Co-occurrence and Exposure Assessment of Parabens and Heavy Metals in Groundwater Sources in Two Rural Communities in Nigeria

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Certification

This is to certify that Oluwakemi Abiola AKINTOBI with matric number LCU/PG/002351 carried out this research work titled "Co-occurrence and Exposure Assessment of Parabens and Heavy metals in Groundwater Sources in Two Rural communities in Nigeria" in the Department of Chemical Sciences (Chemistry Unit), Faculty of Natural and Applied Sciences, Lead City University, Ibadan, Oyo State for the award of Master Degree (MSc) in Environmental and Analytical Chemistry and that this work has not been previously submitted.

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Dedication

This work is dedicated to God Almighty for making all my endeavors a success.

Acknowledgement

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Even though the above-mentioned institutions and persons have assisted in the process of this research work, I alone stand responsible for the errors, if any, found in this work.

Abstract

The constant release of contaminants of emerging concern (CEC) such as parabens and heavy metals into groundwater systems is becoming of great concern due to their numerous negative effects on plants, human and animal health since groundwater is a major source of water supply. In this study, ten (10) randomly selected groundwater sources from two communities were investigated for the concentrations of parabens and heavy metals. Preparation of samples for parabens was done using Solid Phase Extraction (SPE) while analysis was carried out on LC-UV. Instrumental analysis was carried out for heavy metals using Perkin Elmer Inductively Coupled Plasma-Optical Emission Spectrometry optima 8000 (ICP-OES), Shimadzu. The trend of total concentrations of parabens was EtP < PrP < MeP < BuP with values ranging from 30.14 to 400.08 µg L^{-1}. The toxicity of parabens to aquatic organisms was in the order algae < fish < daphnia. In addition, the concentrations of heavy metals such as Fe, Al, Co, Cr and Pb were observed to exceed WHO permissible limits of 0.3, 0.2, 0.01, and 0.05 mg L^{-1}. Furthermore, human health risk assessment data revealed that target carcinogenic risk (TCR) values for heavy metals in children and adults were higher than the permissible limit of 1.0×10^{-4} and were in the order of Ni > Cr >Pb. Conclusively, the human health assessment results from this study revealed that consuming water from these sources is not safe for the dwellers of both communities.

Keywords: Groundwater, Parabens, Heavy metals

Word Count: 240

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List of Acronyms

Abbreviation	Meaning
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
SPE	Solid Phase Extraction
HPLC-UV	High-Performance Liquid Chromatography- Ultra-Violet Spectroscopy
HQ	Hazard Quotient
HI	Hazard Index
WHO	World Health Organization
USEPA	United States Environmental Protection Agency
UL	Upper Intake Level
CDI	Chronic Daily Intake
RDA	Recommended Daily Allowance

Chapter One

Introduction

1.1 Background to the Study

Pharmaceutical and personal care products (PPCPs) are regarded as contaminants of emerging concerns (CECs) in water. They are pervasive in the environment and known to contaminate water bodies through the discharge of treated or untreated sewage from variety of sources such as household and hospital runoffs, industrial facilities, agricultural and recreational activities[1,2,3]. A class of chemicals known as parabens, which are alkyl esters of p-hydroxybenzoic acid, are extensively used in pharmaceutical and personal care products. These chemicals are typically used as preservatives in a variety of foods, beverages, cosmetics, and medicines, primarily to prevent yeast and mold growth. They have antimicrobial and antifungal properties that have the potential to damage the intracellular proteins and plasma membranes of microorganisms, altering enzyme action of these cells[5].

Man is also exposed to these chemicals via inhalation, ingestion, or dermal absorption[6]. Many environmental and human samples, including waste water, drinking water, sludge, soil, urine, serum and seminal plasma, breast tissues, and placenta, contain parabens[6,7,8,9,10,11,12,13,14,15]. Parabens have been labeled as endocrine-disrupting contaminants by the United States Environmental Protection Agency due to significant concerns regarding their impact on human and animal health, hence, it has been classified as endocrine-disrupting contaminants (EDCs)[8]. The normal operation of the endocrine system in the human body may be adversely affected by parabens, which could be harmful to human health[16,17]. Exposure to parabens has also been associated with childhood overweight development by altered Pro-opiomelanocortin-mediated neuronal appetite regulation[18]. Similarly, parabens are said to enable multiple cancer hallmarks

in the human breast, malfunction of the central nervous and immune systems, homeostasis of lipids, hinder the proper functioning of the thyroid, particularly in pregnant women, and telomere shortening (inability for cells to replicate) that leads to ageing, cancer and possibly death[19,20,21,22,23,24]. The most widely used parabens are methyl, ethyl, propyl, butyl, and benzyl (MeP, EtP, PrP, BuP, and BzP, respectively)[25,26].

