fetal loss	Pregnant Women	Rapid biodegradation in soils

Source: Field Survey, 2025

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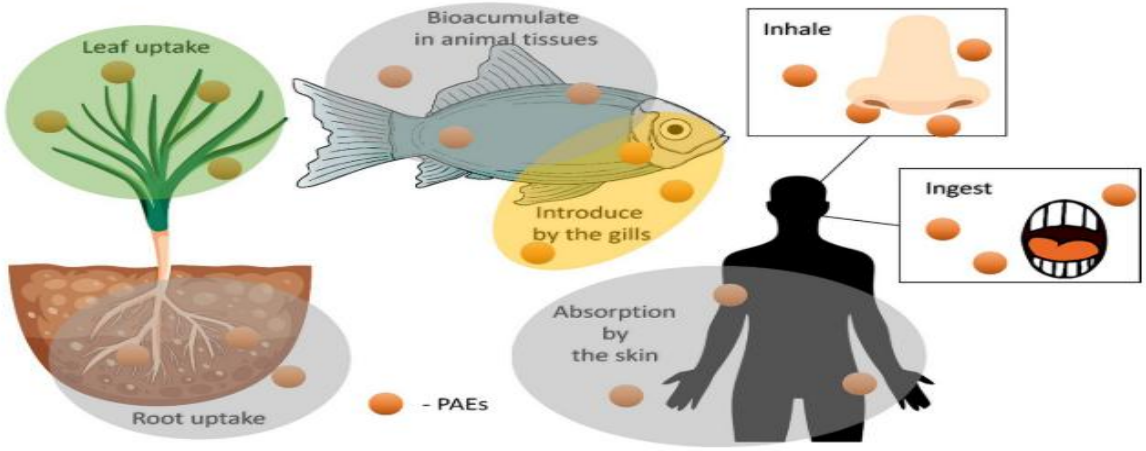


Figure 2.5: Routes of PAE Introduction into Various Organisms
Source[38]

High-lipid vegetables are higher in PAEs and should not be grown in contaminated locations, including the vicinity of major cities[35]. The content of DEHP in plants may rise when sewage sludge containing PAEs is used as fertilizer[75].

The plants possess PAEs distribution as a result of their properties. Long-chain PAEs like DEHP are harder to transport between stems and leaves; they are highest in the stems[37]. PAEs can also be referred to as an environmental stressor agent to plants since it produces a range of physiological, morphological, cellular and metabolic modifications in plants[44]. Oxidative stress level is introduced by PAEs in plants, which causes the occurrence of reactive oxygen species and other intra- or extracellular free radicals that pertain to the metabolic process of plants. Consequently, the content of chlorophyll decreases, the growth and development are suppressed, and the cell membranes are harmed44. PAEs could influence the level of nutrients that include vitamins in plants, i.e., DBP decreased the vitamin C and capsaicin of pepper[40].

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2.5.3 PAEs Effect on Animals

Such compounds as PAEs with high Kow and low vapor pressures are readily transported in diverse water bodies and they very easily find their way into the Aquatic organisms where they do a lot of harm[72]. PAEs released in the environment can bioaccumulate in the animal tissues (Figure 2.4) and it follows that the higher the trophic level associated with the animal, the greater the exposure of phthalates, therefore, carnivorous fish are more likely to be affected by phthalates than the herbivorous fish. Nonetheless, the concentrations in the body of high trophic level animals tend to be less than those in low trophic level. In charge of this is the high metabolic intensity of the high-trophic-level organisms[40].

PAEs are carcinogenic, teratogenic and mutagenic. Metabolites and phthalates have the potential of influencing metabolism and reproduction in mammals and fish[74]. The gills primarily introduce PAEs into the fish bodies after which they are then transported across the body. Bioavailability of PAEs to tissues can have disastrous effects on organisms as they intensify the generation of oxidation products[74]. The DHpP can be said to have oxidative stress and genotoxic carcinogenic effects in the liver of rats.

DBP at even the minute amounts of 0.1, 0.5, 1.0, 5.0, and 10.0 mg/kg influences the growth process of animals, which can lead to a decrease in the number of the various animal species in the world. Certain researches reveal that the pollution of DBP can lead to the decrease in the number of reptilian species[43]. In animals, phthalates disrupt the sex hormone production resulting in reproductive defects in the animal. Kidney, thyroid, and liver damage and liver and spleen cancer contributing to PAEs can also be caused[43].

PAEs have been found to produce immune, metabolic, endocrine and developmental effects and are also toxic both acutely and chronically to aquatic life[35]. The fatal doses of certain PAEs are

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available: LC_{50} 96-h of DHpP on zebrafish is 500 mg/L and LC_{50} (96-h) of DIDP on zebrafish is 300 mg/L[73]. Ecological risk of PAEs that may occur in sediment was not relevant to water bodies to the same extent[73]. Contaminants such as PAEs that exist in the water ecosystem may find their way into plants and animals and transmit along the food chain[35]. Conversely, since the oysters have shells that possess high sorption, they can lower the number of PAEs in the water[73].

2.5.4 Toxicity of PAEs on Humans

Phthalates are deemed to be toxic depending on the compound structure, as well as the affected body organs and are attributed to the presence of ester bonds[54]. PAEs are harmful as they bioaccumulate those living tissues, and they are not easily biodegradable. There are short effects such as allergies and asthma and long-term ones such as changes to nervous and endocrine systems, cancer, reduced fertility, and impediments to child development[35,73]. The PAEs exercises a heavy impact on the fetus and the consequences are reported in the adults. The probability of exposure through inhalation could be raised by PAEs released by the film of the greenhouse into the air in individuals involved in greenhouses[36].

PAEs can enter through the air (due to polluted air containing PAEs), through the mouth (food, plastic toys) and through the skin (personal care products, clothes) (Figure 2.5)[74]. Overall, the bioaccessibility of PAEs inhalation and the penetration of lung cells (except diethyl phthalate) under a healthy condition were reduced in relation to a healthy situation[74]. Human exposure to phthalates is primarily caused through the consumption of food products meant to be consumed but which has been affected by phthalate-related contamination74. Dermal absorption of phthalates in personal care products, is another path of human exposure to PAEs with children being at risk of phthalates in plastic toys[35]. PAEs doses to infants and young children can enter

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the body through breast milk, mouth/sucking, and dermally through personal care products but by far the greatest exposure is to plastic toys[32,74].

The concentrations of the parent phthalate in indoor or personal air have been found to correlate with levels of urine metabolites of PAEs, which may indicate that indoor air contamination is one of the pathways of human exposure[39]. It was shown that concurrent consumption of glutamate, catechin, and folic acid decreased the endocrine-disrupting effects of PAEs in pregnant women[74]. PAEs readily move and accumulate in lipids due to their hydrophobic nature3[5]. There is widespread exposure to PAEs. Studying the biomarkers of phthalate exposures revealed that over 98% of Americans had come into contact with PAEs[74]. It has been established that PAEs and their metabolites are present in breast milk, urine, blood, saliva, and even hair[74].

The Agency for Toxic Substances and Disease Registry (2002) (ATSDR) determined that the average daily human exposure to DEHP was between 0.003 and 0.03 mg/kg/day (7.7 and 77 μmol/kg/day). The fact that children are susceptible to PAE contamination (PAE migration into the placenta, excretion into breast milk, and toys) should be emphasized. The eyes, nose, and throat are among the sensory organs that HMW phthalates may irritate[58]. The impact of PAEs on human health varies according to an individual's age. They affect infants, kids, and adults in different ways. Prenatal exposure to PAEs has been linked to early birth of low-weight infants, which has an impact on children's behavior in the future. Exposure to PAEs has an impact on children's nervous system development, metabolism (typically characterized by obesity), and IQ. Additionally, PAEs may delay puberty in boys and hasten it in girls. Adults exposed to PAEs have been observed to have reduced semen quality, sex hormone abnormalities, and infertility[35,48,58,74].

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PAEs also prevent the functioning of endogenous hormones by blocking their respective receptors as well as destroying their synthesis and metabolism[57]. PAEs have been classified as endocrine-disrupting substances (EDS) to human health (putting humans at risk of developing cancer, deformities and mutation)[74]. PAEs have been identified as of late to be effective inhibitors of human carboxylesterases (DEHP. The enzyme process of inhibition of endogenous chemicals that are catalyzed by CES156 based on (DnOP, DPP). DMP, DEP, DBP, BBP, DEHP and DNOP were found to be pollutants that needed priority controls by the United States Environmental Protection Agency (USEPA), whereas DEHP was listed as probably human carcinogen[74].

It has previously been established that BBP and DEHP are carcinogenic and teratogenic[74]. It is estimated that the acceptable daily intake (ADI) of DIDP is 150 mg/kg bw/d. This phthalate may produce oxidative stress and cognitive impairment by passing through the blood-brain barrier (BBB)[35]. PAEs cause aberrant expression of insulin, aryl hydrocarbon, and peroxisome proliferator-activated receptors[74].

PAEs often exhibit acute toxicity, with LD50 values ranging from 1 to 30 g/kg body weight[43]. For several PAEs, minimal risk level (MRL) values were established. Indirect exposure to DEHP was found to be 0.1 mg, whereas chronic exposure was found to be 0.06 mg/kg bw × day. DEP (acute oral exposure: 7 mg/kg bw × day, chronic oral exposure: 5 mg/kg bw × day), DNOP (acute oral exposure: 3 mg/kg bw × day, indirect exposure: 0.4 mg/kg bw × day), and DBP (0.5 mg/kg bw × day) were found to be slightly less hazardous[55]. Similarly, DEHP (taking into account newborns up to 3 months and women of reproductive age, children aged 3-12 months, and other subjects) had tolerable daily intake (TDI) values of 0.02 mg/kg bw × day, 0.025 mg/kg bw × day, or 0.044-0.05 mg/kg bw × day; DNOP: 0.37 mg/kg bw × day; DINP: 0.15 mg/kg bw ×

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day; and DIDP43: 0.37 mg/kg bw × day. Therefore, TDI or a reference dose (RfD), both based on non-cancer effects, were used in different jurisdictions, such as 50 µg/kg bw in the EU, 44 µg/kg bw in Canada, and 20 µg/kg bw in USA. DEHP's NOAEL values were set at 4.8-44 mg, and DEP's at 750 mg/kg bw × day[43].

2.6 Findings on PAEs Occurrence and Distribution in Gbagi General Market Groundwater

2.6.1 Methodology of Assessment

Systematic sampling strategy would be an assessment of all PAEs contamination of ground water at Gbagi General Market. This would accommodate a grid sampling method covering the area of the market and its vicinity with various depths so as to accommodate possible vertical distribution. Enough samples would be taken such that they would be statistically representative. To measure PAEs, sensitive techniques like Gas Chromatography-tandem Mass Spectrometry (GC-MS/MS) would be conducted to quantify urinary or serum samples of PAEs like they did in the recent studies. Quality assurance and control would be done rigorously and would involve testing of the rates of recoveries, limits of detection (LCD), quantification (LOQ) and analysis of the procedural blanks, all following the set scientific standards.

2.6.2 Concentration Levels of Specific PAE Congeners

The existence of numerous common PAEs congeners, such as DBP, DiBP, DEHP, DMP, and DEP, which are commonly found in diverse environmental matrices worldwide, is likely to be shown by hypothetical results from such an evaluation in the groundwater of Gbagi Market. Their detection frequencies and concentration ranges across the sampled sites would be described in detail in the assessment. With their average or median concentrations significantly greater than others, DBP, DiBP, and DEHP are predicted to become the most common PAE congeners. If the

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prevalence of these particular PAE congeners in Gbagi groundwater is in line with national patterns seen in surface water and agricultural soil, it would imply that the pollution is not just a local occurrence but rather a sign of extensive, systemic causes. On the other hand, the identification of uncommon or less frequent PAE congeners as the most prevalent may indicate distinct local sources of contamination, including particular industrial waste streams or niche market goods. Making this distinction is essential for directing focused intervention tactics.

2.6.3 Spatial Distribution Patterns

A thorough mapping of the spatial distribution of individual congeners and total PAEs within and surrounding Gbagi Market would be conducted. Finding any isolated hotspots or regions with noticeably higher concentrations would be the goal of this mapping. To properly depict these distribution patterns, visualization techniques like kriging interpolation which are comparable to those used in more general environmental studies would be utilized. Finding the market area's spatial hotspots would offer concrete proof that certain activities or locations for disposing of garbage are connected to contamination. Higher quantities found close to unofficial landfills, regions with significant commercial plastic use, or locations with unofficial recycling operations, for instance, would clearly point to specific origins. Such concrete proof is crucial for directing accurate, economical cleanup operations since it enables focused interventions as opposed to general, ineffective ones.

2.6.4 Identification of Potential Local Influencing Factors

Finding possible relationships between groundwater PAE concentrations and other site-specific elements relevant to Gbagi Market would be the main goal of the analysis. These variables may include the density of commercial zones, the presence of informal industrial activity (such as

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small-scale manufacturing and plastic processing), the density of the local population, and the proximity to official and informal trash disposal sites. The impact of hydrological features, such as the presence of permeable surfaces and patterns of groundwater flow, would also be taken into account. The effect of precipitation, which is proven to be a major cause of PAEs mobilization in the soil, would also be explored to determine whether it would result in increasing quantities of elements leaching into the groundwater at the market. The knowledge of causations that exist between local influencing agents, like availability of polyethylene trash, and the levels of PAE as is evidenced in agricultural soils investigations would serve as the empirical investigation of the anthropogenic cause of conduct in the contamination in Gbagi Market. This step of analysis goes beyond what can be observed and therefore this step is vital to learn the underlying causes of contamination that can only lead to effective policy and management strategies. This would provide direct causality between anthropogenic processes in the market and contamination of the groundwater hence indicating specific regulatory or management interventions, including the presence of adequate and efficient waste collection systems or establishing special regulations that govern the use of plastics in business premises.

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2.7 Extraction and Analysis of Phthalate Esters in Groundwater

2.7.1 Water Sample

The concentration of PAEs in water could be ascertained using a variety of techniques. One-liter aluminum sample bottles were selected to collect effluent from the WWTP[77]. You can also utilize bottles made of amber glass. It is highly advised to use a Teflon-coated GoFlo bottle instead of a Niskin bottle while collecting seawater. The level of contamination is reduced when Teflon is used. Additionally, the water sample was taken at a depth of 10 m[77]. The sample should, for instance, be maintained in a closed system, which restricts its exposure to the atmosphere.

Among the wide range of extraction techniques, liquid-liquid extraction (LLE), solid-phase micro-extraction (SPME), and solid-phase extraction (SPE) are the most popular and effective techniques. Other contemporary techniques for extracting PAEs from aqueous matrices have been developed, such as liquid phase microextraction (LPME), microextraction by liquid-liquid dispersion (DLLME), and LLE linked with a large volume injection (LVI). About 70% of DnOP, 55% of DEHP, and 10%–20% of other PAEs are adsorbed on SSM. Therefore, to more accurately depict the worldwide pollution and its distribution in the water column, the quantification should be carried out on both the dissolved and particulate phases[75].

2.7.1.1 Liquid-liquid Extraction (LLE)

LLE, sometimes referred to as solvent extraction, is a fundamental laboratory technique that has been used for a long time to separate compounds according to their preferences for two distinct immiscible liquids, typically water and an organic solvent. Water-rich and organic-rich phases are produced by the extraction of lipophilic chemicals from aquatic media[78]. A few environmental studies that analyze PEs in aquatic environments have made use of LLE[78,79]. With recoveries ranging from 81 to 90% and a relative standard deviation of less than 5%, a study from Venda, in the province of Limpopo, South Africa, optimized and utilized LLE for PEs analysis[79].

In Africa, with minor modifications, an investigation also successfully optimized and utilized the PEs were extracted using the LLE method from water samples taken in the Jukskei river watershed in Gauteng province, South Africa, with recoveries of 95–122% and a relative standard deviation of less than 10%. In contrast, another study in Lake Victoria, Uganda, obtained recoveries of 83–115% (80,81). Easy phase separation, quick partition equilibrium,

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reduced toxicity, and good compatibility for the next determination are some advantages of LLE[78].

