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Identification And Quantification of Phthalate Esters in Asa River, Ilorin, Kwara State Nigeria.

***Ojo Olayiwola Mary,**

University Health Centre, Elizade University, Ilaramokin, Ondo State.

Abstract

The study on the identification and quantification of phthalate esters was conducted in ASA River Ilorin, Kwara State. The research aims at preventing every form of pollution that is harmful to living organisms, the idea is to protect and sustain lives by preventing toxins that can be produced from the pollution. However, water pollution results when unwanted substances enter into the water, which changes either the physical, biological or chemical quality of water which can result in harmful to the environment and human health including discharge of domestic waste, industrial effluent, marine dumping, and radioactive waste are main causes of water pollution. Chemicals are disposed of and industrial waste can accumulate in lakes and rivers, proving harmful to living organisms. The study identified four major degrees of contamination with the fourth degree posing a great threat in the ASA River thus water pollution and chemical discharges were the major types and sources of phthalate in the river based on the result of the study. The result obtained from the report indicated that the continuous discharge of industrial effluent in River ASA and its tributaries has resulted in a marked decline in the whole fish population in general most especially those species that are very sensitive to oxygen depletion due to the effluent pollution. The study however made some vital suggestions which include public awareness on the effect of phthalate esters, treatment of industrial effluent before discharging into water, sanctioning of intruders, discouragement of settling of chemical industries and provision of regulations as guides.

Keywords; Phthalate Esters, Water, Pollution, Health and Environment.

1.0 Introduction

The Federal Environmental Protection Agency (FEPA) Act Section 38 of Cap 131 LFN (1990) defines pollution to mean man-made or man-aided alteration of the chemical, physical, or biological quality of the environment to the extent that it is detrimental to that environment or beyond acceptable limits. Water pollution results when unwanted substances enter into the water, which changes the physical, biological or chemical quality of water which can result in harm to the environment and human health (Mehtab*et al.,* 2017). Man-made activities such as improper waste disposal, agricultural practice, pesticide and fertilizer application, and discharge of plastics and polythene bags into water bodies. Urbanization and weak management systems are the common leading factors influencing water quality in the world (Mehtab*etal*., 2017).

Discharge of domestic waste, industrial effluent, marine dumping, and radioactive waste are the main causes of water pollution. Chemicals are disposed of and industrial waste can accumulate in lakes and rivers, proving harmful to humans and animals (Wang and Yang, 2016). Toxic from industrial waste is the major cause of immune suppression, reproductive failure and acute poisoning. Infectious diseases, like cholera, typhoid fever and other diseases gastroenteritis, diarrhoea, vomiting, and skin and kidney problems can transfer through polluted water. Polluted water can contaminate plants thereby rendering it unfit for human consumption as well as animals which can affect their health when fed (Chen *et al*., 2018). Water pollutants are killing seaweeds, molluscs, marine birds, fishes, crustaceans and other sea organisms that serve as food for humans (Hader et al., 2020).The weakening of water quality is expected to rise over the next decades and this will increase threats to human health, the environment and sustainable development. An estimated 80% of all industrial and municipal wastewater gets into the environment without any prior treatment, leading to the growing deterioration of overall water quality with detrimental impacts on human health and ecosystems in general (UN Water Report, 2018).It was reported that 75 to 80% of water pollution is caused by household sewage, Waste from industries like sugar, textile, electroplating, pesticides and paper pollutes the water, Polluted rivers have intolerable smells and contain fewer plants and animals(Okereke et al., 2016). 80% of the world's population is facing threats to water security. A large amount of domestic sewage is disposed into the rivers and most of the sewage is untreated.The harmful material discharged from the industries is responsible for surface water and groundwater contamination. Contaminant depends upon the nature of industries. Toxic metals enter into water and reduce the quality of water drastically. 25% of pollution is caused by industries and is more harmful than domestic waste (Ipeaiyeda and Onianwa, 2018).Environmental problems respect no limit but intimidate the health and wealth of nations. The UN Third World Water Forum in Japan in March 2003 projected in their statement that the world water crisis would affect many countries in the world by the year 2050, when up to 7 billion people in 60 countries could face serious water shortage, 1.2 billion people do not have access to safe drinking water, more than two million die each year from diseases related with unwholesome water (Wito, 2015).

1.1 Objectives

The major aim of the study is to assess the identification and quantification of phthalate ester in Asa River, Ilorin, Kwara State, Nigeria.

The specific objectives of the study are to;

i. Identify the types of phthalate ester in Asa River, Ilorin, Kwara State, Nigeria.
ii. Quantify the amount of phthalate ester in Asa River, Ilorin, Kwara State, Nigeria.

iii. Proffer ways to reduce the presence of phthalate ester in our river.

2.0 Literature Review

2.1 Water Is Essential for Life.

No living being on the planet Earth can survive without water. Water use has a large impact on the environment in terms of its ecological impact, and economic and agricultural impact. Therefore, water is a basic necessity in daily life, so water needs to be monitored and protected to safeguard the environment and public health (Faust *et al*., 2018). The major part of water on earth is marine water which cannot be used without processing by human beings. The only available freshwater which could be used for drinking purposes arises from the groundwater. The per cent volume of it, however, is sufficient to cater for the needs of the living beings, provided it would have been of high quality. Water quality is important in our lives because it is essential to support the physiological activities of any biological cell (Maduka, 2016).

2.2 Types of Water/Sources of Water

The most common sources of water supply are basically classified into three which include: surface, groundwater, and storm/ rain water (precipitation).