There is evidence that as the alkyl chain length increases, the compound's hydrophobicity and antimicrobial properties also do.

Parabens are the second-most frequently used component in cosmetics and personal care products (PCPs) after water because of their advantageous physicochemical characteristics[27]. These advantageous physicochemical characteristics include small colourless crystals, a lack of flavor or odour, the capacity to function over a broad pH range, and excellent stability following product mixing[27]. Parabens are thought to have progressively overtaken other additives in cosmetics and pharmaceuticals since the 1920s[28]. Compared to the 13,200 products created with parabens in 1981, over 22,000 distinct types of cosmetics used parabens as preservatives in 2006[28].

According to estimates, the value of the worldwide cosmetics market reached 500 billion euros in 2018. As a result of customer desire for cosmetics with a long shelf life, preservative usage is anticipated to increase even more in the near future[29]. Parabens are regarded as high-production volume compounds in Europe, the United States, and Asia. The Environmental Protection Agency reported that MeP was produced at rates of up to 5000 tons per year in the United States throughout the 1990s[30]. The usage of parabens peaked in the Nordic nations' product registers around 2006–2007 and has since decreased, most likely as a result of stringent restrictive norms

and regulations[30]. Yet, according to production information provided by certain manufacturers, China's paraben (MeP, EtP) production rates reached 500 tons per month[28]. Meanwhile, it was stated that PrP was produced at a pace of more than 10,000 tons per month. This is not surprising considering that, in March 2002, China allowed the use of certain food additives, such as MeP, EtP, and PrP, as preservatives in the country with the highest acceptable concentration of 0.5 g kg^{-1} for MeP, EtP and PrP in food[31]. Due to their positive physical properties, MeP, EtP and PrP are expected to replace the other preservatives, such as sodium benzoate and benzoic acid, in the country's A-grade green food products. For these reasons, paraben production and usage in China will likely continue to rise[32].

Heavy metals are defined as metallic elements that have a relatively high density compared to water[33]. Heavy metal pollution of soil and water has become one of the main concerns of human beings recently[34]. Although some elements are essential for humans, they can be dangerous at relatively high exposure levels[34]. Heavy metals are considered as severe pollutants owing to their toxicity, persistence and bio-accumulative nature in the environment[34]. Trace metals gain access into water bodies possibly through anthropogenic and natural sources. Natural sources include geological strata rich in some elements which may contaminate aquifers.

Health risk assessment has been recognized as a useful tool for identifying health risks of human activities[34]. It involves identifying the potential of a risk source to introduce risk agents into the environment, estimating the amount of risk agents that come in contact with the human environment boundaries, and quantifying the health consequences of exposure[34]. Carcinogenic or non-carcinogenic methods can be used to assess potential health risk caused by heavy metals. Non-cancer risk assessment methods based on hazard quotient and hazard index are set by United States Environmental Protection Agency[35].

1.2 Statement of the Problem

Parabens were deemed safe for use by humans in a prior risk assessment conducted before the year 2000[36]. The median lethal dose (LD_{50}) of a single paraben after oral administration was found to range between 2100 and 8000 mg kg^{-1} in early acute toxicity studies in mice[37]. Prior to the year 2000, a summarized study on the short-term, sub-chronic, and long-term toxicity of parabens was published. It found that parabens did not have any hazardous effects on people at the amounts found in consumer products[37]. Parabens were classified as "generally regarded as safe" (GRAS) compounds based on the results of these toxicological research[37]. However, according to current research the endocrine system may be modulated or disrupted by parabens, which could have negative consequences on human health[38].

The persistent release of parabens into the environment has the potential to degrade the quality of groundwater resources. Parabens are converted by carboxylesterases to p-hydroxybenzoic acid in the human body, then are subsequently conjugated to their respective sulfate and glucuronide derivatives, and low molecular-mass parabens (MeP, EtP, and PrP) are then eliminated in the urine[39]. Parabens are absorbed after dietary intake and also through the skin as well as via inhalation. They have also been found in tissues, including placental tissue and breast tumors[40,41]. Epidemiological research has demonstrated that exposure to these chemicals can result in a number of diseases. The shortened menstrual cycle and gestational diabetes mellitus have both been linked to parabens[42,43].