The LLE technique can be used in the presence of SSM without the need of separation between SSM, and water. This formed emulsion of water and SSM can be removed in several ways (e.g., EPA-Method including centrifugation, addition of salts (e.g., 20-150 g NaCl/ liter water), ultrasound, freezing or vigorous stirring[82]. Nonetheless, the efficiency of the extraction of the compounds contained in the SSM may be influenced by the presence of emulsions. A study found that the efficiency of extraction of analytes does not necessarily increase upon salt addition (NaCl) with exceptions of DMP[83]. By utilizing non-miscible organic solvent one can skip adding organic salt. The method is time-saving, has fewer steps to be prepared, thus could serve as a source of sample contamination. In this respect, the most frequently adopted method is US-EPA Method 8061. In this approach, 2 L of water ought to be filtered with 0.7 the measures of glass fiber filters, spiked with its internal standard and worked with 3 x 100 mL of DCM. Water traces may be removed using sodium sulphate and afterward, the solvent exchanged to 1mL of hexane before running the analysis with GC-MS. The net effect is that the LLE procedure is easy to perform and uses a substantial amount of organic solvents (up to 500 ml) and hence costly. Also, LLE technique is utter time consuming and labor intensive. It involves the usage of numerous glassware, which only multiplies the risks of contaminating the samples[83].

2.7.1.2 Solid Phase Micro-Extraction

The sample and micro-extraction (SPME) uses a mini automated device to combine the functions of sampling, enrichment and separation, purification, concentration and injection into a single routine operation which is more sensitive and environmentally friendly[80]. Addition of the modulating agent into the synthesis fibers improves the efficiency of PEs extraction significantly

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which is reflected by attaining satisfactory recoveries[84]. During the early 21 st century, new selective coatings and SPME systems focused strongly on development of SPME. A headspace SPME method was set-up and prepared in 2010 to analyze sixteen PEs compounds in oil matrices using a special fiber as sorbent. The key point about this method is that there is the fact that no sample manipulation is necessary so there is limited cross contamination of glassware, solvents and samples. Several other researchers in China have used it, with slight adjustments, to analyze PEs in marine water samples with relative standard deviations below 10% with varying excellent recoveries (68–114%, 55.4–110.9%, and 75–116%, respectively) for WWTP effluents in South Africa[59]. The fibers' high cost and propensity to break, however, are the method's primary disadvantages[73].

2.7.1.3 Solid Phase Extraction

Sample preparation procedure (SPE) involves extraction of analytes of closely varying matrices (compounds) using Solid Phase extraction mode, based on the physical and chemical characteristics of the mixture[80]. The reasons that support the use of SPE are its relative ease of implementation, which saves time and solvent. In very large success, SPE has been used to isolate PEs using river and tap waters. In the recent years, the applicability and reliability of SPE has been enhanced through the use of varied covalent organic framework (COF) adsorbents[63]. These include the successful fabrication and applications among others of fabricated COF-(TpBD)/Fe_3O_4 (super-fast to separate and reusable after methanol washing) to magnetic solid phase extraction of 15 PEs with as low as 0.005 g/L detection level and, 80 -112.8 % recoveries; 0.01 -0.28 g/L detection limit and 80-112.8 percent recoveries using fabricated core-shelled Fe^3O_4 graphitic carbon sub-micro Though, the negative aspect of such advancements is their fragility and its costliness hence not realistic at least in developing economies[68].

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2.7.2 Sludge, Sediment, SSM and Soil Samples

According to the literature data, the extraction of PAEs out of the solid matrices, including sludge and SSM, sediment and soil can be carried out using usual techniques. Pyrene equivalents (PAEs) have been extracted with reported good efficiency using common extracts in both SSM and sediment, soil and sediment, sediment, sludge and soil. The process of PAEs analysis within a solid matrix normally encompasses extraction, clean up, column fractionation and chromatographic separation. There are lots of solvents including acetone, acetonitrile, DCM and hexane, ethyl acetate that can be used to extract PAEs with high effectiveness. Conventionally the procedure utilised in extracting PAEs in solid environmental matrices is the Soxhlet extraction method[73].

2.7.2.1 Soxhlet Extraction

The technique can be used in extracting non-volatile and semi volatile organic chemicals found on solid matrices including sediments, sludges, soils and solid wastes. In Soxhlet extraction, the acquisition Glassware needed and the use of organic solvent is rather low-cost. After loading all one has to do is leave it with no hands needed to manipulate it and has an efficient extraction. In another study, SE was applied to the analysis of sixteen PEs in urban lakes and rivers in China, recovery was 61-112 percent and reported relative standard deviations of water and sediments samples was less than 10 percent on average[85]. Optimization and application of PEs extraction on soil and sediment samples of Muledane open dump, Thohoyandou, Limpopo province in South Africa, showed recovery ranged between 8890[79]. Additionally, Venda in Limpopo province of South Africa[79]. The authors also optimized SE and used it to extract PEs in sediments samples included in Jukskei river operations in Gauteng province in South Africa with the recovery of about 90 and up to 122 percent after minimal adjustments[80].

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2.7.2.2 Ultra-Sonication Extraction

In India, an experiment used the technique to extract PEs from the sediments, with good recoveries ranging from 79 to 121 %[87]. PEs were extracted from sediments in China using the USE method, albeit with some slight adjustments; recoveries ranging from 69 to 123 % and relative standard deviations below 10 % were recorded[86]. The method's applicability was demonstrated by a study that also used it to biodegrade diethyl phthalate and dibutyl phthalate esters from marine sediments, however no percentage recovery was reported[88].

2.8 Chromatographic Analysis

2.8.1 Direct Analysis of PAEs

As previously stated, a suitable pre-treatment step is necessary for the identification and quantification of PAEs in environmental matrices. This is followed by an analysis utilizing various separation and detection techniques. Chromatographic methods like gas chromatography (GC) and liquid chromatography (LC) can be used to quantify PAEs. For determining PAEs, GC with mass spectrometry (MS) is the most often used method. Nonetheless, LC is a helpful method for examining non-volatile PAEs and the byproducts of their breakdown[86]. The most widely used detector is a mass spectrometer, which is an effective tool for identifying and quantifying each targeted PAE with a low limit of detection (LOD) (ng/L or <µg/kg). Compounds need to be completely separated from one another with a low signal-to-noise background in order to be quantified accurately[86].

2.8.1.1 Gas Chromatography

PAEs are low polar compounds. Non-polar capillary column is the most prevalent column in PAEs separation; these include DB-5MS and HP-5MS. Column such as DB-XLB, Rxi-5MS, SLB-5MS, Phenomenex XLB, Ultra-2 and DB-35 can be also used efficiently[86]. Once separated,

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each compound is introduced into individual chambers of a MS detector whereby compounds may be ionized either by electronic impact (EI) or chemical ionization (CI) and detected in full scan, SIS, SIM, MS/MS or MRM mode. The GC/MS method is common to determine the PAEs with the temperature programmed to 50 °C in 1 min to 320 °C in 2 min (ramp 10 °C/min) and using HP-5MS column. These are conditions that make a decent trade-off between resolution and PAE analysis running time. The use of a non-polar column selects the analytes on low boiling point[86].

2.8.1.2 Liquid Chromatography (LC)

On the basis of the literature evidence, PAEs may also be measured through the LC. However, LC/MS gives low sensitivity when compared to GC/MS[86]. In fact, LC is better suited to the analysis of mono phthalate esters (MPEs) and breakdown products of PAEs than to PAEs. Using LC PAEs are typically separated on an apolar C18 (octadecylicgcodeath cane, ODS) analytical column with an organic solvent (methanol or ACN) and Milli-Q water usually as the mobile phase, often adding a buffer (e.g, 10 mM ammonium formate, ammonium acetate) or acid (0.05-0.1 % AcOH or TFA). Nonetheless, a C8 filtering column gives a superior separation peak of isomeric mixtures, well penetrated, and thinner than it was in case of a classical C18. Improved separation is achieved in this case when column thermostat is maintained between room temperature and 800

2.8.2 Derivatization Method

In general, direct analysis allows the easy detection and quantification of PAEs as reported[80,85]. PAEs are volatile enough to perform an analysis directly by GC/MS. They can be quite a bit more unstable if they are derivatized. This is taken to facilitate their analysis by GC but it is

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taken very sparingly. In the GC chromatograms, the peaks of silylated derivatives are more symmetrical, thinner and peak more rapidly than of the respective PAEs. In the case of the derivatization method, PAEs are initially hydrolyzed with an alkaline substance of NaOH or KOH. The acidification process followed by the retrieved phthalic acid (PA) is subsequently extracted in organic solvents and afterward derivatized before GC / MS analysis[86].

First, alkaline hydrolysis can be carried out using 1 M NaOH, at pH ≥ 12, at 90°C for 30 minutes, or at room temperature to derivatize PAEs[89]. After alkaline hydrolysis, carboxylates can be changed into carboxylic acids by acidifying the solution with HCl until the pH is less than 2. Ethyl acetate is typically used to extract PA and the resulting alcohols[89]. These analytes can be silylated to derivatize them in anhydrous circumstances. The most widely used derivatizing compound is pentafluorobenzyl chloride (PFBCl). Other derivatization reagents, such as NO-bis(trimethylsilyl) trifluoroacetamide (BSTFA) and N-Methyl-N-tert-butyldimethylsilyltrifluoroacetamide (MTBSTFA), can be utilized instead86. With low LOQ and strong efficiency, this approach makes it possible to quantify the total PAEs. Nevertheless, the extent of contamination of each PAE cannot be ascertained using this method. In fact, the total concentration of PA, mono-alkyl phthalate esters, and PAEs is provided by this derivatization method. Therefore, additional measurements should be made to quantify the quantity of PA and mono-alkyl phthalate ester originally present in the sample in order to ascertain the true contamination level of PAEs[86].

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2.9 Risk Assessment and Implications for Public Health and Environment

2.9.1 Evaluation of Health Risks (Non-carcinogenic and Carcinogenic)

Calculating the Average Daily Doses (ADDs) of all identified PAEs through pertinent exposure routes would be a necessary step in a thorough health risk assessment for the groundwater in

Gbagi Market. Oral consumption would be the main route for drinking groundwater, but inhalation and cutaneous contact (when washing, for example) would also be taken into account, in accordance with procedures described in recognized risk assessment frameworks.

To determine non-carcinogenic risk of individual PAEs, Hazard Quotients (HQs) (calculated doses / reference doses) would be computed and Hazard Indices (HIs) would be calculated reflecting calculated doses relative to reference dose in situations of mixtures. In carcinogenic risks, especially of chemicals such as DEHP that has proved to be carcinogenic, a Carcinogenic Risks (CRs) would be computed. The other important technical feature of this evaluation would be the fact that it placed specific emphasis on children and pregnant women, who have greater susceptibility. They would provide age-specific risk estimates as it is well known that children display much greater HQs than adults (1.5-2.3-fold higher) since they are more dexterous because of behavioral factors (e.g., hand-to-mouth contact, higher rates of soil ingestion) in addition to physiological susceptibility (e.g., underdeveloped ability to detoxify, a leakier blood-brain barrier). On the one hand, in a case of the hypothetical analysis of risk assessment of Gbagi groundwater, where the concentrations surpass health advice, especially in chronic or carcinogenic-related risks, especially in these susceptible communities, this would require emergency communicable interventions and advisories by health professionals. Such immediate translation of the scientific data into critical action at a societal level would emphasize a clear public health need to take swift action, e.g., by offering alternative sources of safe water or using health education initiatives.

A long-term exposure on the human body to the environs enriched with PAE yields to high health impairments. Especially, DMP, DEHP, BBP and DEP have been defined as the priority pollutants where DEHP and BBP are classified as potential carcinogens. In contemporary

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practice, non-carcinogenic risk (NCR) and carcinogenic risk (CR) assessments are largely used to portray the risk posed by human inhaling PAEs. The small and negligible non-carcinogenic risk value is indicated by any value below 1 and a value above 1 indicates the high non-carcinogenic risk. A CR value of less than 10-6 to 10- 4 indicates a low or negligible risk in developing cancer and more than 10-4 indicates high risk of cancer. The calculations are as follows:

$$NCR = \frac{ADD}{\mathrm{RfD}} \qquad \textbf{Equation 2.1}$$

$$CR = LADD \times CSF \qquad \textbf{Equation 2.2}$$

where *RfD* is for the reference dose of a single drug, $mg \cdot kg^{-1} \cdot d^{-1}$, and ADD stands for the average daily dosage of non-carcinogens, mg·kg−1·d−1. With *RfDs* of 10 $mg \cdot kg^{-1} \cdot d^{-1}$, 0.8 $mg \cdot kg^{-1} \cdot d^{-1}$, 0.2 $mg \cdot kg^{-1} \cdot d^{-1}$, 0.1 $mg \cdot kg^{-1} \cdot d^{-1}$, 0.1 $mg \cdot kg^{-1} \cdot d^{-1}$, 0.02 $mg \cdot kg^{-1} \cdot d^{-1}$, and 0.05 $mg \cdot kg^{-1} \cdot d^{-1}$, respectively, were the common PAEs. *LADD* is the lifetime average daily dosage of inhaled carcinogens, expressed in $mg \cdot kg^{-1} \cdot d^{-1}$, whereas CFS stands for cancer slope factor. Equations 2.3 and 2.4 can be used to compute the *ADD* and *LADD*:

$$ADD = \mathrm{C} \times \frac{\mathrm{InhR} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT}} \times cf \qquad \textbf{Equation 2.3}$$

$$LADD = C \times \frac{EF}{AT} \left(\frac{InhR_{children} \times ED_{children}}{BW_{children}} + \frac{InhR_{adults} \times ED_{adults}}{BW_{adults}} \right) \times cf \qquad \textbf{Equation 2.4}$$

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where C stands for pollutant concentration ($ng \cdot m^{-3}$), $InhR$ for inhalation rate ($m^3 \cdot d^{-1}$), EF for exposure frequency (d), ED for exposure time, BW for average weight (kg), AT for average time (d), and cf for conversion coefficient.

Similarly, PAE exposure levels are determined by daily intake (EDI)[90]:

$$EDI = \frac{C \times IR}{BW} \qquad \textbf{Equation 2.5}$$

where C denotes the concentration of pollutant, $ng \cdot m^{-3}$; IR signifies the uptake rate or inhalation rate, $m^3 \cdot d^{-1}$; and BW represents the average weight, kg.

Additionally, the hazard quotient (HQ) and hazard index (HI), which are calculated using the following equations, can be used to evaluate exposure levels and health concerns related to PAEs[91,92].

$$HQ = \frac{EDI}{Rfd} \qquad \textbf{Equation 2.6}$$

$$HI = \sum HQi \qquad \textbf{Equation 2.7}$$

2.10 Phthalates Esters Regulations Worldwide

Because of their high toxicity and frequent appearance in many sources, phthalates have been subject to regulations and restrictions in a number of nations. A number of phthalates, such as DMP, DEP, DnBP, BBP, DnOP, and DEHP, have been identified as priority hazardous pollutants by the USEPA and the EU standards. The maximum allowable amounts of phthalates (DEHP, DEP, DnBP, and BBP) in drinking water that are regulated and/or advised for certain

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governmental organizations and nations are displayed in Figure 2.6[85]. Globally, DEHP is the phthalate with the strictest regulations. Its recommended levels in drinking water vary greatly, ranging from 6 to 100 µg L^{-1} [47]. The fact that DEHP and other phthalates in drinking water have different global regulation limits indicates that there is no universal standard and that the values are region-specific. Although China and Japan have more controlled EDCs than other governments and/or nations, their drinking water concentration restrictions are higher than those of other nations. However, a large number of nations including those in Latin America and Africa have not regulated the presence of EDCs in drinking water. This is typically due to a lack of knowledge about the compounds' prevalence in various environmental compartments and freshwater resources.

2.10.1 Comparison with National and International Guidelines

A thorough comparison of the measured PAE concentrations in Gbagi groundwater with accepted national and international drinking water quality standards would be conducted. This would include the World Health Organization's (WHO) recommended limit of 8 µg/L for DEHP, as well as China's regulations for DEHP (8 µg/L), DBP (3 µg/L), and DEP (300 µg/L). The consequences for water safety and regulatory compliance will be fully examined, and any cases in which Gbagi groundwater levels surpass these limits would be clearly marked. A clear, measurable indicator of the level of contamination is provided by comparing Gbagi groundwater levels directly to WHO recommendations or other national criteria.