2.2.1 Surface Water

According to Hanasaki*et al.,* (2018), surface water is the water on the surface of the planet such as rivers, lakes, wetlands, oceans and dams.

2.2.2 Groundwater

Is the water found below Earth's surface in soil pore spaces and the fractures of rock formations? A unit of rock or an unconsolidated deposit is called an aquifer when it can yield a usable quantity of water. The depth at which soil pore spaces or fractures and voids in rock become completely saturated with water is called the water table. (Jia *et al.,* 2017).

2.2.3 Rainwater /Precipitation

Is any form of water inthe form of snow, rain, or from the atmosphere (Vlastos*et al.*, 2019).

2.3 Importance of Water

Wholesome water is important in health and developmental issues, both at the global level and local levels in some areas of investment, water supply and sanitation can result in the promotion of the economic status of an area, by reducing health causes. According to Westall*et al*. (2018), water is essential to life because is the ingredient of life and also for chemical reactions. However, water is used to determine the early emergence of life, it is also used in metabolic processes, are also used for maintaining the body system (homeostasis) (Kambar, 2015). Water is important in Agricultural activities, and agriculture is the bedrock of the economic sector for many countries as a result the water used in agricultural activities in countries like Brazil and Argentina became major world players in the agricultural commodities at the world market contributing to 13% of global green water export and at lower-level agriculture yet play some vital roles for the food security of the population (Erika *et al*., 2014). Water also plays a vital role in domestic activities in the community. Many communities use surface water and shallow wells, as their main sources of water supply in urban areas of developing nations. Some use this water for bathing, drinking and washing.

2.4 Pollution

It is the introduction of contaminants into the natural environment that causes adverse effects. Pollution can take the form of chemical substances such as noise, heat or light. The components of many pollutants may be either foreign substances/energies or naturally occurring contaminants. The increasing population is creating many issues but it also plays a negative role in polluting the water. Increasing population leads to an increase in solid waste generation. Solid and liquid waste is discharged into rivers. Water is also unhygienic by human excreta. In polluted water, a huge number of bacteria are also established which is unsafe for human health. The government is not sufficiently expected to supply important needs to citizens because of an increasing population. Hygiene facilities are more in city areas than in rural areas. Polythene bags and plastic waste a major source of pollution. Waste is thrown away by putting it into plastic bags. It is estimated that three core people of urban areas defecate in the open. 77% of people are using flush latrines and 8% are using pit latrines. Urbanization can cause many infectious diseases. Overcrowding, unhygienic conditions, and unsafe drinking water are major health issues in urban areas. One-quarter of the urban population is susceptible to disease. Pesticides are used to kill bacteria, pests and different microorganisms. Chemical-containing pesticides are directly polluting the water and affecting the quality of water. Industries that produce waste contaminate water sources and drastically affect water quality (Ho *et al*., 2012).

If pesticides are excess in amount or poorly managed, then it would be hazardous to the agricultural ecosystem. Only 60% of fertilizers are used in the soil other chemicals leach into soils polluting the water, cyanobacteria are rich in polluted water and excess phosphate runoff leads to eutrophication. Residues of chemicals mix with river water due to flooding, heavy rainfall, and excess irrigation and enter the food chain. These chemicals are lethal for living organisms and many vegetables and fruits are contaminated with these chemicals. Trace amounts of pharmaceuticals in water also cause water pollution and it is dangerous to human health. Domestic sewage is contributing to water pollution in Nigeria. Many household wastes are discharged directly into water bodies without being treated which seriously is becoming a major public health concern and this hurts the environment (Kamble, 2014). Pollution is often classified as a point and non-point source (Causey et al.,2015).

2.5 Sources of Water Pollution

Water pollution either in groundwater or surface water is contaminations or alterations of the chemicals, physical, and biological characteristics of water that cause them to be unfit

or dangerous to public health, to plants, animals, or aquatic life dependent on water. (Hasan *et al*, 2019).

The high global occurrence of phthalates in different environmental media has resulted in the detection of their metabolites in human urine, blood, and breast milk, indicating widespread human exposure. In addition, the notorious endocrine-disrupting effects of phthalates have shown that they mimic or antagonize the action of endogenous hormones, consequently producing adverse effects on reproduction, growth and development. (Olujimi, 2017). Many studies showed that there is a significant occurrence of phthalate esters (PEs) in water, sediment and biota example fish, a classic example was the research conducted from two lagoons (Epe and Lagos) in Nigeria. Two fish species (*Tilapiaguineensis*, and *Chrysichthysnigrodigitatus*) and a crustacean (the African river prawn Macrobrachiumvollenhovenii). Phthalate esters level was discovered and analyzed showing bioconcentration factor (BCF), in fish, biota-sediment accumulation factor (BSAF) and phthalate pollution index (PPI) in the biota and environment. (Olujimi, 2017). Some facts show the presence of phthalate esters in the fish species which interferes with the growth and health condition of the fish species and also is found in water and Sediment PE at different levels in the rivers. Various research showing concentrations of phthalate esters such as DEHP and DEPDBP were observed in fish, river and sediment

2.5.1 Non-Point Source

Refers to wastewater that comes from different sources such as farmland, street and storm water flow. (Evans et al., 2019). Non-point source is water pollution that is caused by the different dispersed sources of pollution, non-point majority of non-point sources cause pollution problems related to pollutants carried by runoff from rain and snow melt, other pollutant sources such as spills and leaks, atmospheric deposition and hydrologic modification. (Ahmed and Ismail, 2018). Non-point pollutants affect groundwater and surface water, examples of non-point sources of water pollution are runoff from urban and rural areas, industrial sites, mines sites, livestock, oil spillage, waste disposal areas land landfills, lodges and manure. Road runoff and urban stormwater discharge, car parks are large runoff produce areas that are often contaminated with sediment, litter, oil and petrol, and with toxic metals from motor vehicles. Water carrying this contaminant is washed into dries and directly into nearby water bodies, most surface water drains are collected directly to water bodies or courses.