Parabens interfere with the receptors for androgens, estrogens, progesterone, glucocorticoids, and peroxisome proliferator-activated receptors, according to in-vitro studies (PPARs)[44]. Similar to this, studies using cell cultures have shown that parabens can cause human breast epithelial cells

to acquire carcinogenic processes[44]. Even low concentrations of MeP (10 nM) caused the formation of MCF-7 (breast cancer cell line by Michigan Cancer Foundation-7) xenograft tumors and increased the size of tumor xenograft derived from the estrogen receptor (ER)-positive breast cancer patients[45]. Long-term exposure to parabens increased breast cancer cell proliferation and migration[45]. Unfortunately, there is little information available on the presence of parabens in Nigeria's various water matrices.

1.3 Justification of the Study

Parabens are one of the most widely used preservatives because of their advantageous properties such as low toxicity based on early assessments. However, recent findings indicate that parabens may act as endocrine-disrupting chemicals (EDCs) and thus, are considered as chemicals of emerging concerns (CECs) that have adverse human health effects[16]. Furthermore, data from developed countries have shown that parabens are ubiquitous in the environment. But data from developing countries like Nigeria are scarce, and when available are limited to Urban areas[9].

1.4 Aim and Objectives of the Study

The main aim of this study is to determine the concentrations of parabens (Methylparaben, Ethylparaben, Propylparaben and Butylparaben) and heavy metals (Ca Mg, K, Na, Fe, Cu, Zn, Mn, P, Co, Se Cd, Cr, Ni and Pb) in groundwater samples.

The specific objectives are:

i. determine the physico-chemical parameters (Temperature, pH, Conductivity, Total Dissolved Solids, Dissolved Oxygen).
ii. evaluate the exposure and health risk of humans to these contaminants.

iii. assess the relationship between the studied parameters.

1.5 Research Questions

i. What are the concentrations of parabens in the groundwater samples?

ii. What are the concentrations of heavy metals in the groundwater samples?

iii. What is the relationship between these contaminants?

iv. What are the health implications of these contaminants in drinking water?

1.6 Significance of the Study

Groundwater samples was selected randomly from the sampling sites to test for the presence of parabens and heavy metals. The analysis of these groundwater samples will provide new set of data and information on presence and concentrations of these contaminants in these communities because data on parabens concentrations in groundwater in Nigeria are scarce and are limited to urban areas.

1.7 Scope of the Study

This study investigated the concentrations of parabens (Methylparaben, Ethylparaben, Propylparaben and Butylparaben) and heavy metals (Ca Mg, K, Na, Fe, Cu, Zn, Mn, P, Co, Se Cd, Cr, Ni and Pb) in groundwater samples collected from two communities in Oyo and Ogun states respectively. Five (5) groundwater samples were collected from each community making total of Ten (10) groundwater samples.

1.8 Limitation of the Study

This study considers the determination of parabens and heavy metals in groundwater samples only. The study was carried out in two rural communities which lies between Oyo and Ogun States.

1.9 Operational Definition of Terms

Contaminant: this is an unwanted substance which has harmful effects on the environment. The presence of these substances in the environment affects both living and non-living things.

Heavy Metals: Heavy metals are defined as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids such as arsenic, that are able to induce toxicity at low levels of exposure.

Parabens: any of a group of compounds used as preservatives in pharmaceutical and cosmetic products and in the food industry.

Groundwater: groundwater is water that exists in the pore spaces and fractures in rock and sediments beneath the earth's surface.

Endocrine System: the glands and organs that make hormones and release them directly into the blood so they can travel to tissues and organs all over the body.

Antimicrobial: a substance that kills microorganisms such as bacteria or mold, or stops them from growing and causing disease.

Nervous System: the organized network of nerve tissue in the body. It includes the central nervous system (the brain and spinal), the peripheral nervous system and other nerve tissue.

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Chapter Two

Literature Review

2.1 Water

Water is a substance composed of hydrogen and oxygen. It is odourless and tasteless at room temperature and it has the ability to dissolve other substances, hence called a universal solvent[1]. Aside from being useful as a solvent, water also has a wide range of other applications in living organisms. It is believed that life began in the oceans, and living organisms rely on the various components of the water's aqueous solutions for their biological processes[1]. Because of its properties, water is a vital component of the environment, and it can be used for transportation and recreation and as a habitat for a myriad of plants and animals[1]. The fact that water is readily changed to vapour (gas) allows it to be transported through the atmosphere from the oceans to inland areas where it condenses and as rain nourishes plant and animal life. The water on the surface of the earth is found mainly in its oceans (97.25 %) and polar ice caps and glaciers (2.05 %), with the balance in freshwater lakes, lakes, rivers and groundwater[1].