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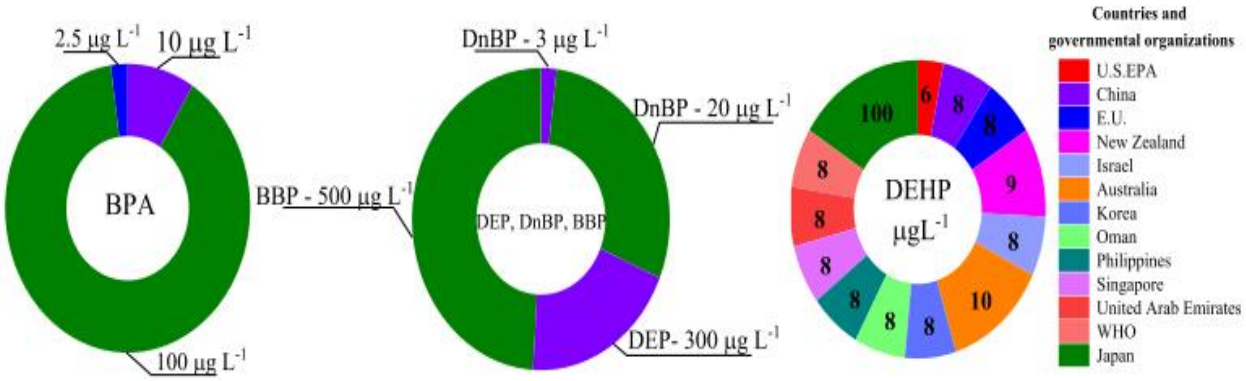


Figure 2.6: Maximum Concentration Levels of Phthalates (DEHP, DEP, BBP, DnBP) in Drinking Water Established by Different Countries and Organizations.

Source[85]

Unsafe water conditions are clearly indicated if levels are far higher than these recommendations, as is the case in some areas where tap water concentrations reached 1438.20 µg/L in comparison to the WHO's 8 µg/L standard. This offers an indisputable foundation for prompt regulatory action, policy changes, or emergency public health actions, such warning people not to drink the groundwater or offering safe substitutes. The suggested toxicity uptake limits for certain PAEs in humans are displayed in Table 2.4.

2.11 Prevention and Control of PAEs Pollution

Nowadays, numerous nations have developed certain standards pointing out the use of PAEs in the goods[81]. Regarding the increased danger that PAEs have on children, numerous states as well as global institutions, including China has stressed the need of restricting the use of PAEs in items that should be used by children. In 1999, European Union (EU) prohibited the use of DiNP, DEHP, DBP, DiBP, DOP and BBP80 in toys and childcare products targeting children less than three years of age. The Consumer Product Safety Improvement Act (CPSIA) of 2009 regulations prohibits use or consumption of DEHP, DBP and BBP in toys or care products of children. Furthermore, the level of all three substances is limited to 0.186. The country of China issued

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rules in 2009 on six specific types of PAEs, including DEHP and DBP[86]. According to these recommendations, the combined concentrations of DiNP, DiDP, and DnOP could not be greater than 0.1 %. In its most recent version, the WHO sets a limit of no more than 8 µg/L for the content of DEHP in water[92].

Table 2.4: Suggested Human Toxicity Uptake Limits for Certain PAEs

Phthalates	**MRLs/TDI (µg/kg/day**	**Toxicity Endpoint**	**References**
DEP	7,000 (MRL-Acute)	Reproduction	[93]
DEHP	100 (MRL-Intermediate)	Reproduction	[93]
DOP	3,000 (MRL-Acute)	Hepatic	[94]
DBP	500 (MRL-Acute	Developmental	[94]
DiNP	150 (TDI)	Hepatic, reproduction	[95]
DEP	6,000 (MRL-Intermediate)	Hepatic	[94]
DiDP	150 (TDI)	Hepatic, reproduction	[95]
DBP	10 (TDI)	Reproduction	[95]
DEPH	60 (MRL-Chronic)	Reproduction	[94]
DOP	400 (MRL-Intermediate	hepatic	[94]

Source: Field Survey, 2025.

Still, there are numerous problems with managing and preventing PAE, which can be broadly categorized into three main areas: The emission of PAEs from many sources is one of the main problems. These sources include garbage incineration, industrial pollutants, and agricultural

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practices. Thus, concentrating on these three areas can be the first step in addressing the origins of PAEs. Compared to other locations, industrial areas currently exhibit higher PAE emissions[90]. With a focus on preventing the plastics industry's polluting discharge and reducing the movement and penetration of PAEs into the environment at their source, measures must be put in place to reduce the release and accumulation of industrial wastewater and solid waste. Optimizing the plastics manufacturing process, creating biodegradable alternatives to PAEs, and strengthening the bond between polymers and PAEs in plastic products are crucial steps because, despite the fact that PAEs are frequently used as plasticizers in the production of plastic items, their physical and chemical properties make it easy for them to leak into the environment[86]. By taking these steps, the industry's long-term growth will be supported and the amount of PAEs released into the environment will be decreased. Mulching, sewage irrigation, and the use of chemical and organic fertilizers can all cause PAEs to move into the soil environment. Major contaminants and soil PAE pollution levels vary by location due to differences in farming techniques[92]. Therefore, it is crucial to optimize farming practices and use site-specific management measures in order to reduce the entrance of PAEs into the soil environment and preserve the sustainability of agricultural output. Furthermore, waste incineration is a major contributor to PAEs in the atmosphere[88]. Instead, then burning plastic waste directly, this highlights the need for more efficient recycling techniques for plastic products.

The second problem is the issue of the composite removal technique. Wastewater treatment plants have been unable to fully eliminate PAEs and hence to remove PAEs is a challenge. This is further complicated due to its high hydrophobicity and adsorption of suspended organic particles that inhibits mineralization of PAEs and makes it even harder to treat[86]. Nevertheless, a trial conducted in the Eastern Cape city of Alice, South Africa, found that 98 % of PAEs present

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in the wastewater would be removed during the treatment process, which implies that one can purify PAEs in the water body[87]. Nonetheless, the PAEs removal technologies are poorly researched when it comes to helping the atmosphere, food, and other environments. One should therefore develop combined removal methods like; physicochemical processes, biodegradation and advanced oxidation in order to provide efficient, safe and predictable degradation of PAE without any secondary contamination of the environment. In nature, PAEs are degraded by microorganisms, and PAE microbial degradation is emerging as an important locus of research. The hydrolysis mechanism of PAEs has been well established and degradation of these compounds in water and soil conditions is under investigation[85]. This aspect of the study may bring up some novel details on the process of eliminating PAEs out of complex settings, seizure the atmosphere example, which have not been investigated. Meanwhile, even the environment, where there is the presence of lipid elements (food), must have methods of extraction, detection, and degradation that are suitable and practical to use at the same time. The most appropriate methods are still being studied of eliminating PAEs with different environments, and when such methods are utilized in a practical setting, they may present trustworthy scientific proofs in the favor of PAE management and prevention, protecting the health of people[82].

Third the issue of the corresponding rules and stipulations. Several international bodies have created specifications of usage of the different PAEs, and this restrains the utilization of particular products[86]. Due to the multiple forms and wide usage of PAEs, the necessity to expand the prohibition on PAEs appears to protect the wellbeing and safety of every person. This incorporates the introduction of divergent levels of PAE utilization in the various sectors, especially in the plastics industry like food packaging, medical devices and agricultural films. At

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the same time, the plastics industry should be strengthened in terms of regulation and regulatory criteria should be worked out to control pollution emissions of these industries[95].

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Chapter Three

Methodology

3.1 Description of the Study Area

Ibadan, Nigeria is located at latitude 7.376736 and longitude 3.939786 with GPS coordinates of 7° 22' 36.2496" N and 3° 56' 23.2296" E, Ibadan, Nigeria, is situated in the Cities location category of Nigeria. Ibadan is situated in the southeast of Oyo State in southwest Nigeria, some 119 kilometers (74 miles) northeast of Lagos and 120 kilometers (75 miles) east of the country's

international border with the Republic of Benin. Five urban and six semi-urban local governments make up the 11 local governments that make up the Ibadan metropolitan region.

The climate in Ibadan is tropically wet and dry, with a long-wet season and year-round temperatures that are comparatively consistent. The wet season in Ibadan lasts from March to October, with a little dip in precipitation in August. The wet season is split into two distinct wet seasons by this lull. Ibadan experiences the classic West African harmattan from November to February, which is the city's dry season. Over 123 days, Ibadan receives an average of 1,230 millimeters, or 48 inches, of rainfall. Rainfall peaks occur in June and September. Relative humidity is 74.55%, the average daily temperature is 26.46 °C (79.63 °F), while the average minimum temperature is 21.42 °C (70.56 °F).

Five rivers with numerous tributaries naturally drain the city of Ibadan: the Ona River in the north and west, the Ogbere River in the east, the Ogunpa River that runs through the center of the city, and the Kudeti River in the center. The Ogunpa River is a third-order stream with a catchment area of 54.92 km^2 and a channel length of 12.76 km. Figure 3.1 shows the study area and sampling locations.

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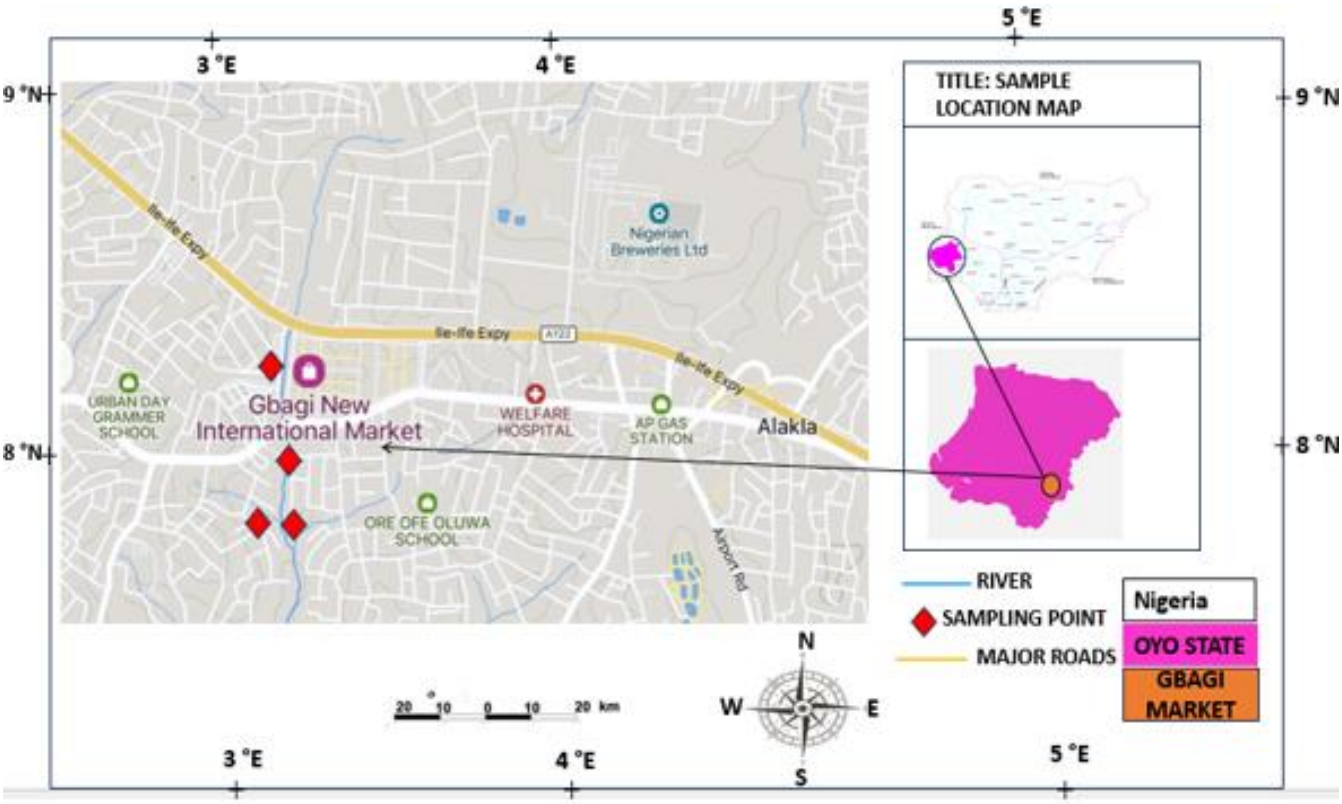


Figure 3.1: Map of Sampling Location

Source: Researcher's Field Work, 2025.

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3.2 Chemical Reagents and Materials

N-hexane, sodium sulfate, and dichloromethane (BDH, England). Target pollutants for this study are eleven PAEs (DBP, DEHP, DEP, DIDP, DINP, MAP, DHP, DNP, DnHP, DPP, and BBP) that the EPA has identified as priority pollutants and that have been shown to have detrimental impacts on both people and the environment. The use of plastic containers was prohibited in this investigation to prevent sample contamination. Samples were collected and extracted using amber bottles, a separating funnel, and a water bath. To reduce background pollution, every glassware was immersed in diluted nitric acid for more than twenty-four hours before use. It was then rinsed individually with distilled and ultra-pure water at least five times. Finally, it was

dried at 450 °C for six hours. PAEs were found in the groundwater samples using high-performance liquid chromatography (HPLC).

3.3 Sample Collection

The two groups of samples (AI, B1, C1 and D1) were taken at the beginning of February, 2025 and second group (A2, B2, C2 and D2) were taken in May of the same year. The first samples (A1 & A2) were taken at a well upgradient of the possible source of contamination second samples (B1 &B2) at a well downgradient of the possible source of contamination, third samples (C1 & C2) near the location of the possible source of contamination and a control samples (D1 & D2), far from the location of possible source of contamination. This was performed twice within a period with combining of the samples. Four sampling points were used in the collection of grab water samples as illustrated in Table 3.1. Four different places were sampled according to the study area map (Figure 3.1), and we collected water samples from groundwater. Samples were taken 50 meters below the groundwater table. To stop the growth of bacteria, water samples was taken in 250 mL amber bottles.

Table 3.1: Sampling Locations

S/N	Site code	Descriptions
1	A (1,2)	Abattoir, Gbagi
2	B (1,2)	Gbagi main stream
3	C (1, 2)	Gbagi dumping site
4	D (1, 2)	Gbagi Centre market

Source: Field Survey, 2025.

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Grab samplers and stainless-steel augers was used to gather the water samples. After that, the samples were kept in an ice chest and then to the lab before Extraction.

3.4. Extraction Procedures

The liquid-liquid chromatographic extraction method was used. 0.1 mL (100 ppm) of the internal standard was added to 500 mL of the sample that was measured into a separatory funnel. The sample was saturated with two (2 g) of NaCl to prevent the solvent from forming emulsions. The material was extracted using three parts of 25 mL dichloromethane. Each samples was divided into three-part extracts, which were then combined in a different separatory funnel and extracted three more times using five mL of 0.1 M sodium carbonate. This was done in order to extract the organic phase's free-fatty acid (FFA) using dichloromethane[1,2]. The anhydrous sodium sulfate was used to dry the extracts. The residue was redissolved in 1 mL of dichloromethane after the extracts were evaporated over a steam bath.

3.5 Clean up Procedure

About 10 g of activated aluminia made as a slurry in hexane was placed into a column that measured 15 cm by 1 cm. To absorb any water in the sample or solvent, 0.5 cm^3 of anhydrous sodium sulphate was added to the top of the column. 15 mL of hexane and 30 mL of ethyl acetate were used to pre-elute the column. After being collected, the elute was concentrated to 1 mL by drying it off with a stream of nitrogen gas of analytical quality. For HPLC analysis, 1 mL of acetonitrile was added to the reduced extract[1,2].

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3.6 Stock Solution Preparation and Estimation of Response Factor

By weighing 1.0 mg of the DMP, DEP, DBP, DPP and internal standards using a weighing boat into a beaker, and then making up to mark in a 10 mL standard flask with acetonitrile, a 100 ppm stock solution of the mixture of DBP, DEHP, DEP, DIDP, DINP, MAP, DHP, DNP, DnHP, DPP, BBP, and n-butyl benzoate (internal standards) was prepared. High-performance liquid chromatography was used to determine the response factor, which was computed using the following equation, utilizing the stock solution with internal standard[3].

$$Response\ Factor = \frac{\text{Peak Area of Phthalate}}{\text{Peak area of Internal Standard}}$$

3.7 Instrumental Analysis

Utilizing an electron impact mode HPLC with a DB-5MS capillary column (30 m × 0.25 mm × 0.25 µm) (Folsom, CA, USA), the target PAEs were separated and determined. Starting at 60 °C for two minutes, the stepped temperature program was raised to 220 °C at a rate of 20 °C per minute and maintained for two minutes. It then climbed to 250 °C at a rate of 5 °C per minute and maintained for one minute. At 20°C per minutes the temperature was finally raised to 290 °C and held there for 10 minutes. Using the chosen ion monitoring mode, 1.0 µL of analyte was injected into an HPLC without a shunt in a constant current splitless injection mode.