2.5.2 Point Source

It is a source of water pollution that comes from an identifiable source such as industries, abattoir discharge and household effluent. (Causey et al.,2015). Point source pollutant in surface water is mostly found in a plume that has the greatest concentration of pollutants nearest the source, the different types of point source pollutants found in water mostly come from businesses, industries, domestic, animal waste treatment, hospital waste point source in groundwater from industries include discharge of chemicals commonly called volatile organic compound, which include manufacture and refined substances oil, paint fuel products. In general, it takes only a small amount to raise health concerns for example approximately 4 litres (about 1 gallon) of pure trichloroethylene, a common solvent, will contaminate over one billion litres (300,000 gallons of water). (EPA, 2018). Once the ground is contaminated it is difficult, costly, and even sometimes it is difficult to clean up the area. (EPA, 2018). The most common sources of point source pollutants in water are higher temperature discharge, and micro-organisms such as bacteria, and viruses. (EPA, 2018).

2.6 Types of Pollution

The different types of pollution include but are not limited to air pollution, soil pollution, and water pollution.

2.6.1 Air Pollution

It is the introduction of harmful substances into the air which alter it is original quality as a result of human activities or natural occurrences. Human activities such as industrial, and domestic activities, are natural as a result of volcanic eruptions, earth quakes. However, air pollution is associated with many health impacts including chronic obstructing pulmonary diseases and acute disease as well as cerebra-vascular cancer, and heart diseases (Evelyn, and Tyav, 2012).

2.6.2 Soil Pollution

It is the contamination of land as a result of improper waste disposal, dumping of chemical waste by factories and industries, and deforestation. (Evelyn and Tyav 2012).

Soil is formed by the decomposition of rocks and organic matter over a decade due to the process of weathering, soli properties differ from place to place with the differences in bet rock compositions, climate and other factors, certain chemical elements occur naturally as the compositions of minerals, and still may be toxic at some concentration (aware &Ohlmeyer, 2014). Other potentially harmful substances can get into the soil through human activities, soil contamination may be responsible for health effects costing millions of Euros, especially in infancy health problems from cancer (arsenic, asbestosis) and kidney diseases as a result of lead, mercury and cadmium exposure, and persistent organic chemicals examples VOCs are of particular concerns due human activities to our soil pollution through mines, agriculture, industries. Soil contamination Over 200 years has contributed to causing soil contamination and become very widespread in Europe, decision-makers, scientists, businesses, and individual citizens generally agree that air and water pollution hurt human health, but the impact of soil pollution on our health has had a much lower profile and are not so well understood. In a country like Europe the health impact of long-term, low-level exposure to soil contaminants is of particular interest, among decision-makers and researchers who both realize the lack of information in this area (Tang et al., 2019).. In some cases, there are clear explanations that show specific types of contaminants in air or water and their health effect (Nematu*et al, 2012).* However, until recently, the impact of soil pollution on our health has had a much

lower profile even though researchers are trying to point out the problems associated with soil pollution such as soil sealing, erosion and soil contamination

Soil pollution can be caused as a result of intensive industrial activities, inadequate waste disposal, mining, military activities, or accidents all those have introduced excessive amounts of contamination in the soil in this case the plant can also absorb contaminants in the soil, and the contaminant can be washed and taken to water bodies (storm water). Therefore, soil quality must be ensured by looking at physical, chemical and biological parameters since soil serves as environmental media where agricultural activities are carried out and serves as habitation for humans, plants, and animals as well as microorganisms, good quality of soil is directly proportional to the human, plant and animal. (Nematu*et al., 2012).*

2.6.3 Water Pollution

It is defined as any impairment in its native characteristics by natural or addition of anthropogenic contaminants to the extent that it either cannot serve humans for drinking purposes and/or to support biotic communities, such as fish. (Babayemi et al., 2016) Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater by human activities.(Obi china and Rimande, 2018) All water pollution affects organisms and plants that live in these water bodies and in almost all cases the effect is damaging not only to the individual species and populations but also to the natural biological communities. It occurs when pollutants are discharged directly or indirectly into water bodies without adequate treatment to remove harmful constituents. The water of rivers, ponds, as well and the like as well as industry's purpose in most cases there is little treatment of water this brought the issues of about 80% of freshwater flowing on the surface of the land are polluted, these polluted passing through the surface poison waste estimated of about 16,662,000000 litres of contaminated water is produced daily in towns with a population of million in India (Mekonnen and Hoekstra, 2015). The commonest water pollution is ground and surface water pollution, which is mainly the result of improper waste disposal, industrial activities and poor sanitary landfills caused by municipal solid waste management (Kamar Uddin et al., 2017). In Nigeria, most of the industries are situated along the river banks for easy availability of water and also disposal of the wastes. These wastes often contain a wide range of contaminants such as petroleum hydrocarbons, chlorinated hydrocarbons and heavy metals, various acids, alkalis, dyes and other chemicals which greatly change the pH of water. The waste also includes detergents that create a mass of white foam in the river waters. All these chemicals are quite harmful or even fatally toxic to fish and other aquatic populations (Adewoye, 2013).