2.2 Groundwater

Groundwater refers to all the water occupying the voids, pores and fissures within geological formations. Usually, the water comes from atmospheric precipitation that's either directly caused by rainfall or indirectly from nearby waterways such as lakes and canals[1]. Some of the sources of groundwater supply come from the limestone, sand, and gravel formations, though some may be drawn from impervious rocks such as granite when they have an over burden of sand or gravel. It's believed that groundwater supplies about two-third of the world's fresh water reserves[1].

According to experts, the world's groundwater reservoir is around 5.0 trillion liters. This is more than twice the volume of water that's in the world's rivers and over 30 times bigger than the world's fresh water lakes[2]. It is used for industrial and domestic purposes. Around half of the world's livestock and irrigation activities rely on groundwater. In rural areas, almost all of the domestic water supply comes from groundwater[3]. Groundwater is increasingly being used for domestic, municipal, agricultural, and industrial purposes, mostly as a result of the high initial investment and ongoing maintenance costs of surface water production through dams, particularly in developing nations[4].

Improved technology, which is demonstrated by deep boring in the form of a borehole that satisfies WHO drinking water quality standards, is another aspect that is responsible for the focus being shifted to this source[5]. Hand-dug wells, shallow wells driven by hand pumps, deep wells operated by submersible pumps, and boreholes are all used to extract groundwater[6]. In addition to its physical composition, groundwater also has high mineral content due to the chemical composition of the rock surface[3]. Water holes are considered to be the oldest method of obtaining sub-surface water[7]. They have been classified into four types that require a full conventional treatment before they can be used. A water hole is a structure that's located in the ground that's designed to intersect the water table and allow the flow of water from the aquifers to flow into the subsurface. There are two types of wells: deep and shallow[8]. They can be categorized into three different categories depending on the type of construction.

1. Hand-dug well

2. Bored well

3. Driven well[9].

Generally, shallow wells are less than 15 meters deep while deep wells are deeper than 50 meters[10]. They have different characteristics such as their bacteriological quality and yield with the water becoming purer and more constant with increase in depth. Deep wells are usually boreholes with depth above 100 and 150 m diameter especially in the sedimentary formations[6]. Although they have higher yield, deep wells are typically more expensive to maintain and operate. One of the most important factors that are considered when it comes to maintaining and operating a deep well is the condition of its screen. This is because it can prevent the well from working properly. being clogged and corroded, thus reducing its effectiveness and efficiency. Unlike deep wells, hand-dug wells are usually constructed manually. They are prone to pollution since they're usually located near the water table. However, they can still be improved by adding certain features such as a cover, apron, and cement ring. A properly constructed hand-dug well should ideally yield around 2,500 to 7,500 m^3 of water per day. Unfortunately, most domestic hand-dug wells only produce around 500 to 1,000 m^3 of water per day. Although groundwater pollution is not as easily categorized as surface water contamination[3]. It is still important to note that it can still be affected by sources that are not directly related to the water bodies.

Contaminant analysis is carried out on groundwater contamination. It usually involves analyzing the various characteristics of the ground, such as its geology, hydrogeology, and temperature. Aside from chemicals, other factors such as pathogens and sensory changes can also contribute to the development of groundwater pollution. High levels of naturally-occurring substances such as iron, manganese, and calcium can negatively affect the aquatic life in the area. Their concentration can also determine the type of water that's considered a natural component. Contaminants that are also caused by human activities can also negatively affect the water quality. Other natural and anthropogenic substances may cause turbidity and other negative

effects[11]. Turning raw water into a usable form is the process of groundwater treatment. This process involves removing toxic substances and pathogens from the water. Depending on the source of the contamination and the physical processes involved, water can be made potable. The various methods that can be used for this process include aeration, coagulation, filtration, and flocculation. The use of low-cost treatment processes can help improve the water quality and prevent water borne diseases. Some of the effective methods that can be used include the use of pot storage, disinfection, and chlorination[12].

2.3 Groundwater Quality

The various characteristics of groundwater can also be used to determine its useful uses. For instance, determining the concentration of certain inorganic constituents can be performed. Aside from this, other factors such as the pH level of the water and specific electrical conductance can also be analysed. A physical analysis is also performed to determine the various characteristics of the water, such as its temperature, colour, and odour (Table 2.1). Bacteria analysis is carried out to determine the presence of harmful organisms. It was highlighted that pathogenic organisms are infrequently discovered in groundwater since most well pathogenic contamination results from poor well construction or from being connected to bedrock aquifers with big gaps that allow direct communication between the surface and groundwater[13]Also, it was noted that any or all of the following may be connected to and responsible for the water quality issue[14].