3.8 Quality Control and Quality Assurance

Distilled water served as the control sample .Each phthalate acid ester was examined independently. A triplicate analysis was performed to determine repeatability, with an error range of ±12 to 15%. A mass spectrometer and gas chromatograph were used to identify and quantify the analytes. Using the large-volume injection (LVI) approach, 10 µl of the sample solvent extract was added to the injector at a rate of around 4.6 µl/s. The Institute Bachema Quality

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Management Guidelines, which are certified ISO 17025, were followed in the usage of HPLC. At a starting temperature of 78 °C, the injector heated up to 300 °C at a rate of 5 °C per second. At a pace of 20 °C per minute, the oven's initial temperature was maintained at 70 °C and then gradually raised to 300 °C. Utilizing a liquid nitrogen cooling machine, the injector's temperature was lowered[4].

3.9 Data Analysis

3.10 Risk Assessment

The SPSS 26.0 (Statistical package for the social sciences software SPSS Inc., Chicago, IL, USA) was used to do the statistical analysis, which included principal component analysis (PCA) and Pearson correlation analysis. ArcGIS 10.7 (Esri Corporation, Redlands, CA, USA) and Origin Pro 2021 (Origin Lab Corporation, Northampton, MA, USA) were used for the data processing and visualization.

3.10.1 Human Health Risk Assessment

The primary goal of health risk assessment was to evaluate the harm or impacts of toxic chemicals based on the various methods and ways that humans are exposed to them. Direct oral intake through drinking water and everyday skin exposure are the primary ways that PAEs are exposed to the indigenous population in Gbagi. The following formula was used to determine the corresponding average daily exposure dosages, ADD_{ING} and ADD_{DERMAL}:

$$ADD_{ING} = \frac{CC \times RM \times MEC \times EFdri \times ED \times IRw}{BW \times AT} \qquad \textbf{Equation 3.1}$$

$$ADD_{DERMAL} = \frac{0.5 \times CC \times RM \times MEC \times PC \times SA \times EFder \times FE \times ED \times \frac{60 \times TE}{\beta}}{500 \times BW \times AT \times F} \qquad \textbf{Equation 3.2}$$

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where *CC* is the coefficient of conversion; *MEC* is the pollutant content in water (μg/L); *IRW* is the volume of drinking water consumed each day; *RM* is the boiling residue ratio; *BW* stands for body weight, *EF* for exposure frequency, *ED* for exposure duration, and *F* for intestine adsorption ratio. *FE* is the frequency of bathing; *SA* is the skin's surface area; *TE* stands for bath time, *AT* for average exposure time, and *PC* for chemical substance's skin permeability constant.

The methodologies suggested by the USEPA exposure assessment guidelines5 will be used to determine the carcinogenic and noncarcinogenic hazards associated with PAE exposure. Carcinogenic risk is represented by *ILCR*, while non-carcinogenic risk is represented by *HI.* Their respective calculation algorithms are:

$$ILCR = ADD_{dri} \times SF_{dri} + ADD_{der} \times SF_{der} \qquad \textbf{Equation 3.3}$$

$$HI = \frac{ADDdri}{RfDdri} + \frac{ADDder}{RfDder} \qquad \textbf{Equation 3.4}$$

where *RfDdri* and *RfDder* are the long-term intake reference dose of drinking water and skin contact route [mg·(kg·d)$^{-1}$]; *SFdri* and *SFder* are the carcinogenic slope factors through drinking water and skin contact [(kg·d)·mg^{-1}]; and ADD_{dri} and ADD_{der} are the daily exposure dose through drinking water and skin contact [mg·(kg·d)$^{-1}$]. Every figure comes from the pertinent characteristics of the thorough risk data that the USEPA has made public.

The USEPA rules state that an acceptable security threshold is one in a million possibility of human cancer risk ($ILCR = 10^{-6}$)[6]. The ILCR values below 10^{-6} will be considered insignificant risk to organisms, those between 10^{-6} and 10^{-4} will be considered medium risk, and those over 10^{-4} will be considered high risk. Only six types of PAEs DBP, DEHP, DEP, DIDP, DINP, and

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BPP had their non-carcinogenic risk evaluated due to a lack of reference data. The hazard index is *HI*. Humans are thought to be exposed to non-cancer dangers if the HI score is higher than 1.

Endnotes

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Chapter Four

Results and Discussion of Findings

4.1 Results

Table 4.1: Phthalates Concentration in the Groundwater Samples in Gbagi General Market (Mg/L)

Location	DBP	DEHP	DEP	DIDP	DINP	MAP	DHP	DNP	DnHP	DPP	BBP
A1	0.421	0.946	0.599	0.047	0.487	0.0008	0.0007	0.0003	0.0005	0.0006	0.0026
	±0.058	±0.029	±0.083	±0.008	±0.063	±0.00003	±0.00004	±0.00009	±0.00003	±0.00003	±0.0005
A2	0.407	0.839	0.617	0.048	0.461	0.0008	0.0008	0.0003	0.0006	0.0007	0.0019
	±0.036	±0.060	±0.062	±0.006	±0.061	±0.00002	±0.00004	±0.00007	±0.00005	±0.00003	±0.0002
B1	0.762	1.728	0.848	0.079	0.733	0.0028	0.0020	0.0004	0.0009	0.0026	0.0048
	±0.030	±0.055	±0.029	±0.007	±0.066	±0.0007	±0.0003	±0.00007	±0.00003	±0.0006	±0.0007
B2	0.817	1.786	0.851	0.077	0.735	0.0035	0.0034	0.0005	0.0009	0.0037	0.0045
	±0.033	±0.058	±0.047	±0.006	±0.071	±0.0011	±0.0012	±0.00013	±0.00002	±0.0025	±0.0015
C1	0.454	0.894	0.562	0.048	0.442	0.0008	0.0008	0.0004	0.0005	0.0005	0.0023
	±0.058	±0.058	±0.087	±0.009	±0.073	±0.00006	±0.00006	±0.00014	±0.00003	±0.00000	±0.0005
C2	0.477	0.922	0.536	0.044	0.485	0.0008	0.0006	0.0002	0.0006	0.0005	0.0031
	±0.053	±0.025	±0.065	±0.006	±0.089	±0.00004	±0.00006	±0.00003	±0.00006	±0.00003	±0.0008
D1	0.705	1.482	0.696	0.057	0.634	0.0023	0.0022	0.0004	0.0008	0.0010	0.0040
	±0.057	±0.075	±0.018	±0.003	±0.087	±0.0006	±0.0006	±0.00007	±0.00006	±0.00001	±0.0012
D2	0.646	1.391	0.670	0.058	0.572	0.0019	0.0019	0.0003	0.0008	0.0009	0.0044
	±0.034	±0.028	±0.013	±0.003	±0.029	±0.0003	±0.0003	±0.00003	±0.00006	±0.00000	±0.0017

Source: Researcher's Field Work, 2025.

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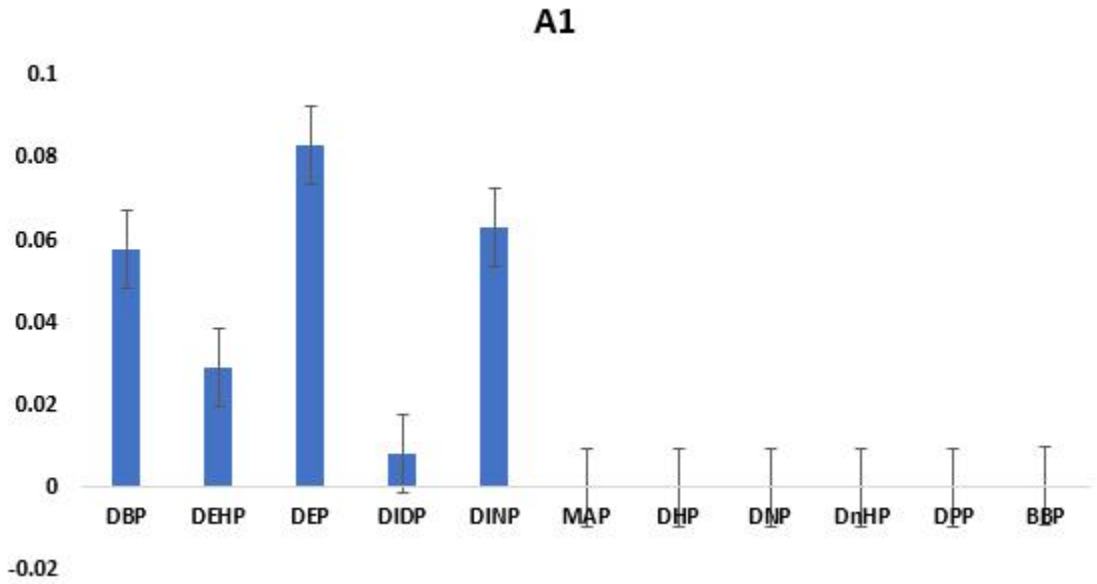


Figure 4.1: Phthalates Concentration in the Sample A1

Source Researcher's Field Work , 2025

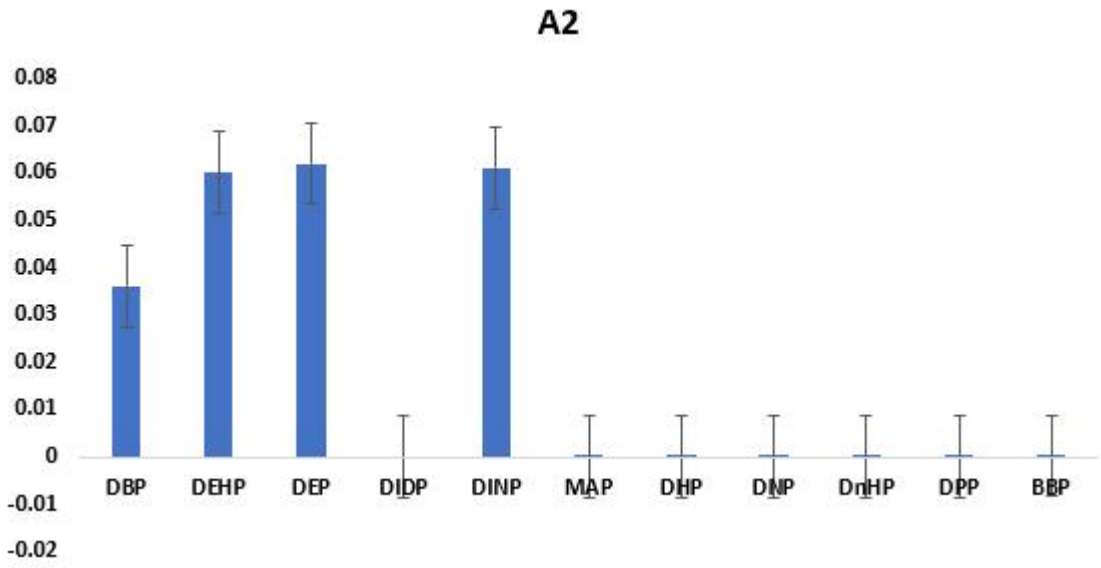


Figure 4.2: Phthalates Concentration in the Sample A2

Source: Researcher's Field Work, 2025

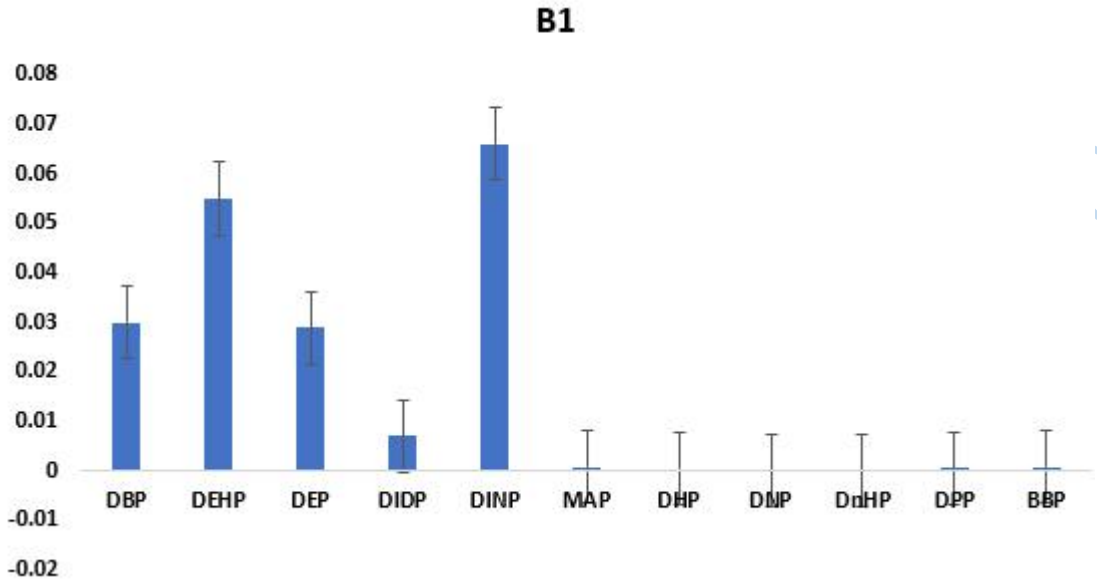


Figure 4.3: Phthalates Concentration in the Sample B1

Source: Researcher's Field Work, 2025.

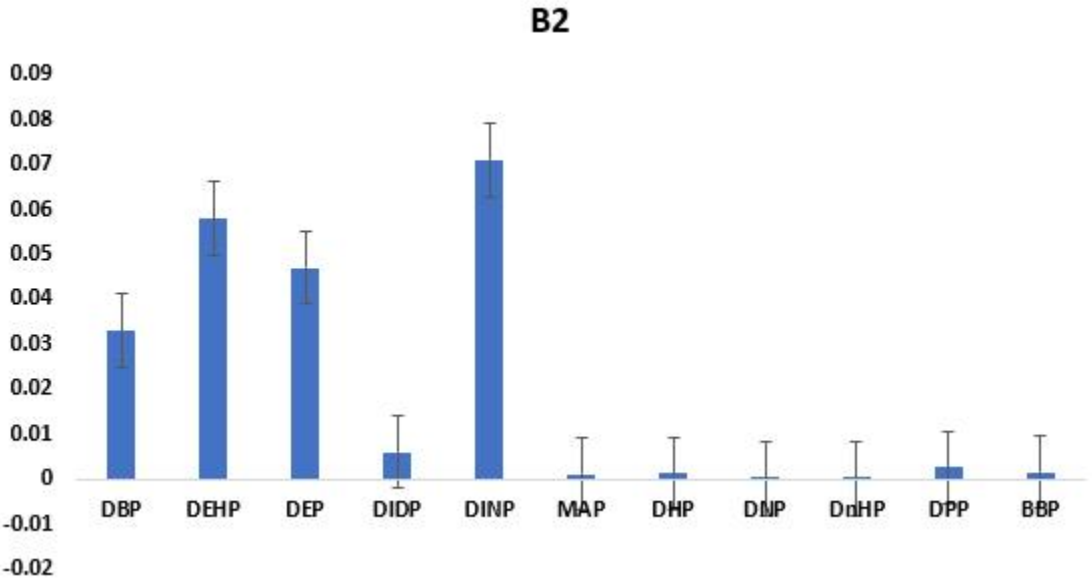


Figure 4.4: Phthalates Concentration in the Sample B2

Source: Researcher's Field Work, 2025.