It is found that one-third of the total water pollution in Nigeria comes in the form of industrial effluent discharge, solid wastes and other hazardous wastes. Most of these defaulting industries are petrochemical industries, sugar mills, soap and detergent, distilleries, leather processing industries, paper mills, agrochemicals and pesticides manufacturing industries and pharmaceutical industries. For such industries surface water is the main source for waste disposal (Elleta and Ogundiran, 2015).

In Nigeria, it is estimated that 80% of industrial effluents and emissions are discharged without any form of treatment. Major coastal towns and cities such as Lagos, Warri and Port-Harcourt have large human populations but invariably lack sewage treatment plants except in a few relatively new and isolated residential or industrial estates. Most residents use septic tanks whose contents when dislodged are discharged into coastal rivers, lagoons and near shore waters without further treatment. The associated problems include increases in BOD and the introduction of pathogenic microorganisms and intestinal parasites which pose risks to swimmers and fishermen as well as the general public (Ahmed and Ismail, 2018).

Untreated or allegedly treated industrial effluents often contain variable amounts of heavy metals such as arsenic, lead, nickel, cadmium, copper, mercury, zinc and chromium. These heavy metals have a marked effect on the aquatic flora and fauna which through bio-magnification enter the food chain and ultimately affect human beings as well. Heavy metal pollution is an ever-increasing problem for aquatic bodies. These toxic heavy metals entering an aquatic environment are adsorbed onto particulate matter, although they can form free metal ions and soluble complexes that are available for uptake by biological organisms (Adewoye, 2013).

However, in Kano Nigeria study conducted reveals that unprocessed wastewater from Challawa and Sharada industries which are being discharged into Challawa river is the major factor responsible for its contamination hence, regular monitoring is needed given that the river is used for a variety of purposes including, fishing irrigation, domestic and water supply (Bernard and Ogunleye, 2015). The parameters of interest were common waste-derivable chemical constituents such as nitrate (NO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}) and indicator microorganisms like *Escherichiacoli*. The study showed that about 22% of the samples had concentrations of NO_3^- higher than the WHO permissible level (45mg/L) while 80% of the samples analyzed to test the bacteriological quality of the groundwater showed evidence of sewage and industrial effluent contaminations. The identification of *E. coli* in the water indicates faecal contamination (Nurliyana et al., 2018). Improvement in the management of both domestic and industrial wastes would improve the quality of both surface and ground water hence, the necessity for the reduction or rather elimination of water pollution.

The river water is mainly used for irrigation, watering livestock and vegetable fields, fishing, washing and bathing, effluent and waste disposals. Oseere River is found in the upper regions of the water body which receives industrial wastes except for domestic sewage, refuse and wastewater from homes, and agricultural wastes. Okun River is found downstream of Oseere and shares a direct border with Asa River and it is the point of discharge of industrial, agricultural and domestic wastes. Both Oseere and Okun provide no recreational and fishing activities. Asa River is located downstream, where water from Asa Dam, Oseere

and Okun drains; unlike in the past its recreational and commercial fishing activities have been greatly reduced and this may be linked to the gross misuse of the river.

2.7 Industries Along Asa River

Several numbers of large and small-scale industries and industrial units are located along the stretch of these rivers and they all use these water bodies as their waste-discharging points. Among these are: the soap and detergent industry, foam-producing outlets, flour mill, pharmaceutical industry, breweries, photo laboratories, several cassava processing units, poultry farms, countless agricultural premises and mechanical workshops. Unluckily, all the above-mentioned units are without proper effluent treatment facilities and the effluents from them end – up in the Okun stream which eventually empties into the Asa River, either directly or indirectly through canals and urban run-offs. These pollutants have not only deteriorated the river water and sub-surface water but also there has been a continuous impairment in the aquatic population of edible species. The populace living at the river banks has also been complaining about the deteriorating trend of the river, which is very obvious and has often resulted in periodic fish kills as reported by the local fish farmers in the area. It has also been reported that the continuous discharge of industrial effluent in River Asa and its tributaries has resulted in a marked decline in the whole fish population in general; especially those species that are very sensitive to oxygen depletion due to the effluent pollution (Opasola et al, 2019). River Asa runs through an industrial area in Ilorin, Kwara state, and the river flows through the town of Ilorin resulting in the contamination of the river water due to the continuous discharge of industrial effluents (Olawale et al, 2019).

2.8 Volatile Organic Compound (Vocs)

Are organic chemicals that have high vapour pressure at ordinary room temperature surrounding air, a trait known as volatility. For example, Semi-Volatile Organic Compounds (SVOCs), such as phthalate, formaldehyde, acetaldehyde, hex aldehyde, benzaldehyde, benzene e.t.c (Cicolella, (2018).

2.8.1 Phthalate Esters (Paes)

Phthalate esters (PAEs) are well-known polymer additives and are widely used in industries as plasticizers for polymeric products especially cellulose esters and vinyl chloride copolymers (Gobas et al., 2020). A non-plasticizer such as paints, varnishes, cosmetics, insect repellants, insecticides carriers, propellants building materials, automobile parts and food packaging to improve their flexibility, transparency, durability, longevity and altering physical properties like malleability and flame resistance of synthetic products (Clara et al., 2010). Phthalates are also found in many household products including children, plastic toys, adhesive materials, polish, perfumes, and air fresheners, polish exposure to phthalates can predispose individual health (Swan et al., 2015). An estimate of 8 billion tons of phthalate esters is reported being used globally each year, particularly as additives to plastics products, industrial chemicals and parts of several consumer products.