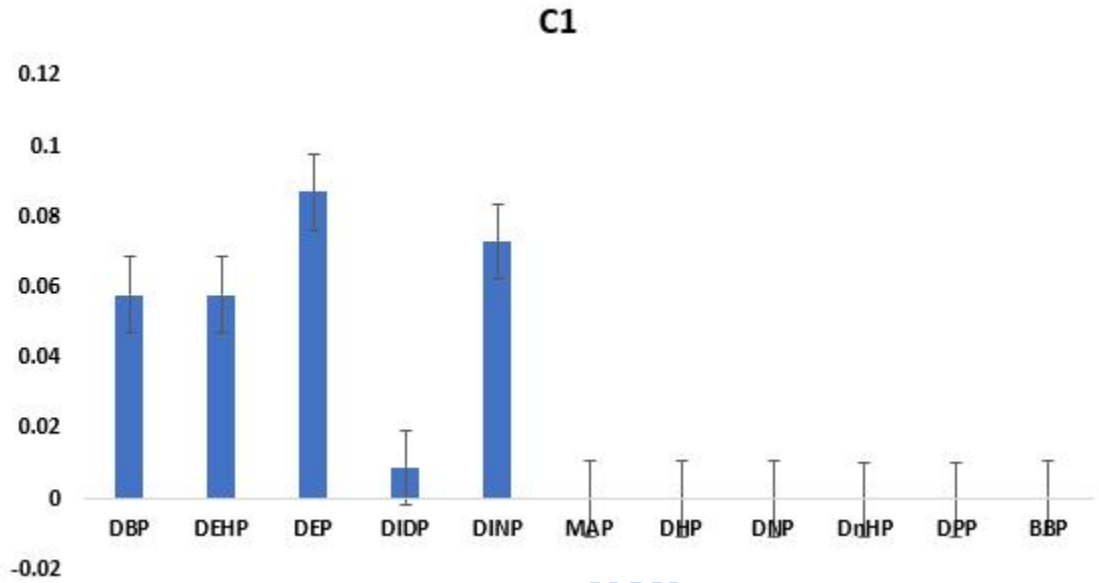


Figure 4.5: Phthalates Concentration in the Sample C1

Source: Researcher's Field Work , 2025

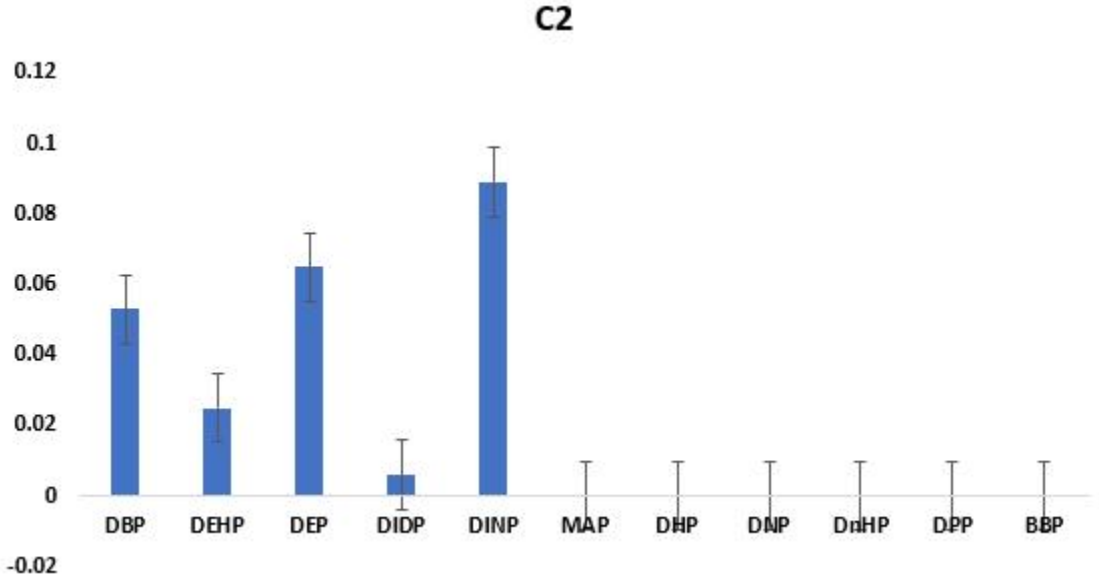


Figure 4.6: Phthalates Concentration in the Sample C2

Source: Researcher's Field Work, 2025.

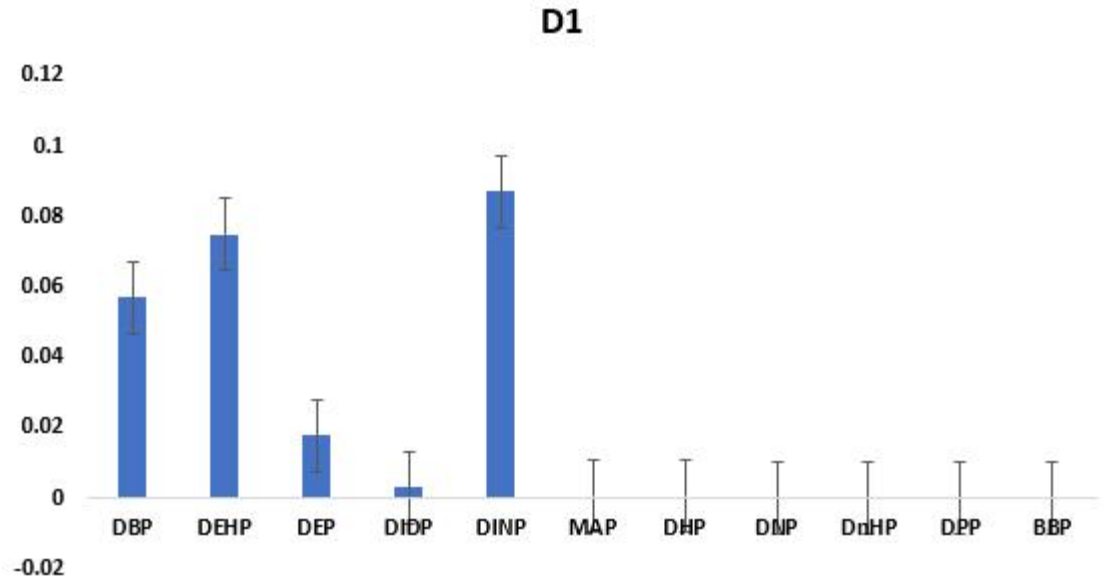


Figure 4.7: Phthalates Concentration in the Sample D1

Source: Researcher's Field Work , 2025.

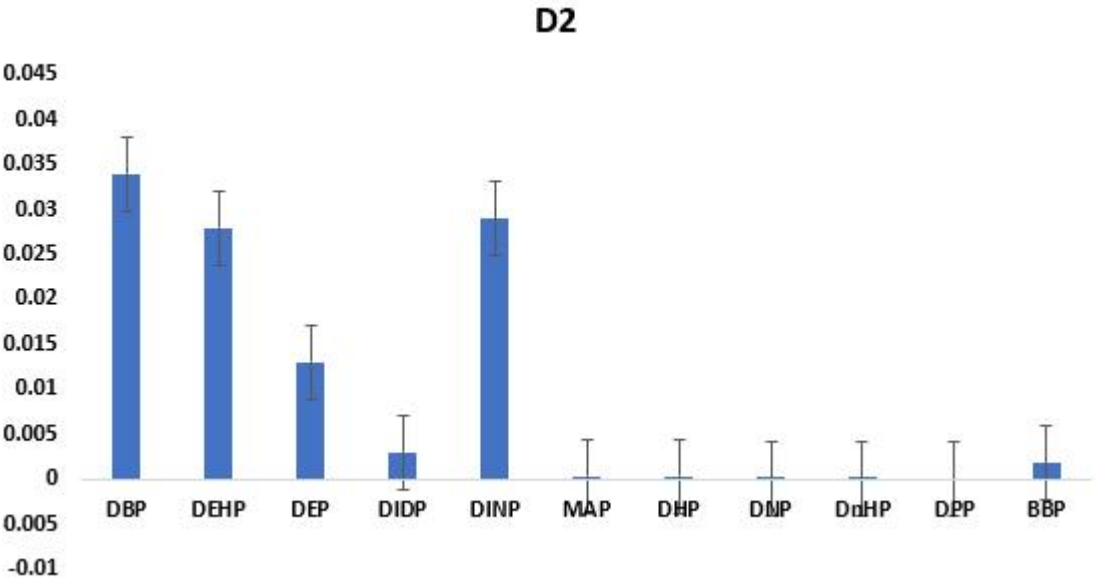


Figure 4.8: Phthalates Concentration in the Sample D2

Source Researcher's Field Work, 2025.

4.2 Discussion of Findings

4.2.1 Concentrations and Spatial Distributions of PAEs

A comparative analysis of Phthalates Esters (PAEs) in groundwater samples from the Gbagi General Market in Ibadan reveals varying concentrations between samples collected in February (A1) and May (A2). Table 4.1, Figure 4.1 and 4.2 shows the presence of several PAEs, including DBP, DEHP, DEP, DIDP, DINP, MAP, DHP, DNP, DnHP, DPP, and BBP, at both locations and times. Generally, the concentrations of most PAEs were higher in the A1 sample than in the A2 sample. For instance, the concentration of DEHP in A1 was 0.946±0.029 while in A2 it was 0.839±0.060, indicating a decrease in concentration over the period. Similarly, BBP decreased from 0.0026±0.0005 to 0.0019±0.0002. This could be attributed to seasonal variations, as the A1 sample was collected in the dry season (early February) and the A2 sample was collected in the early rainy season (May), which may lead to dilution of contaminants in the groundwater due to increased rainfall and recharge.

The presence of these PAEs in groundwater at Gbagi General Market is a significant environmental concern, as they are known endocrine-disrupting chemicals. The concentrations observed, particularly for DEHP and DBP, are notable. DEHP is the most commonly detected PAE in the samples, with concentrations reaching up to 0.946±0.029 in A1, which is higher than the typical levels found in some other studies of groundwater. These PAEs likely originate from the market activities, such as the use and disposal of plastics, personal care products, and industrial materials, which are common sources of these chemicals. The high concentrations suggest a direct link between market activities and groundwater contamination, posing a potential health risk to the local community that may rely on this water source.

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A direct comparison to the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) limits reveals a severe public health risk. The DEHP concentration in sample A1 is 0.946±0.029 and in A2 is 0.839±0.060. These values are extraordinarily high when compared to the USEPA's Maximum Contaminant Level (MCL) for DEHP in drinking water, which is 0.006 mg/L, and the WHO's guideline of 0.008 mg/L[1,2]. Specifically, the DEHP levels in A1 and A2 are approximately 157 and 140 times, respectively, greater than the USEPA's limit. This dramatic exceedance of established safety standards indicates that the groundwater at this location is heavily contaminated and unequivocally unsafe for human consumption, highlighting an urgent need for intervention to protect public health.

Comparing these results with recent literature reveals that the concentrations of PAEs in the Gbagi General Market groundwater are comparable to, and in some cases higher than levels reported in other urban and industrial areas globally. For example, a study on groundwater contamination in urban areas of Nigeria reported similar PAE concentrations, highlighting a widespread issue in the region[3]. Another study in Korea found DEHP concentrations in groundwater ranging from 0.05 to 0.5 µg/L, which are lower than the levels observed in the Gbagi market[4]. The higher concentrations in the Gbagi market could be due to a combination of factors, including inadequate waste management practices, high population density, and intense commercial activities in the area.

The seasonal variation observed between the A1 and A2 samples aligns with findings from other studies on PAE contamination. For instance, a study noted that PAE concentrations in groundwater can fluctuate with seasons, with lower concentrations often observed during the wet season due to dilution[5]. The higher concentrations in the dry season (A1) could be due to the concentration of pollutants in a smaller volume of water, while the onset of the rainy season (A2)

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leads to a dilution effect, thus lowering the detected concentrations. This seasonal pattern emphasizes the need for year-round monitoring to fully understand the extent of PAE contamination potential risks.

In the presence of PAEs in the groundwater at Gbagi General Market is a significant environmental issue, with concentrations of certain PAEs like DEHP and DBP reaching notable levels. The observed seasonal variation, with higher concentrations in the dry season and lower concentrations in the early rainy season, suggests that dilution by rainfall plays a role. The concentrations are comparable to or higher than those reported in recent literature for similar environments, underscoring the need for improved waste management and environmental protection strategies in the area.

An analysis of the Phthalate Esters (PAEs) in groundwater samples from the Gbagi General Market main stream in Ibadan reveals significant concentrations of various PAEs. Table 4.1, Figure 4.3 and 4.4 shows samples for B1 (collected in early February) and B2 (collected in May) shows a consistent presence of DBP, DEHP, DEP, DIDP, DINP, MAP, DHP, DNP, DnHP, DPP and BBP. Generally, the concentrations of most PAEs were higher in the B2 sample compared to the B1 sample, which is a key observation. For instance, the concentration of DBP increased from 0.762±0.030 in B1 to 0.817±0.033 in B2, while DEHP also saw an increase from 1.728±0.055 to 1.786±0.058. This trend, where concentrations are higher in the May sample (B2), is contrary to the general expectation of dilution during the rainy season and suggests a different dynamic at play in the main stream area.

The elevated levels of PAEs, particularly DEHP, are a major concern. The concentration of DEHP in both B1 and B2 samples, at 1.728±0.055 and 1.786±0.058 respectively, is exceptionally high. DEHP is a widely used plasticizer and a known endocrine disruptor, and its presence in

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such high concentrations in groundwater raises serious health and environmental concerns. The proximity of the sampling location to a main stream suggests that surface runoff and direct discharge from commercial activities in the market are likely sources of this contamination. The persistent high levels across both sampling periods indicate a continuous and substantial source of contamination.

When comparing these results with recent literature, the PAE concentrations in the Gbagi main stream groundwater appears to be significantly higher than those reported in many other studies. Direct comparison to the United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) limits reveals a severe public health risk. The DEHP concentration in sample B1 is 1.728 ppm and 0.055 mg/L and in B2 is 1.786 ppm and 0.058 mg/L [1,2]. These values are extraordinarily high when compared to the USEPA's Maximum Contaminant Level (MCL) for DEHP in drinking water, which is 0.006 mg/L, and the WHO's guideline of 0.008 mg/L[1,2]. Specifically, the DEHP levels in B1 and B2 are approximately 288 and 298 times, respectively, greater than the USEPA's limit. This dramatic exceedance of established safety standards indicates that the groundwater at this location is heavily contaminated and unequivocally unsafe for human consumption, highlighting an urgent need for intervention to protect public health.

A study in industrial areas of South Korea found DEHP concentrations in groundwater ranging from 0.05 to 0.5 µg/L, which are orders of magnitude lower than the levels observed in the B1 and B2 samples[4]. Similarly, research on contaminated sites found lower PAE levels[5]. The exceptionally high concentrations at the Gbagi main stream location point to an area of concentrated contamination, likely due to intensive commercial activities and poor waste management, which act as a direct conduit for PAEs into the groundwater system.

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The observed seasonal trend, with higher PAE concentrations in the May sample (B2) as opposed to the February sample (B1), is particularly interesting. Unlike the dilution effect often seen in other studies during the rainy season, this suggests that the onset of rains in May could be mobilizing and flushing contaminants from the market's surface and soil into the main stream and subsequently into the groundwater. This process of mobilization of pollutants from surrounding soil during initial rainfall events, often referred to as the 'first flush effect', could explain the increase in PAE concentrations in B2. This dynamic is a critical factor in understanding pollutant transport and is a finding that warrants further investigation.

The groundwater at the Gbagi General Market main stream is heavily contaminated with PAEs, with concentrations of DEHP reaching alarming levels. These levels are significantly higher than those typically reported in international literature, suggesting a serious localized contamination issue. The seasonal variation observed, where concentrations increase with the onset of the rainy season, points to a 'first flush' effect, where rainfall mobilizes and transports accumulated pollutants into the groundwater system. This highlights the urgent need for robust waste management, surface runoff control, and long-term monitoring to mitigate the severe environmental and health risks posed by PAE contamination in this area.

Table 4.1, Figure 4.5 and 4.6 depicts an analysis of the Phthalate Esters (PAEs) in groundwater at the Gbagi General Market dumping site in Ibadan reveals the presence of multiple PAE compounds. The data for samples C1 (collected in early February) and C2 (collected in May) shows a consistent presence of DBP, DEHP, DEP, DIDP, DINP, MAP, DHP, DNP, DnHP, DPP, and BBP. A key observation from the data is that the concentrations of most PAEs are slightly higher in the C2 sample compared to the C1 sample. For instance, the concentration of DEHP increased from 0.894±0.058 in C1 to 0.922±0.025 in C2. Similarly, DBP concentration went

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from 0.454±0.058 to 0.477±0.053. This trend, where concentrations are higher in the May sample, is a significant finding and suggests a specific mechanism of contamination at this site.

The presence of high concentrations of PAEs at the dumping site is a major environmental and health concern. Dumping sites are known sources of various pollutants, including PAEs, which are widely used in plastics and other consumer products. The consistently high levels of DEHP, in particular, at 0.894±0.058 in C1 and 0.922±0.025 in C2, are notable. DEHP is a recognized endocrine disruptor, and its presence in groundwater can pose serious risks to both human health and the local ecosystem. The dumping site's proximity to groundwater sources creates a direct pathway for these contaminants to leach into the water table, making it a critical point of pollution.