Due to the additive's nature of these contaminants, phthalates exist freely and are not chemically bound to the polymer chain in a freely mobile phase and drain away; hence they can drain away, migrate or evaporate into the environment via domestic and industrial effluents, sewage sludge, storm water, runoffs and indiscriminate dumping of phthalate products. These contaminants have been found in air, food, water and soil, organisms, tissues and fluids of wildlife (Gobas et al. 2020).

2.9 Types of Phthalate Esters

According to Kanchanamayoo et al., (2012), the following are types of phthalate esters.

Di-ethyl Phthalate (DEP)

Di-ethyl Phthalate (DEP): Associated with changes in hormone levels and genital development in humans.

Di-n-butyl Phthalate (DBP)

Di-n-butyl Phthalate (DBP): Recognized as a reproductive toxicant by the National Toxicology Program and the State of California. It can lead to changes in genital development.

Di-isobutyl Phthalate (DIBP)

Di-isobutyl Phthalate (DIBP): Associated with changes in male genital development

Dimethyl Phthalate (DMP)

Dimethyl Phthalate (DMP): Inconclusive evidence has shown reproductive toxicity in animal studies

Di-isohexyl Phthalate (DIHP)

Di-isohexyl Phthalate (DIHP): Limited toxicity testing has shown that DIHP is probably a developmental and reproductive toxicant.

2.10 Industrial Uses of Phthalate Esters

Phthalates are used in industries for the manufacturing of different products such as packaging, children's toys, adhesives and glues, paints, pharmaceutical and personal care products, detergents, textiles, vinyl flooring, electronics, medical devices and insect repellants, insecticide carriers, propellants building materials, air fresheners, automobile parts food packaging with aim of improving their flexibility, transparency, durability, longevity and altering physical properties like malleability flame resistant of synthetic products (Godwin *et al*., 2016).

2.11 Health Implication of Phthalate Ester on Human

Phthalate has a great effect on the excretory system and also affects newborn babies because is a toxic chemical and newborn babies have low immature metabolism (Colon et al., 2010). Phthalates act as endocrine disruptors that have reproductive effects in the human body that cause low sperm count, low levels of estrogen, and infertility generally speaking (Hoppin, et al., 2014). Testicular cancer, male infertility, genital malformations and reproductive abnormalities including hypospadias and cryptorchidism are known as the Testicular Digenesis Syndrome (TDS), which is affected by a combination of genetic predisposition, and lifestyle. The age and development stage of the organism seems to be a very important factor that determines the system that will be injured and the extent of the adverse outcome of the phthalate effect (Latini, 2017). Phthalates have something to do with the reproductive system of

domestic animals in many ways One of the few reports in farm animals indicating endocrine disruption caused by environmental pollutants such as phthalate regarding heifers that were drinking water in direct contact with a sewerage overflow. These animals showed increased age at first calving (Hoppin et al., 2014)

2.12 Environmental Effect of Phthalates

Because of their large and widespread application, phthalates or phthalic acid esters (PAEs) are found in all the environmental media. They have been widely detected throughout the worldwide environment. Indoor air where people spend 65−90% of their time is also highly contaminated by various PAEs released from plastics, consumer products as well as ambient suspended particulate matter. Because of their widespread application, PAEs are the most common chemicals that humans are in contact with daily. Based on various exposure mechanisms, including the ingestion of food, drinking water, dust/soil, air inhalation and dermal exposure the daily intake of PAEs may reach values as high as 70 µg/kg/day (Nematu et al., 2012). PAEs are involved in endocrine disrupting effects, namely, upon reproductive physiology in different species of fish and mammals. They also present a variety of additional toxic effects for many other species including terrestrial and aquatic animals and plants. Therefore, their presence in the environment has attracted considerable attention due to their potential impacts on ecosystem functioning and public health. PAEs are found in every part of environmental matrices: air, water, sediment, sludge, wastewater, soil, and biota (Nematu et al 2012).

3.0 Materials and Methods

3.1 Study Area

River Asa is located in Ilorin, Kwara State Nigeria. Ilorin has an area of bout 100km^2 (Adewoye, 2010) and according to UN projection, the population of Ilorin is 1,450,000 million as of the year 2023. Ilorin is on latitude 8 30'N and 4 35'E and has an elevation of about 273m to 333 m above sea level. It is a humid tropical city characterized by both wet and dry seasons. The wet season starts in April and ends in October, while the dry season starts in November and ends in March (Adeniran et al., 2018). The mean annual rainfall is 1150mm while the mean annual temperature ranges from 25-28.9^{o}C. The city has a relative humidity which ranges from 65-80%. Due to the level of waste management, some residents in the city empty their wastes into the river and some of its tributaries such as Aluko, Alalubosa, Okun, Agba, Oseere and Atikeke. The basin ranges in size between 5.8 and 7.1 km^2. Okun, Aluko and Oseere tributaries are located on the western part of Asa River, while the others can be found on the eastern part. Asa River and two of its major tributaries (i.e. Okun and Oseere) are prone to contamination because of their visible location along the stretch of the city's industrial estate. The runoff discharge in the studied area reflects closely the rainfall pattern with periods of peak maximum discharge coinciding with periods of heavy rainfall. Total rainy season runoff values in Okun and Oseere are between 94.6% and 85.8% while about 14.3mm and 12.2 mm in the dry season. (Adeniran et al. 2018).

3.2 Collection of Samples

Water samples were collected from three points; upstream, mid and downstream along the river Asa into a clean glass bottle, preserved with dilute nitric acid and stored in an ice pack until arrival to the laboratory for analysis.

3.3 Samples Handling and Pre-Treatment

Water was collected in an amber glass container. Conventional sampling practices were followed. No special sample preservation and storage were taken since phthalates are stable at pH 7.0 samples were collected and sealed with a glass stopper followed by a metal clip. The samples were refrigerated at 4^{0}C free from light from the time of collection until extraction.

3.4 Extraction of Water Samples

Cyclohexane internal standard solution and then 9ml cyclohexane. With the aid of glass glass-coated magnet, the sample was the liquid/liquid intensity extracted for a minimum of an hour. Using an upward delivery glass separating funnel, the solvent extract was then isolated in a 10ml vial. The sample volume is 1L in 10ml cyclohexane

3.5 Analysis of Phthalate Ester in Water

The new method for analysis of phthalate in water samplesGC/ MSwas validated (Godwin *et al, 2016*).

3.6 Instrumental Analysis

High-performance liquid chromatography (HPLC) was done with Agilent HPLC 1260 infinity series; which was used in determining the presence and level of phthalate ester in the water and sediment samples. The HPLC conditions were as follows: Zorbax Eclipse AAA C18 column 150 mm × 4.6 mm i.d., particle size of 3.5 µm, 228 nm wavelength, temperature 40ºC, injection volume 20 µl and gradient elution condition using acetonitrile and water (90:10 v/v) as mobile phase. Under this condition, separation lasted for about 4 min with a flow rate of 1 mL/min for the first four minutes then 2 ml/ min. Identification of individual phthalate ester was established based on its retention time and quantification was performed by a combination of internal standardization and response factor.

4.0 RESULTS AND DISCUSSION

The efficiency and reliability of the analytical method employed were determined by the analysis of the response factor, retention time and percentage recovery. The phthalates were eluted from the column in the order of dim ethyl- (DMP), diethyl- (DEP), dibutyl- (DBP), and biphenyl phthalates(DPP).The response factor and retention time are indicated in Table 1. The recovery analysis was done to prove the reliability of the analyticalmethodemployed.Thepercentagerecoveriesrangedf rom78.0%in diethyl-and 94.3% indiphenyl-phthalates(DPP).

The quantitative results of phthalates in water at the designating sampling locations along the stream are presentedinTable2.The concentrations of phthalates obtained in this study showed several occurrences of phthalate inAs stream.

Table 2 presents the levels of phthalate esters in water

samples. The phthalates esters determined in the water >DBP. A glance at the concentrations of phthalate esters showed the presence of dim ethyl phthalate in all sites. Generally, the levels of DMP are higher than all other phthalate compounds. Deputy phthalate was detected only in Sample 4 while biphenyl phthalate was detected in Sample 4 and 5. The mean levels of phthalate in the stream water ranged from 1.29 µg/L for dibutyl phthalate to 938 µg/L for dim ethyl phthalate. The level of dilution between DBP and DMP was above 450-fold. The presence of phthalate ester in this water body could be due to local contamination from industrial wastes including disposable plastic materials (suchastiles, wire coatings, syntheticleathers, wallpapers, wrapping materials and plastic soft drink bottles)and agricultural wastes, from the motor park and market area thrown into the water body at Sp 1(stream), farming as well as recreational activities occurring along the stream bank. Burning oftyres at an abattoir located at Sp 1(stream) and refuse incineration could also be a good source of phthalates in this water body. The values reported in this study for the stream are above the USEPA water criteria of 3 µg/L for the survival of fish and other aquatic life in rivers (USEPA,1980).
Other aquatic life in rivers (USEPA,1980).

Table1. Valuesofresponsefactor, retentiontimeandper centre coveries.

Compound	Response factor	Retention time(min)	%Recovery
DEP	0.27	1.86	78.0
DBP	0.85	2.96	85.5
DMP	0.21	1.62	88.7
DPP	0.47	2.25	94.3
n-Butylbenzoate:		1.28	

Table2. Levelsofphthalateesters(µg/L)in water samples from ASA stream.

Station	DEP	DBP	DMP	DPP	Σ4Pes
Sp1	ND	ND	74.8±45	ND	75
Sp2	ND	ND	1980±62	ND	1980
Sp3	505±74	ND	1440±570	ND	1945
Sp4	ND	6.43±3.10	81.4±48	21.3±13	109
Sp 5	ND	ND	1110±560	6.35±9.0	1116
Mean	101±16	1.29±1.3	938±780	5.53±6.5	

5.0 Conclusion and Recommendation

5.1 Conclusion

This study provides information on the contamination levels of four PAE sintheAsa River, Ilorin, Kwara State Nigeria. The levels of phthalate esters recorded in this study were at levels that raise concern. The state Environmental Protection Agency needs to adopt a constant monitoring plan so that the concentrations of this persistent organic pollutant discharged into the water body conform with international standards.

5.2 Recommendation

- Treatment of industrial effluent before discharge into water source
- Regular monitoring of the concentration of pollutants in water by environmental protection agencies to ensure conformity with international standard
- Industries discharging their effluent into water bodies without adequate treatment should be sanctioned.
- Sitting industries especially production industries that make use of phthalates should be discouraged.
- Public awareness on the effect of phthalate esters.

References

Ahmed, S., & Ismail, S. (2018). Water pollution and its sources, effects & management: a Case Study of Delhi. *Shahid Ahmed and Saba Ismail (2018)' Water Pollution and its Sources, Effects & Management: A Case Study of Delhi', International Journal of Current Advanced Research*, *7*(2), 10436-10442.

Babayemi, J. O., Ogundiran, M. B., &Osibanjo, O. (2016). Overview of environmental hazards and health effects of pollution in developing countries: a case

study of Nigeria. *Environmental Quality Management*, *26*(1), 51-71.