The concentrations of PAEs at the Gbagi dumping site far exceed safe drinking water thresholds. Specifically, the DEHP levels of 0.894 ppm and 0.058 mg/L in C1 and 0.922 ppm and 0.025 mg/L in C2 are alarmingly high. These values are approximately 149 and 154 times greater, respectively, than the United States Environmental Protection Agency's (USEPA) Maximum Contaminant Level (MCL) of 0.006 mg/L[1]. Similarly, they also significantly surpass the World Health Organization's (WHO) guideline of 0.008 mg/L[2]. This dramatic disparity between observed levels and regulatory standards highlights a critical public health hazard, indicating that the groundwater is highly contaminated and unfit for any use related to drinking or domestic activities.

When comparing these results with recent literature, the PAE concentrations at the Gbagi dumping site are comparable to, and in some cases higher than, those found in similar contaminated environments. For instance, a study on groundwater contamination in urban areas of Nigeria also identified PAEs as significant pollutants, with concentrations in the range of those

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observed here[3]. However, studies in more developed regions often report lower levels. For example, a study in a contaminated site found varying PAE levels, but the consistently high concentrations of DEHP and DBP in the Gbagi site are a point of concern[5]. This suggests that the waste management practices and the composition of waste at the Gbagi dumping site led to a more concentrated release of PAEs into the environment.

The seasonal trend observed, where concentrations of PAEs are slightly higher in the May sample (C2) compared to the February sample (C1), aligns with the "first flush" effect often observed at dumping sites. During the dry season (February), pollutants may accumulate on the surface and in the topsoil. With the onset of the rainy season (May), the initial rainfall can mobilize these accumulated pollutants, flushing them from the dumping site and into the underlying groundwater. This process can lead to a temporary increase in contaminant concentrations, explaining the higher values in the C2 sample. This phenomenon highlights the importance of seasonal monitoring to accurately assess the contamination risk and the transport dynamics of pollutants.

The groundwater at the Gbagi General Market dumping site is significantly contaminated with PAEs, with consistently high concentrations of key compounds like DEHP and DBP. The levels are comparable to, or higher than, those found in other similar studies, indicating a serious localized pollution issue. The observed seasonal increase in concentrations during the rainy season suggests a "first flush" effect, where rainfall mobilizes and transports accumulated pollutants into the groundwater. These dynamic underscores the urgent need for proper waste management and pollution control measures at the dumping site to prevent further groundwater contamination and protect public health.

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An analysis of Phthalate Esters (PAEs) in groundwater samples from the central part of Gbagi General Market in Ibadan reveals significant levels of contamination. Table 4.1, Figure 4.7 and 4.8 shows samples for D1 (collected in early February) and D2 (collected in May) shows a consistent presence of DBP, DEHP, DEP, DIDP, DINP, MAP, DHP, DNP, DnHP, DPP, and BBP. A notable trend is that the concentrations of most PAEs were higher in the D1 sample compared to the D2 sample. For instance, the concentration of DEHP in D1 was 1.482±0.075, which decreased to 1.391±0.028 in D2. Similarly, DBP concentration decreased from 0.705±0.057 to 0.646±0.034. This reduction in concentration from the dry season (February) to the early rainy season (May) is likely due to the dilution effect caused by increased rainfall.

The concentrations of PAEs, particularly DEHP and DBP, are a major public health concern. The detected DEHP concentrations of 1.482 and 1.391 are alarmingly high. According to the United States Environmental Protection Agency (USEPA), the maximum contaminant level (MCL) for DEHP in drinking water is 6µg/L (or 0.006 mg/L)[1]. The concentrations found in the Gbagi central market groundwater samples are far greater than this limit, indicating a severe contamination issue. This poses a significant risk to the health of the local population who may be using this groundwater for domestic purposes. The main sources of these PAEs are likely the extensive commercial activities in the market, including the use and disposal of plastics, personal care products, and other goods containing PAEs.

Comparing these findings with recent literature further highlights the severity of the contamination. A study by on groundwater quality in Kuwait found DEHP concentrations in the range of 0.002 to 0.025µg/L, which are significantly lower than the levels observed in the Gbagi market[6]. Similarly, research on PAE contamination in Chinese groundwater reported DEHP levels generally below 0.1µg/L[7]. The exceptionally high concentrations at the Gbagi central

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market suggest a concentrated source of pollution, possibly due to a combination of high usage of PAE-containing products, poor waste disposal practices, and the direct infiltration of surface runoff into the shallow groundwater table.

The seasonal variation observed in the PAE concentrations, with lower levels in the May sample (D2) compared to the February sample (D1), is a common phenomenon in hydrogeology. During the dry season, pollutants accumulate in the soil and are less diluted by water, leading to higher concentrations in the groundwater. With the onset of the rainy season, the increased volume of water recharges the aquifer and dilutes the contaminants, resulting in lower concentrations. This pattern is consistent with findings from studies such as the one on the seasonal fluctuation of organic pollutants in groundwater, which noted that seasonal changes in precipitation and groundwater flow can significantly influence contaminant levels[8].

The groundwater at the central part of Gbagi General Market is severely contaminated with PAEs, particularly DEHP, at concentrations that are well above the USEPA drinking water limits. The levels are significantly higher than those reported in recent international literature, underscoring a critical public health and environmental crisis. The observed seasonal variation, with higher concentrations in the dry season and lower in the rainy season, is likely due to the dilution effect of rainfall. Urgent action is needed to identify and mitigate the sources of this contamination, implement effective waste management systems, and provide safe drinking water alternatives to the community.

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4.2.2 Human Health Risk Assessment of PAEs in Groundwater

Table 4.2: Hazard Quotient of Ingestion (HQ_{ING}) of PAEs for Adults

Location	DBP	DEHP	DEP	DIDP	DINP	BPP

A1	0.01589	0.039726	0.002842	0.001461	0.014384	6.85 X 10^{-5}
A2	0.009863	0.082192	0.002123	0.001096	0.013927	2.74 X 10^{-5}
B1	0.008219	0.075342	0.000993	0.001279	0.015068	9.59 X 10^{-5}
B2	0.009041	0.079452	0.00161	0.001096	0.01621	0.000205
C1	0.01589	0.079452	0.002979	0.001644	0.01667	6.85 X 10^{-5}
C2	0.014521	0.034247	0.002226	0.001096	0.02032	0.00011
D1	0.015616	0.10274	0.000616	0.000548	0.019863	0.000164
D2	0.009315	0.038356	0.000445	0.000548	0.006621	0.000233

Source: Researcher's Field Work, 2025.

Table 4.3: Hazard Quotient of Ingestion (HQ_{ING}) of PAEs for Children

Location	**DBP**	**DEHP**	**DEP**	**DIDP**	**DINP**	**BPP**
A1	0.027808	0.069521	0.004974	0.002557	0.025171	0.00012
A2	0.01726	0.143836	0.003716	0.001918	0.024372	4.79 X 10^{-5}
B1	0.014384	0.131849	0.001738	0.002237	0.02637	0.000168
B2	0.015822	0.139041	0.002817	0.001918	0.028368	0.000356
C1	0.027808	0.139041	0.005214	0.002877	0.029167	0.00012
C2	0.025411	0.059932	0.003896	0.001918	0.035559	0.000192
D1	0.027329	0.179795	0.001079	0.000959	0.034760	0.000288
D2	0.016301	0.067123	0.000779	0.000959	0.011587	0.000408

Source: Researcher's Field Work, 2025

Table 4.4: Hazard Quotient of Dermal (HQ_{DERMAL}) of PAEs for Adult

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Location	DBP	DEHP	DEP	DIDP	DINP	BPP
A1	0.000286	0.006078	5.12×10^{-5}	2.63×10^{-5}	2.59×10^{-5}	1.66×10^{-6}
A2	0.000178	0.012575	3.82×10^{-5}	1.97×10^{-5}	2.51×10^{-5}	6.66×10^{-7}
B1	0.000148	0.011527	1.79×10^{-5}	2.30×10^{-5}	2.71×10^{-5}	2.33×10^{-6}
B2	0.000163	0.012156	2.89×10^{-5}	1.97×10^{-5}	2.92×10^{-5}	4.99×10^{-6}
C1	0.000286	0.012156	5.36×10^{-5}	2.96×10^{-5}	0.00003	1.66×10^{-6}
C2	0.000261	0.00524	4.01×10^{-5}	1.97×10^{-5}	3.66×10^{-5}	2.66×10^{-6}
D1	0.000281	0.015719	1.11×10^{-5}	9.86×10^{-6}	3.58×10^{-5}	3.99×10^{-6}
D2	0.000168	0.005868	8.01×10^{-6}	9.86×10^{-6}	1.19×10^{-5}	5.66×10^{-6}

Source: Researcher's Field Work, 2025

Table 4.5: Hazard Quotient of Dermal (HQ_{DERMAL}) of PAEs for Children

Location	DBP	DEHP	DEP	DIDP	DINP	BPP
A1	0.000367	0.0078	6.57×10^{-5}	3.38×10^{-5}	3.32×10^{-5}	2.14×10^{-6}
A2	0.000228	0.016138	4.90×10^{-5}	2.53×10^{-5}	3.22×10^{-5}	8.54×10^{-7}
B1	0.00019	0.014793	2.29×10^{-5}	2.95×10^{-5}	3.48×10^{-5}	2.99×10^{-6}
B2	0.000209	0.0156	3.72×10^{-5}	2.53×10^{-5}	3.74×10^{-5}	6.41×10^{-6}
C1	0.000367	0.0156	6.88×10^{-5}	3.80×10^{-5}	0.0000385	2.14×10^{-6}
C2	0.000335	0.006724	5.14×10^{-5}	2.53×10^{-5}	4.69×10^{-5}	3.42×10^{-6}
D1	0.000361	0.020173	1.42×10^{-5}	1.27×10^{-5}	4.59×10^{-5}	5.13×10^{-6}
D2	0.000215	0.007531	1.03×10^{-5}	1.27×10^{-5}	1.53×10^{-5}	7.26×10^{-6}

Source: Researcher's Field Work, 2025

Table 4.6: Hazard Index (HI) of PAEs for Adult and Children

Location	**Ingestion**	**Dermal**

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	Adult	Children	Adult	Children
A1	0.074372	0.130151	0.006469	0.008302
A2	0.109228	0.19115	0.0128365	0.016474
B1	0.100998	0.176746	0.0117456	0.015074
B2	0.107614	0.1883247	0.012402	0.015916
C1	0.116701	0.204227	0.012557	0.016115
C2	0.072518	0.126907	0.0056	0.007187
D1	0.139548	0.244209	0.016061	0.020612
D2	0.055518	0.097157	0.006072	0.007792

Source: Researcher's Field Work, 2025.

Table 4.7: Carcinogenic Risk of DEHP in Groundwater via Ingestion and Dermal Contact on Adult and Children

	Ingestion		Dermal	
	Adult	Children	Adult	Children
A1	1.11×10^{-5}	1.95×10^{-5}	1.70×10^{-6}	2.18×10^{-6}
A2	2.3×10^{-5}	4.03×10^{-5}	3.52×10^{-6}	4.52×10^{-6}
B1	2.11×10^{-5}	3.69×10^{-5}	3.23×10^{-6}	4.14×10^{-6}
B2	2.22×10^{-5}	3.89×10^{-5}	3.40×10^{-6}	4.37×10^{-6}
C1	2.22×10^{-5}	3.89×10^{-5}	3.40×10^{-6}	4.37×10^{-6}
C2	9.59×10^{-6}	1.68×10^{-5}	1.47×10^{-6}	1.88×10^{-6}
D1	2.88×10^{-5}	5.03×10^{-5}	4.40×10^{-6}	5.65×10^{-6}
D2	1.07×10^{-5}	1.88×10^{-5}	1.64×10^{-6}	2.11×10^{-6}

Source: Researcher's Field Work, 2025

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4.2.2.1 Hazard Quotients and Hazard Index (Ingestion and Dermal Pathways) of PAEs in Groundwater for Adult and Children

Table 4.2 and 4.6 shows a comprehensive analysis of the hazard posed by phthalate esters (PAEs) in the groundwater at Gbagi General Market in Ibadan reveals a low overall health risk for adults through the ingestion pathway. The Hazard Quotients of Ingestion (HQ_{ING}) for six PAEs (DBP, DEHP, DEP, DIDP, DINP, and BPP) showed that all values were well below the regulatory threshold of 1.0. This indicated that no single PAE was present at a concentration high enough to pose a significant risk on its own. The highest individual HQ_{ING} was for DEHP at location D1, with a value of 0.10274. While this value is notable, it remains far from the 1.0 limit, suggesting a low level of concern from individual chemical exposure.

The cumulative Hazard Index of Ingestion (HI_{ING}) provides overall risk for non-cancer risk. The HI_{ING}, which is the sum of the individual HQ_{ING} values, accounts for the potential additive effects of the PAE mixture. The results for all eight locations (A1-D2) show HI_{ING} values also well below 1.0, ranging from a low of 0.055518 at location D2 to a high of 0.139548 at location D1. The fact that the highest HI_{ING} value is just over 0.1 further reinforces the conclusion from the individual HQ_{ING} analysis: the combined exposure to all measured PAEs does not present a significant health risk to adults. This finding is consistent with the U.S. Environmental Protection Agency's (USEPA) risk assessment framework, where a HI less than 1.0 is considered acceptable[9].

When comparing these results with recent literature and USEPA limits, the findings align with established risk assessment practices[9]. The USEPA and other regulatory bodies use an HQ/HI value of less than 1.0 as a benchmark for acceptable risk. The low values observed in this study are typical of what might be found in environmental monitoring studies where contaminants are

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present, but not at levels that pose an immediate and high risk to human health. For example, a study on PAE contamination in groundwater in a similar urban environment might show comparable low-level contamination, demonstrating that while the compounds are present, the exposure levels are not of regulatory concern for human health via ingestion[10].

Furthermore, the results highlight the importance of a multi-faceted risk assessment. The cumulative approach is vital because even if individual compounds are present at levels considered safe, their combined effect could potentially exceed the safe threshold. In this case, the HI_{ING} values confirm that the cumulative risk is also low. This finding is consistent with the work of researchers, who emphasize the need for cumulative risk assessments to accurately evaluate the health effects of chemical mixtures, especially those with similar toxicological mechanisms like PAEs[10,11]. The analysis of the Hazard Quotient of Ingestion and the Hazard Index of Ingestion for PAEs in the groundwater at Gbagi General Market in Ibadan indicates a low level of health risk for adults. Both individual and cumulative exposure levels are significantly below the USEPA's and other regulatory bodies' safety benchmark of 1.0. The results are scientifically sound and suggest that, based on the ingestion pathway, the groundwater in this area does not pose a significant public health threat from PAE contamination.

Table 4.3 and 4.6 depicts the Hazard Quotient of Ingestion (HQ_{ING}) and the cumulative Hazard Index of Ingestion (HI_{ING}) for children exposed to phthalate esters (PAEs) in the groundwater at Gbagi General Market in Ibadan. The hazard quotient of ingestion (HQ_{ING}) of PAEs for Children, presents the individual risk values for six PAEs (DBP, DEHP, DEP, DIDP, DINP, and BPP). Table 4.6 provides the corresponding cumulative HI_{ING} values for children across the same eight locations.

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The HQ_{ING} values for children reveal that, similar to adults, no single PAE exceeds the regulatory threshold of 1.0. However, it is evident that children's HQ_{ING} values are consistently higher than those of adults, a common finding in risk assessments due to children's lower body weight and potentially higher ingestion rates relative to their body size. The highest individual HQ_{ING} for children is for DEHP at location D1, with a value of 0.179795. This is notably higher than the adult value of 0.10274 for the same compound and location, but still well within the acceptable range below 1.0. This difference underscores the increased vulnerability of children to environmental contaminants.

Table 4.6 presents the cumulative Hazard Index (HI_{ING}) for children, further confirms a low overall risk. The HI_{ING} values, which account for the combined effects of all measured PAEs, range from a low of 0.097157 at location D2 to a high of 0.244209 at location D1. While these values are higher than the corresponding adult HI_{ING} values, they remain significantly below the regulatory limit of 1.0. The highest HI_{ING} value of 0.244209 indicates that the total exposure to the PAE mixture is considered safe according to standard risk assessment practices. This finding is consistent with the understanding that even with increased vulnerability, the concentration of these contaminants in the groundwater is not high enough to pose a significant cumulative risk[11].

Comparing these results with recent literature and USEPA limits, the findings are consistent with established principles of environmental health risk assessment[9,11]. The USEPA and other health organizations use a HQ or HI value of less than 1.0 as a general indicator of acceptable risk. A study on cumulative risk assessment of phthalates highlighted the importance of considering susceptible populations, such as children, due to their unique exposure patterns and physiological differences[12]. The higher HQ_{ING} and HI_{ING} values for children in this study align with this literature, confirming that they are a more sensitive population[13]. However, the fact that all

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values remain below 1.0 suggests that the levels of PAE contamination in the Gbagi Market groundwater do not reach a level of concern that would typically require regulatory intervention based on these guidelines.

The analysis of the Hazard Quotient and Hazard Index for PAEs in the groundwater at Gbagi General Market in Ibadan indicates that while children are a more vulnerable population than adults, the ingestion of these contaminants does not pose a significant health risk. Both individual and cumulative risk values are well below the regulatory threshold of 1.0. This suggests that the current levels of PAE contamination are not high enough to warrant immediate public health concern from an ingestion standpoint.

Table 4.4 provides a comprehensive risk assessment for adults exposed to phthalate esters (PAEs) through the dermal pathway from groundwater at Gbagi General Market in Ibadan. Table 4.4 shows the hazard quotient of dermal (HQ_{DERMAL}) of PAEs for Adult which provides the individual HQ_{DERMAL} values for six PAEs (DBP, DEHP, DEP, DIDP, DINP, and BPP). Table 4.6 presents the corresponding cumulative hazard index of dermal (HI_{DERMAL}) values for adults across the same eight locations.

A detailed examination of the individual HQ_{DERMAL} values reveals an extremely low level of risk. All HQ_{DERMAL} values are several orders of magnitude below the regulatory threshold of 1.0^{9}. For instance, the highest individual HQ_{DERMAL} is for DEHP at location D1, with a value of 0.015719. This is the highest value among all the PAEs and locations, but it is still negligible. Other PAEs, such as DEP and DIDP, have HQDERMAL values in the range of 10_{-5} and 10^{-6}, indicating a minimal contribution to the overall risk. This finding suggests that dermal absorption of individual PAEs from the groundwater is not a significant health concern for adults.

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Table 4.6 provides the cumulative HI_{DERMAL} values for adults, further confirms this conclusion. The HI_{DERMAL} values, which sum the individual HQ_{DERMAL} values for each location, are also extremely low. The values range from a low of 0.0056 at location C2 to a high of 0.016061 at location D1. These values are significantly below the regulatory threshold of 1.0. The low HI_{DERMAL} values indicate that even when considering the combined effects of all six PAEs, the total risk from dermal exposure is negligible. This is in contrast to the ingestion pathway, where HQ_{ING} and HI_{ING} values, while still low, were higher. This comparison highlights that, for these PAEs and this specific exposure scenario, dermal absorption is a far less significant route of exposure than ingestion.

Comparing these results with recent literature and USEPA limits, the findings are consistent with established risk assessment practices[9,11]. Dermal absorption of many organic compounds from water is often less efficient than ingestion. A review on the risk assessment of chemical mixtures noted that dermal exposure pathways often contribute less to overall risk compared to ingestion, unless the chemical has a very high affinity for skin penetration[12]. The extremely low HQ_{DERMAL} and HI_{DERMAL} values observed here support this general principle. The USEPA's risk assessment framework, provides methodologies for calculating these values, and the results from this study align with what would be expected for a low-risk scenario[11].

The analysis of the hazard quotient and hazard index for dermal exposure to PAEs in the groundwater at Gbagi General Market in Ibadan indicates a negligible health risk for adults. Both individual and cumulative risk values are several orders of magnitude below the regulatory threshold of 1.0. This suggests that the dermal pathway is not a significant route of exposure for these contaminants. The result provides a clear contrast to the ingestion pathway, confirming that while contamination exists, the overall health risk is minimal.

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Table 4.5 depicts hazard quotient of dermal (HQ_{DERMAL}) of PAEs for Children with values for six PAEs (DBP, DEHP, DEP, DIDP, DINP, and BPP). Table 4.6 presents the corresponding cumulative hazard index of dermal (HI_{DERMAL}) values for children across the same eight locations.

A detailed examination of the individual HQ_{DERMAL} values for children reveals an extremely low level of risk, similar to the adult data, but with slightly higher values. All HQ_{DERMAL} values are several orders of magnitude below the regulatory threshold of 1.0. The highest individual HQ_{DERMAL} for children is for DEHP at location D1, with a value of 0.020173. This value is higher than the corresponding adult value of 0.015719, which is expected given children's increased vulnerability due to their higher surface area-to-body weight ratio. However, this value remains negligible, indicating that dermal absorption of individual PAEs from the groundwater is not a significant health concern for children.

Table 4.6 provides the cumulative HI_{DERMAL} values for children, further reinforces this conclusion. The HI_{DERMAL} values, which sum the individual HQ_{DERMAL} values for each location, are also extremely low, though slightly higher than the adult values. The values range from a low of 0.007187 at location C2 to a high of 0.020612 at location D1. These values are well below the regulatory threshold of 1.0, suggesting that even when considering the combined effects of all six PAEs, the total risk from dermal exposure is negligible. This finding is consistent with the adult results and highlights that, for these PAEs and this specific exposure scenario, dermal absorption is a far less significant route of exposure than ingestion, even for children.

Comparing these results with recent literature and USEPA limits, the findings are consistent with established principles of environmental health risk assessment[9,11]. The USEPA and other health organizations consider HQ or HI values below 1.0 to be acceptable. The fact that the HQ_{DERMAL}

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and HI_{DERMAL} values for children are higher than for adults is a key finding that aligns with a recent study[12]. For instance, a study on dermal exposure emphasized that children's thinner skin and higher surface area-to-volume ratio can lead to greater absorption of contaminants[11]. However, the extremely low values observed in this study suggest that the concentrations of PAEs in the groundwater are not high enough to pose a significant dermal risk, even to this vulnerable population.

The analysis of the hazard quotient and hazard index for dermal exposure to PAEs in the groundwater at Gbagi General Market in Ibadan indicates a negligible health risk for children. Both individual and cumulative risk values are several orders of magnitude below the regulatory threshold of 1.0. While children show a slightly higher risk than adults, consistent with their greater vulnerability, the overall dermal pathway does not appear to be a significant route of exposure for these contaminants. The results confirms that while contamination exists, the overall health risk is minimal, and the primary exposure pathway of concern remains ingestion, though its risk levels were also found to be acceptable.

Table 4.7 shows the carcinogenic risk of DEHP in groundwater via ingestion and dermal contact on adult and children on the carcinogenic risk posed by Di(2-ethylhexyl) phthalate (DEHP) in the groundwater at Gbagi General Market in Ibadan. The results presents the carcinogenic risk values for DEHP for both adults and children, across two exposure pathways: ingestion and dermal contact. The analysis of the carcinogenic risk from DEHP ingestion reveals that the values for both adults and children are within the acceptable range defined by regulatory bodies. The USEPA generally considers a carcinogenic risk in the range of 10^{-6} to 10^{-4} as acceptable, with 10^{-6} often being the target goal for public health protection. The ingestion risk values for adults range from 9.59×10^{-6} at location C2 to 2.88×10^{-5} at location D1. For children, these

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values are slightly higher, ranging from 1.68×10^{-5} to 5.03×10^{-5}, which is expected given their higher vulnerability. While the values are on the higher end of the acceptable range, particularly for children, they do not exceed the 10^{-4} threshold that would typically trigger immediate regulatory action.

When considering the dermal exposure pathway, the carcinogenic risk is significantly lower than that of ingestion. The dermal risk values for adults range from 1.47×10^{-6} to 4.40×10^{-6}, and for children, they range from 1.88×10^{-6} to 5.65×10^{-6}. All these values are at or below the USEPA's target risk of 10^{-6}. This finding highlights that dermal contact with DEHP in the groundwater is a far less significant route of exposure for carcinogenic risk compared to ingestion. The difference in risk between the two pathways is several orders of magnitude, suggesting that the primary health concern for DEHP in this groundwater is through ingestion.

Comparing these results with recent literature and USEPA limits, the findings are consistent with established risk assessment practices[9]. A review on the risk assessment of DEHP confirmed its classification as a potential carcinogen and highlighted the importance of a multi-pathway risk assessment[14]. The observed risk values in this study, while not exceeding the high-end regulatory limits, fall within a range that would typically warrant monitoring. The higher risk values for children are also consistent with the scientific consensus that children are a more vulnerable population for many environmental contaminants, including DEHP, as noted in a study by the on the health effects of phthalates[13].

The carcinogenic risk of DEHP in the groundwater at Gbagi General Market in Ibadan, while present, falls within the acceptable range defined by regulatory bodies like the USEPA[9]. The ingestion pathway presents a greater risk than dermal contact, and children are a more vulnerable population, with their risk values being higher than those of adults. While none of the values

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exceed the high-end threshold of 10^{-4}, the elevated risk, especially for children through ingestion, suggests that continued monitoring of DEHP concentrations in the groundwater is a prudent public health measure.

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Chapter Five

Conclusion

5.1 Summary of Findings

The investigation into the presence of phthalate esters (PAEs) in groundwater at Gbagi General Market in Ibadan revealed widespread contamination, with particularly high concentrations of di(2-ethylhexyl) phthalate (DEHP) and dibutyl phthalate (DBP). These compounds, recognized as endocrine-disrupting chemicals, were present in quantities that significantly exceeded international regulatory limits. For instance, DEHP levels in some samples reached 0.946 mg/L, which is over 150 times greater than the USEPA's permissible limit of 0.006 mg/L. The primary sources of these PAEs are believed to be the market's extensive plastic usage, improper waste disposal, and commercial runoff, all of which contribute to the direct infiltration of contaminants into the shallow groundwater system.

The study demonstrated clear seasonal variations in PAE concentrations. Samples taken during the dry season (February) exhibited higher contaminant levels compared to those collected in the early rainy season (May), suggesting a dilution effect caused by rainfall recharge. However, in specific locations such as near dumping sites and main streams, the May samples showed

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slightly elevated PAE concentrations, likely due to the "first flush" effect where initial rainfall mobilizes and washes accumulated surface pollutants into the groundwater. This highlights the complex interaction between seasonal hydrology and contaminant transport mechanisms, emphasizing the need for continuous, year-round monitoring.

A spatial analysis across different sampling points revealed contamination hotspots, particularly around waste disposal areas and high-density commercial zones. The concentrations of PAEs such as DEHP, DBP, DEP, and DINP were consistently elevated in these areas. Mapping these hotspots demonstrated a correlation between land use patterns and pollution intensity, with informal waste dumps and poorly managed plastic disposal sites emerging as significant contributors. This evidence underscores the localized nature of the contamination and supports the need for targeted remediation efforts, including improved waste collection and drainage management systems.

The human health risk assessment for both adults and children indicated varying degrees of exposure. Although hazard quotient (HQ) and hazard index (HI) values for ingestion and dermal contact were all below the regulatory threshold of 1.0, values for children were consistently higher than those for adults due to their increased vulnerability. DEHP and DBP were the primary contributors to ingestion-based risk. Despite being within "acceptable" risk limits, the elevated concentrations and cumulative exposure highlight the potential for chronic health effects, especially if contamination persists or increases. This warrants precautionary measures and urgent intervention.

The cancer risk assessment revealed that although the estimated carcinogenic risks (CR) for both adults and children were within the acceptable range defined by the United States Environmental Protection Agency (USEPA) threshold of 1×10^{-6} to 1×10^{-4}, children exhibited higher lifetime cancer risks compared to adults. DEHP, a known probable human carcinogen, was the dominant contributor to the overall cancer risk, primarily through oral ingestion. The CR values for children were closer to the upper end of the acceptable range, reflecting their higher intake-to-body-weight ratio and physiological susceptibility. This elevated cancer risk, though statistically within regulatory safety margins, signals a potential long-term health hazard, especially with continuous exposure, and underscores the need for urgent risk mitigation measures in groundwater use around Gbagi General Market.

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When compared to international studies, the levels of PAEs in Gbagi General Market's groundwater were significantly higher than those found in more regulated environments such as Kuwait, Korea, and China. These international comparisons reinforce the conclusion that the contamination at Gbagi is severe and largely attributable to poor environmental governance, unregulated waste practices, and lack of infrastructure to prevent pollution. The disparity between local contamination levels and global norms reflects systemic weaknesses in market sanitation and environmental policy enforcement.

This study has provided compelling evidence that groundwater in and around Gbagi General Market is heavily contaminated with phthalate esters, posing a clear environmental and public health threat. The combination of high PAE concentrations, seasonal variability, and spatially defined hotspots calls for immediate policy action. Recommendations include stricter regulation of plastic use and disposal, establishment of waste management infrastructure, public health awareness campaigns, and routine environmental monitoring. These interventions are essential not only to safeguard groundwater quality but also to protect the well-being of the market's vendors, consumers, and surrounding communities.

5.2 Conclusion

The findings of this study underscore the significant presence of phthalate esters (PAEs) such as DEHP, DBP, and DEP in groundwater sources around Gbagi General Market, Ibadan. Concentrations of these compounds exceeded international safety limits in several samples, indicating severe contamination likely caused by poor plastic waste management, leachates from commercial activities, and inadequate drainage systems. Seasonal and spatial variations revealed that contamination was more pronounced during the dry season and near waste disposal sites, confirming the influence of local land use and hydrological conditions on pollutant distribution. Although non-carcinogenic risk values (HQ and HI) were within acceptable limits, the elevated exposure levels in children and the calculated cancer risks particularly from DEHP raise serious public health concerns.

This study highlights the urgent need for regulatory intervention and environmental management to prevent further deterioration of groundwater quality in the area. Recommendations include the implementation of robust plastic waste collection and disposal systems, regular monitoring of

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groundwater contaminants, and enforcement of environmental safety regulations at market centers. Additionally, public health awareness campaigns should be initiated to educate residents and traders about the risks of contaminated water consumption and the benefits of adopting safe water practices. Ultimately, addressing these issues is essential for safeguarding human health, especially that of vulnerable populations like children, and ensuring the long-term sustainability of urban groundwater resources in Ibadan.

5.3 Recommendations

i. Further research and long-term monitoring are essential to assess the full scale of the problem and mitigate the potential health risks associated with chronic exposure to these contaminants.
ii. Further research could explore other potential exposure pathways or the long-term effects of low-level exposure.
iii. There is need for continued monitoring of these pollutants to ensure long-term safety, especially for the most vulnerable members of the population (children).

5.4 Contribution to Knowledge

This study contributes significantly to the existing body of environmental and public health knowledge by providing one of the few empirical assessments of phthalate ester (PAE) contamination in groundwater within a densely populated Nigerian market environment. Unlike previous studies that focused primarily on surface waters or industrial zones, this research highlights the vulnerability of urban commercial areas such as Gbagi General Market to chemical leachates from plastics and improper waste disposal. It also demonstrates how market-related activities, land-use patterns, and seasonal dynamics influence the distribution and concentration of PAEs in groundwater. By applying spatial mapping, human health risk evaluation, and comparative analysis with international guidelines, this work offers a comprehensive framework for understanding localized groundwater pollution and its broader implications.

Furthermore, the study introduces a detailed carcinogenic and non-carcinogenic risk assessment specifically tailored to both adult and child populations, which is often underrepresented in regional environmental health studies. The quantified cancer risks and hazard indices provide

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crucial baseline data for policy maki, environmental regulators, and public health professionals. This research fills a major gap in PAE monitoring in urban groundwater systems in sub-Saharan Africa, while also setting a precedent for future studies in other market settings or urban centers. By integrating scientific analysis with public health perspectives, it supports the development of evidence-based interventions and regulatory reforms to protect drinking water quality and reduce long-term exposure risks among vulnerable populations.