Bernard, E., & Ogunleye, A. (2015). Evaluation of tannery effluent content in Kano Metropolis, Kano State Nigeria. *International Journal of Physical Sciences*, *10*(9), 306-310.

Blount BC, Milgram KE, Silva MJ, Malek NA, Reidy JA, Needham LL2009 Quantitative Detection of Eight Phthalate Metabolites in Human Urine Using HPLC-APCI-MS/M. AnalyticalChemistry72(17):4127-4134.

Chang BV, Yuan SY, Liu C, Liao CS (2002). Occurrence and microbial degradation of phthalateestersinTaiwanriversediments. Chemosphere 40:1295-1299.

Chen W, Kan AT, Pu G, Vignona LC, Tomson MB (1999). Adsorption-desorptionbehavioursofhydrophobicorganiccompoundsinsediments of Lake Charles Louisiana, USA. Environ. Toxicol. Chem.18:1610-1616.

ClaraM, WindhoferG, HartlW, BraunK, SimonM, GansO, Scheffknecht C, Chovanec A (2010). Occurrence of phthalates in surface run off, untreated and treated waste water and fate during waste water treatment. Chemosphere 78:1078-1084.

ColonI, CaroD, BourdonyCJ, RasarioO(2010). Identification of Phthalate EstersintheSerumofYoungPuertoRicanGirlswithPrematureBreastDevelopment,Environ.HealthPerspect.108(9):895-900.Doi:10.1289/ehp.00108895

Elleta, 2006; Ogundiran*et al*., (2015). European Union Risk Assessment Report on Bis (2-ethylhexyl)Phthalate(DEHP).InstituteofHealthandConsumer

Erika *et al* MP(2014).Socialandeconomicinterest in the control of phthalic acid esters, Trends Anal. Chem.22:847-857.

Evans, Alexandra EV, et al. "Agricultural water pollution: key knowledge gaps and research needs." *Current opinion in environmental sustainability* 36 (2019): 20-27.

Evelyn, M. I., &Tyav, T. T. (2012). Environmental pollution in Nigeria: The need for awareness creation for sustainable development. Journal of research in forestry, wildlife and environment, 4(2), 92-105.

Faust *et al*., AO (2018). Procedural clean-up technique fordetermination of phthalate esters in an aquatic environment. Int. J.Environ.Stud.44(4):237-243.Doi:10.1080/00207239308710864

FEPA (1990).Flame ionization gas chromatographic determination of phthalate esters in water surface sediments and fish species in the Ogun River catchments , Ketu, Lagos, Nigeria. Environ. Monit. Assess. 172:561-569.

Opasola, O. A., Adeolu, A. T., Iyanda, A. Y., Adewoye, S. O., & Olawale, S. A. (2019). Bioaccumulation of Heavy Metals by Clarias gariepinus (African Catfish) in Asa River, Ilorin, Kwara State. *Journal of Health and Pollution*, *9*(21).

Olawale, S. A., Emmanuel, A., & Aishat, A. (2016). Concentrations of heavy metals in water, sediment and fish parts from Asa River, Ilorin, Kwara State. *Imp J Interdiscip Res [Internet]*, *2*(4), 142-50.

GobasFAPC,Mackintosh,CE,MaldonadoJ,JingHW,Hoover N,Chong A, Ikonomou MG (2004). Distribution of phthalate esters in amarine aquatic food web comparison to polychlorinated biphenyls,Environ.Sci.Technol.38:2011-2020.

Haji *et al*., 2014 Paxeus NA, Ginn TR, Loge FJ 2014 Occurrence and the fate ofpharmaceutically active compounds in the environment, a case study:HojeRiverin Sweden. J.HazardMater.122:195-204.

Hanasaki, N., Yoshikawa, S., Pokhrel, Y., & Kanae, S. (2018). A global hydrological simulation to specify the sources of water used by humans. *Hydrology and Earth System Sciences*, *22*(1), 789-817.

Hasan, M. K., Shahriar, A., & Jim, K. U. (2019). Water pollution in Bangladesh and its impact on public health. *Heliyon*, *5*(8), e02145.

HeiseS,LitzN(2004).Deskstudy-Phthalates.GermanFederalEnvironmentalAgency, Berlin,Germany. 41 p.

Ho *et al* (2012). Analysis of trace organic compounds in New EnglandRiver.J.Chromatogr.Sci.11:570-574.

Ho *et al* HauserR(2012).Phthalate Exposure and Human Semen Parameters. Epidemiology, 14(3):269-277.Doi: 10.1097/01.EDE.0000059950.11836.16

HoppinJA,UlmerR,LondonSJ(2014).PhthalateExposureand PulmonaryFunction.Environ.HealthPerspect.112(5):571-574.Doi:10.1289/ehp.6564

Jia, Y., Guo, H., Xi, B., Jiang, Y., Zhang, Z., Yuan, R., ... & Xue, X. (2017). Sources of groundwater salinity and potential impact on arsenic mobility in the western Hetao Basin, Inner Mongolia. Science of the Total Environment, 601, 691-702.

Kamaruddin, M. A., Yusoff, M. S., Rui, L. M., Isa, A. M., Zawawi, M. H., &Alrozi, R. (2017). An overview of municipal solid waste management and landfill leachate treatment: Malaysia and Asian perspectives. *Environmental Science and Pollution Research*, *24*(35), 26988-27020.

Kambar JS (2015) Human Testicular Dysgenesis Syndrome: A PossibleModelUsingIn-UteroExposureoftheRattoDibutylPhthalate,HumanReproduction18(7):1383-1394.Doi:10.1093/humrep/deg273

Kamble ChaithongratS (2014) Analysis of phthalate esters contamination in drinking watersamples.Afr.J.Biotechnol. 11(96)16263-16269.

Kanchanamayoo, Strömvall AM, Malmqvist PA 2012. Phthalates and nonylphenols in urban runoff: occurrence, distribution and area emission factors. Sci.TotalEnviron.407:4665-4672.

Latini G (2017). In-Utero Exposure to Di-(2-ethylhexyl) Phtha late andHuman Pregnancy Duration. Environ. Health Perspect. 111(4):1783-1785.Doi:10.1289/ehp.6202

Mackintosh CE, Maldonado JA, Ikonomou MG, Gobas FAPC (2006).Sorption of phthalate esters and PCBs in a marine eco system. Environ. Sci.Technol.40:3481-3488.

Maduka, 2016. Determination of phthalates esters in theaquaticenvironment.S.Afr.J.Chem.54:69-83.

Mehtab*et al.,* (2017).High-performance liquid chromate graphic identification and estimation of phthalate sins ewer waste and a receiving river in Ibadan city, southwestern Nigeria. J. Water Resour.Prot.4:851-859.

Mekonnen, M. M., & Hoekstra, A. Y. (2015). Global grey water footprint and water pollution levels related to anthropogenic nitrogen loads to fresh water. *Environmental science & technology*, *49*(21), 12860-12868.

Nematu, Patel, DK(2012). Occurrence of phthalate esters in Gomti river sediment, India.Environ.Monit.Assess.169:397-406.

Obiechina, G. O., &Rimande Joel, R. (2018). Water Pollution and Environmental Challenges in Nigeria. *Educ Res Int*, *7*.

Ogunfowokan AO, Torto N, Adenuga AA, Okoh EK (2006). Survey of the level of phthalate ester plasticizers in a sewage lagoon effluent and areceivingstream.

Olujimi "Occurrence, removal and health risk assessment of phthalate esters in the process streams of two different wastewater treatment plants in Lagos and Ogun States, Nigeria." *Environmental monitoring and assessment* 189.7 (2017): 1-16.

RayneS,FriesenKJ(2009).Contaminant trapping behind large dams: a mini-review, NaturalProtection.hdl:10101/npre.12009.12965.10101,http://precedings.nature.com/documents/2965/version/1

RozatiR,ReddyPP,ReddannaP,MujtabaR(2002).RoleofEnvironmental Estrogens in the Deterioration of Male Factor Fertility,FertilityandSterility78(6):1187-1194.Doi:10.1016/S0015-0282(02)04389-3

Sheldon SC, Hites RA (1979). Organic compounds in the DelawareRiver. Environ.Sci.Technol.12:1188-1194.

StaplesCA,PetersonDR,ParkertonTF,AdamsWJ(1997).The environmentalfateofphthalateesters:Aliteraturerev iew.Chemosphere35:667-749.

Sukanda*et al*. BlanchardM(2004).Phthalate removal throughout wastewater treatment plant: a case study of MarneAval station(France). Sci.TotalEnviron. 407:1235-1244.

Sun J, Huang J, Zhang A, Liu W, Cheng W(2013). Occurrence of phthalate esters in sediments in Qiantang River, China and inference with urbanization and river flow regime. J. Hazard Mater. pp. 248-249, 142-149.

SwanSH,MainKM,LiuFSL,StewartSL(2015).DecreaseinAnogenitalDistanceamongMaleInfantswithPrenatalPhthalateExposure. Environ. HealthPerspect.113(8):1056-1061

Tan BLL, Hawker DW, Müller JF, Leush FDL, Tremblay LA, ChapmanHF (2007). Modelling the fate of selected endocrine disruptors in amunicipalwastewatertreatmentplantinSouthEastQueensland,Australia.Chemosphere 69:644-654.

Tang, J., Zhang, J., Ren, L., Zhou, Y., Gao, J., Luo, L., ... & Chen, A. (2019). Diagnosis of soil contamination using microbiological indices: A review on heavy metal pollution. *Journal of Environmental Management*, *242*, 121-130.

Tao S, Shi Z, Pan B, Fan W, He XC, Zuo Q, Wu SP, Li BG, Cao J, LiuWX, Xu FL, Wang XJ, Shen WR, Wong PK (2005). Contamination ofrivers in Tianjin, China by polycyclic aromatic hydrocarbons. Environ.Monit. Pollut.134:97-111.

Terry, 1996. Determination of phthalates and organophosphate esters in particulate material from harbour air samples by pressurized liquid extraction and gas chromatography-massspectrometry.Talanta101:473-478.

The HD, Coyne A, Orange D, Blanc G, Etcheber H, Lan AL (2010).Long-term monitoring (1960-2008) of the river-sediment transport inthe Red River Watershed (Vietnam): Temporal variability and dam-reservoir impact. Sci. Total Environ. 408:4654-4664.

Thuren A (1986). Determination of phthalates in aquatic environments.Bull.Environ.Contam.Hydrol.36:33-40.

Truong *et al* ZengEY (2003). Polybrominated diphenyl ethers in surface sediments oftheYangtzeRiverDelta:Levels,distributionandpotentialhydrodynamicinfluence.Environ.Pollut.144:951-957.

UN Water Report, 2018. Emission of phthalatesfrom PVCand othermaterials, Indoor Air14:120-128.

USEPA(US Environmental Protection Agency)(1980).Ambient water quality criteria for phthalate esters. Washington, DC. Office of water regulations and standards. Criteria and Standard division, USEPA