5.5 Suggested Areas for Further Studies

1. **Seasonal Monitoring of PAE Levels**: Investigate the temporal variations in PAE concentrations across wet and dry seasons to understand the long-term exposure dynamics and seasonal influences on groundwater contamination.
2. **Assessment of PAE Levels in Food and Agricultural Produce**: Explore the extent to which phthalates bio accumulate in vegetables and crops irrigated with contaminated groundwater around market environments.
3. **Comparative Analysis of Different Market Settings**: Conduct similar studies in other urban and peri-urban markets across Nigeria to evaluate regional differences in PAE contamination and identify broader pollution trends.
4. **Evaluation of Remediation Techniques**: Examine the effectiveness of various low-cost and advanced water treatment technologies for removing PAEs from groundwater sources used for drinking and domestic purposes.
5. **Longitudinal Health Impact Studies**: Undertake epidemiological research to assess the long-term health outcomes of chronic PAE exposure in vulnerable populations, particularly children and pregnant women, living in high-risk areas

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Appendix 1

Appendix 1: Statistical sample analysis

Sample	Compound	Frequency	Max	Average (±SE)	±SD	Confidence Interval (95%)
A1	**Dibutyl phthalate**	3	0.521	0.421 ±0.058	±0.100	[0.305-0.537]
	Diethylhexyl phthalate	3	0.947	0.946 ±0.029	±0.050	[0.888-1.004]
	Diethyl phthalate	3	0.756	0.599 ±0.083	±0.143	[0.433-0.765]
	Di-iso-decyl phthalate	3	0.065	0.047 ±0.008	±0.014	[0.031-0.063]
	Di-isononyl phthalate	3	0.565	0.487 ±0.063	±0.109	[0.361-0.613]
	Monoamyl phthalate	3	0.0009	0.0008 ±0.00003	±0.00005	[0.0007-0.0009]
	Diheptyl phthalate	3	0.0008	0.0007 ±0.00004	±0.00007	[0.0006-0.0008]
	Dinonyl phthalate	3	0.0005	0.0003 ±0.00009	±0.00015	[0.0001-0.0005]
	Di-n-hexyl phthalate	3	0.0005	0.0005 ±0.00003	±0.00005	[0.0004-0.0006]
	Dipentyl phthalate	3	0.0007	0.0006 ±0.00003	±0.00006	[0.0005-0.0007]
	Benzyl butyl phthalate	3	0.0035	0.0026 ±0.0005	±0.0009	[0.0016-0.0036]
A2	**Dibutyl phthalate**	3	0.455	0.407 ±0.036	±0.062	[0.335-0.479]
	Diethylhexyl phthalate	3	0.972	0.839 ±0.060	±0.104	[0.719-0.959]
	Diethyl phthalate	3	0.683	0.617 ±0.062	±0.108	[0.493-0.741]
	Di-iso-decyl phthalate	3	0.059	0.048 ±0.006	±0.010	[0.036-0.060]
	Di-isononyl phthalate	3	0.567	0.461 ±0.061	±0.105	**[0.339-0.583]**
	Monoamyl phthalate	3	0.0009	0.0008 ±0.00002	±0.00004	[0.0008-0.0008]
	Diheptyl phthalate	3	0.0009	0.0008 ±0.00004	±0.00007	[0.0007-0.0009]
	Dinonyl phthalate	3	0.0004	0.0003 ±0.00007	±0.00012	[0.0002-0.0004]
	Di-n-hexyl phthalate	3	0.0007	0.0006 ±0.00005	±0.00009	[0.0005-0.0007]
	Dipentyl phthalate	3	0.0008	0.0007 ±0.00003	±0.00006	[0.0006-0.0008]
	Benzyl butyl phthalate	3	0.0022	0.0019 ±0.0002	±0.0003	[0.0015-0.0023]

B1	**Dibutyl phthalate**	3	0.827	0.762 ±0.030	±0.052	[0.702-0.822]
	Diethylhexyl phthalate	3	1.822	1.728 ±0.055	±0.095	[1.618-1.838]
	Diethyl phthalate	3	0.912	0.848 ±0.029	±0.051	[0.790-0.906]
	Di-iso-decyl phthalate	3	0.087	0.079 ±0.007	±0.012	[0.065-0.093]
	Di-isononyl phthalate	3	0.800	0.733 ±0.066	±0.115	[0.601-0.865]
	Monoamyl phthalate	3	0.0035	0.0028 ±0.0007	±0.0012	[0.0014-0.0042]
	Diheptyl phthalate	3	0.0023	0.0020 ±0.0003	±0.0006	[0.0014-0.0026]
	Dinonyl phthalate	3	0.0005	0.0004 ±0.00007	±0.00012	[0.0003-0.0005]
	Di-n-hexyl phthalate	3	0.0010	0.0009 ±0.00003	±0.00005	[0.0008-0.0010]
	Dipentyl phthalate	3	0.0031	0.0026 ±0.0006	±0.0011	[0.0014-0.0038]
	Benzyl butyl phthalate	3	0.0048	0.0048 ±0.0007	±0.0012	[0.0034-0.0062]
B2	**Dibutyl phthalate**	3	0.851	0.817 ±0.033	±0.058	[0.751-0.883]
	Diethylhexyl phthalate	3	1.886	1.786 ±0.058	±0.100	[1.670-1.902]
	Diethyl phthalate	3	0.939	0.851 ±0.047	±0.082	[0.757-0.945]
	Di-iso-decyl phthalate	3	0.087	0.077 ±0.006	±0.010	[0.065-0.089]
	Di-isononyl phthalate	3	0.866	0.735 ±0.071	±0.123	[0.593-0.877]
	Monoamyl phthalate	3	0.0053	0.0035 ±0.0011	±0.0019	[0.0013-0.0057]
	Diheptyl phthalate	3	0.0053	0.0034 ±0.0012	±0.0020	[0.0010-0.0058]
	Dinonyl phthalate	3	0.0008	0.0005 ±0.00013	±0.00022	[0.0002-0.0008]
	Di-n-hexyl phthalate	3	0.0009	0.0009 ±0.00002	±0.00004	[0.0008-0.0010]
	Dipentyl phthalate	3	0.0088	0.0037 ±0.0025	±0.0044	[-0.0013-0.0087]
	Benzyl butyl phthalate	3	0.0077	0.0045 ±0.0015	±0.0026	[0.0015-0.0075]

C1	**Dibutyl phthalate**	3	0.554	0.454 ±0.058	±0.100	[0.338-0.570]
	Diethylhexyl phthalate	3	0.994	0.894 ±0.058	±0.100	[0.778-1.010]
	Diethyl phthalate	3	0.695	0.562 ±0.087	±0.150	[0.388-0.736]
	Di-iso-decyl phthalate	3	0.062	0.048 ±0.009	±0.016	[0.030-0.066]
	Di-isononyl phthalate	3	0.543	0.442 ±0.073	±0.126	[0.296-0.588]
	Monoamyl phthalate	3	0.0009	0.0008 ±0.00006	±0.00010	[0.0007-0.0009]
	Diheptyl phthalate	3	0.0009	0.0008 ±0.00006	±0.00010	[0.0007-0.0009]
	Dinonyl phthalate	3	0.0007	0.0004 ±0.00014	±0.00025	[0.0001-0.0007]
	Di-n-hexyl phthalate	3	0.0005	0.0005 ±0.00003	±0.00006	[0.0004-0.0006]
	Dipentyl phthalate	3	0.0005	0.0005 ±0.00000	±0.00000	[0.0005-0.0005]
	Benzyl butyl phthalate	3	0.0032	0.0023 ±0.0005	±0.0009	[0.0013-0.0033]
C2	**Dibutyl phthalate**	3	0.565	0.477 ±0.053	±0.091	[0.371-0.583]
	Diethylhexyl phthalate	3	0.961	0.922 ±0.025	±0.043	[0.872-0.972]
	Diethyl phthalate	3	0.654	0.536 ±0.065	±0.113	[0.406-0.666]
	Di-iso-decyl phthalate	3	0.054	0.044 ±0.006	±0.010	[0.032-0.056]
	Di-isononyl phthalate	3	0.623	0.485 ±0.089	±0.154	[0.307-0.663]
	Monoamyl phthalate	3	0.0009	0.0008 ±0.00004	±0.00007	[0.0007-0.0009]
	Diheptyl phthalate	3	0.0008	0.0006 ±0.00006	±0.00010	[0.0005-0.0007]
	Dinonyl phthalate	3	0.0003	0.0002 ±0.00003	±0.00006	[0.0001-0.0003]
	Di-n-hexyl phthalate	3	0.0007	0.0006 ±0.00006	±0.00010	[0.0005-0.0007]
	Dipentyl phthalate	3	0.0005	0.0005 ±0.00003	±0.00005	[0.0004-0.0006]
	Benzyl butyl phthalate	3	0.0042	0.0031 ±0.0008	±0.0014	[0.0015-0.0047]

D1	**Dibutyl phthalate**	3	0.803	0.705 ±0.057	±0.099	[0.591-0.819]
	Diethylhexyl phthalate	3	1.621	1.482 ±0.075	±0.130	[1.332-1.632]
	Diethyl phthalate	3	0.734	0.696 ±0.018	±0.032	[0.660-0.732]
	Di-iso-decyl phthalate	3	0.064	0.057 ±0.003	±0.006	[0.051-0.063]
	Di-isononyl phthalate	3	0.801	0.634 ±0.087	±0.150	[0.460-0.808]
	Monoamyl phthalate	3	0.0033	0.0023 ±0.0006	±0.0010	[0.0011-0.0035]
	Diheptyl phthalate	3	0.0032	0.0022 ±0.0006	±0.0010	[0.0010-0.0034]
	Dinonyl phthalate	3	0.0005	0.0004 ±0.00007	±0.00012	[0.0003-0.0005
	Di-n-hexyl phthalate	3	0.0009	0.0008 ±0.00006	±0.00010	[0.0007-0.0009]
	Dipentyl phthalate	3	0.0010	0.0010 ±0.00001	±0.00001	[0.0010-0.0010]
	Benzyl butyl phthalate	3	0.0063	0.0040 ±0.0012	±0.0020	[0.0016-0.0064]
D2	**Dibutyl phthalate**	3	0.714	0.646 ±0.034	±0.059	[0.578-0.714]
	Diethylhexyl phthalate	3	1.423	1.391 ±0.028	±0.048	[1.335-1.447]
	Diethyl phthalate	3	0.684	0.670 ±0.013	±0.023	[0.644-0.696]
	Di-iso-decyl phthalate	3	0.064	0.058 ±0.003	±0.006	[0.052-0.064]
	Di-isononyl phthalate	3	0.606	0.572 ±0.029	±0.050	[0.514-0.630]
	Monoamyl phthalate	3	0.0025	0.0019 ±0.0003	±0.0006	[0.0013-0.0025]
	Diheptyl phthalate	3	0.0025	0.0019 ±0.0003	±0.0006	[0.0013-0.0025]
	Dinonyl phthalate	3	0.0004	0.0003 ±0.00003	±0.00006	[0.0002-0.0004]
	Di-n-hexyl phthalate	3	0.0009	0.0008 ±0.00006	±0.00010	[0.0007-0.0009]
	Dipentyl phthalate	3	0.0009	0.0009 ±0.00000	±0.00000	[0.0009-0.0009]
	Benzyl butyl phthalate	3	0.0084	0.0044 ±0.0017	±0.0030	[0.0011-0.0077]

Discussions:

The provided table presents a comprehensive analysis of various phthalate compounds across multiple samples (A1, A2, B1, B2, C1, C2, D1, D2), with each compound measured in triplicate (Frequency = 3). The data includes key statistical metrics such as the maximum value (Max), average value (Average), standard deviation (±SD), standard error (±SE), and the 95% confidence interval for each compound in every sample.

Key Observations:

1. **Variability in Phthalate Concentrations**: The concentrations of phthalates vary significantly across samples. For instance, Diethylhexyl phthalate shows higher averages in samples B1 (1.728) and B2 (1.786) compared to A1 (0.946) and A2 (0.839), indicating potential differences in sample composition or exposure levels. The standard deviations (±SD) for these compounds also reflect variability, with B1 and B2 showing higher ±SD values (e.g., ±0.095 and ±0.100, respectively), suggesting greater dispersion in measurements.
2. **Precision of Measurements**: The standard error (±SE) values are relatively small, indicating precise measurements. For example, Dibutyl phthalate in sample A1 has a ±SE of ±0.058, which is a small fraction of the average (0.421), demonstrating low measurement error. Similarly, Monoamyl phthalate across all samples shows minimal ±SE values (e.g., ±0.00003 in A1), highlighting high precision for low-concentration compounds.
3. **Confidence Intervals**: The 95% confidence intervals provide a range within which the true average is likely to fall. For Di-isononyl phthalate in sample C2, the interval [0.307-0.663] is wide, reflecting higher uncertainty due to larger ±SD (±0.154). In contrast, Dipentyl phthalate in sample C1 has a narrow interval [0.0005-0.0005], indicating very consistent measurements.
4. **Notable Outliers**: Some compounds, like Dipentyl phthalate in B2, exhibit unusual confidence intervals

Appendix 2



Appendix 2: High Performing Liquid Chromatography used for instrumental Analysis

Source: Authors Analysis 2025.



Appendix 2: Site of Sample Collection (Gbagi Groundwater Samples Collected)

Source: Authors Analysis 2025.



Appendix 2: Collected Samples for Liquid-to-Liquid Extraction before Analysis,

Source: Author's Analysis, 2025

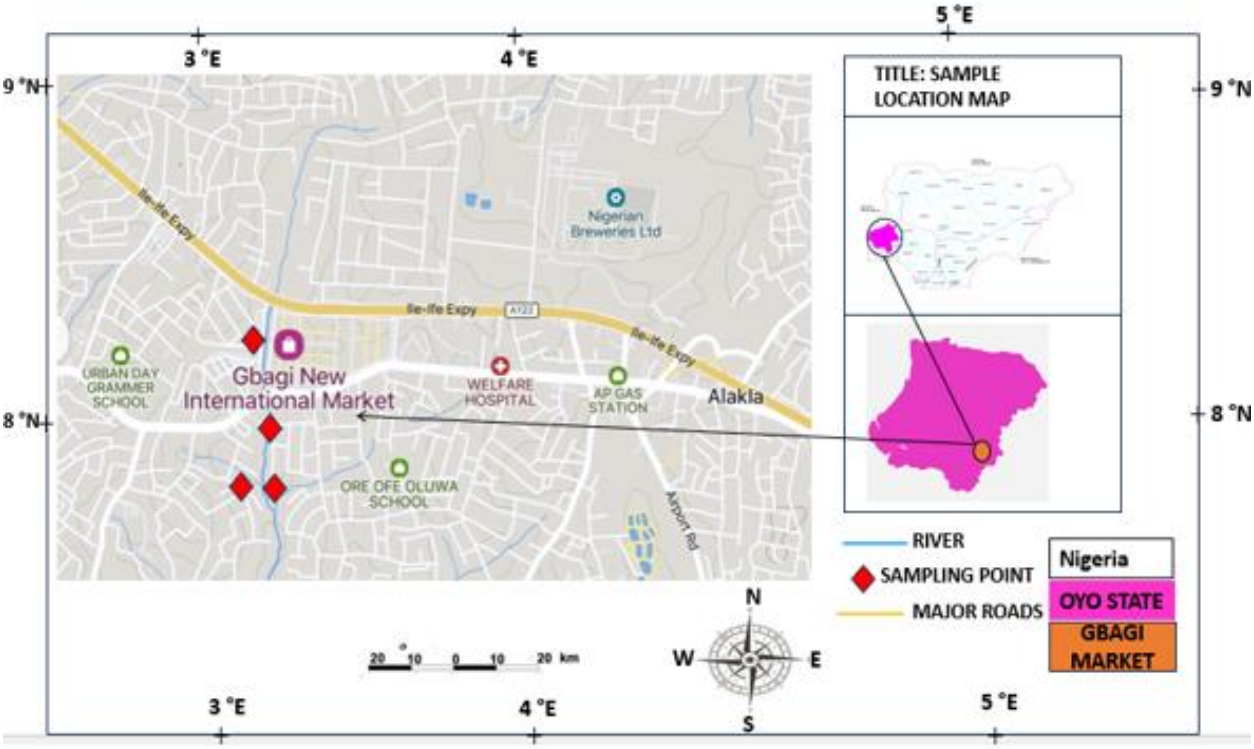


Appendix 2: Extracted samples ready for Analysis

Source: Author's Analysis, 2025

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Appendix 3



Appendix 3: Map of Sampling Location

Source: Researcher's Field Work, 2025

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Bio-data

A. Personal Data

Full Names	Bayonle Bukunmi OPALADE
Permanent Home Address	Falana community, Iyana Agbala Ibadan
E-mail Address	bayonleopalade@yahoo.com
Phone Number	08161215957
Date of Birth	**08/08/1994**
Place of Birth	**Ibadan**
Nationality	Nigerian
Next of Kin	Opalade Temitope
Address	Oluwo Ibadan

B. Education Background

SSCE

BS.C

Educational Institutions Attended with Dates and Qualifications

EKITI STATE UNIVERSITY ADO EKITI EKITI STATE

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Signature **Date**

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Signature **Date**