1. Poor quality source of water,

2. Poor site selection or protection such as apron and lining

3. Construction difficulties and

4. Structural deterioration with age

Parameters	Undesirable effects produced	Highest desirable level	Minimum desirable level
A. Physical			
Colour	Discolouration odour	5	50
Odour	Taste	Unobjectionable	Unobjectionable
	Gastrointestinal irritation	Unobjectionable	Unobjectionable
Total solids (mg L^{-1})	Gastrointestinal irritation	500	1500
Suspended matter	Turbidity	5	5
	Gastrointestinal irritation		
B. Chemicals			
pH	Taste, excessive scale formation	7.0 to 8.5	6.5 to 9.2
Calcium (mg L^{-1})	Taste, corrosion in hot water system	75	200
Chloride (mg L^{-1})	Mottling of teeth	200	600
	Disfiguring of skeletons		
Fluoride (mg L^{-1})	Excessive scale formation	1.0	1.5
Total hardness as mg L^{-1} of $CaCO_3$	Taste odour	100	500
Mineral oil (mg L^{-1})	Taste		
Phenolic subs. (mg L^{-1})	Toxic	0.01	0.30
C. Trace elements			
Copper (mg L^{-1})	A stringent taste, discolouration, corrosion of pipe fittings and utensils	0.05	0.05
Cyanide (mg L^{-1})	Toxic		
Iron (mg L^{-1})	Taste, discolouration constipation turbidity growth of bacteria	0.1	0.05
Lead (mg L^{-1})	Toxic		
Manganese (mg L^{-1})	Taste, discolouration, turbidity, deposits in pipes	0.05	0.05
Zinc	A stringent taste	5.0	15.0
D. Pesticides			
DDT (mg L^{-1})	Toxic		0.05
PCB	Toxic		NIL

Table 2.1: Drinking Water Quality

Source adapted from World Health Organization[15]

2.3.1 Microbial Quality

Safe guarding the microbial quality of drinking water is regarded as the most important objective, even ahead of its physical and chemical quality, since water represents an obvious mode of transmission of enteric diseases[16,17]. Aside from human and animal excreta, other sources such as sewage can also contribute to the contamination of drinking water[18]. Microbial qualify is determined using various methods of bacterial examination. The indication organism's method is basically the concept of using organisms usually abundant in human and animal excrement, as evidence of contamination and possible presence of other potentially dangerous microorganisms[19]. The use of indicator organisms for determination of the microbial quality of water saves the time, labour and expenses involved in attempting to test for all pathogens that a water sample might possibly contain. For an organism to be ideal for use as an indicator, it must meet the following criteria:

1. The method of isolation, identification and enumeration should be simple and unambiguous.

2. It should be resistant to chlorine and have a higher survival rate in water than pathogens.

3. It should be more neutral than all pathogens in the environment.

The significant that can be attached to the presence or absence of a particular fecal indicator varies with each organism and with the degree to which that organism can be specifically associated with faeces.[19] The recommended standards for testing contamination during transportation or storage is the most probable number (MPN) count of less than 10 per 100 ml

for total coli forms and 2.5 per 100 ml for E. coli. The World Health Organization also recommends that countries implement comprehensive fecal contamination control measures.

2.3.2 Physicochemical Quality

The term "physicochemical quality" refers to the characteristics of water that can affect its acceptability. These include its colour and taste, as well as its toxic effects, which can include reactions to laxatives[20].

2.3.2.1 Taste and Odour

The development of taste and odour is influenced by the activation of the human receptor cells. These cells are located in the taste-buds and nasal cavity[19]. When people taste water, they stimulate the gustatory and olfactory nerves. In all taste it is actually flavour that is being measured, the combination of taste, smell, and temperature is referred to as the flavour. The lack of flavour in many food products can also explain the link between smell and taste. This is because the sense of smell is lost when one's nose is cold. The prevalence of taste and odour problems in drinking water supplies is considered to be the largest consumer complaint area. These issues are usually caused by various factors such as the water source, the distribution system, and the treatment method[19]. Taste in drinking water is measured by taste tests such as the threshold test or taste rating tests. In order to determine the level of odour in drinking water, smell tests are carried out. This method is more sensitive to the senses than the analytical method commonly used. For instance, if the threshold for cyanide in drinking water would be 1/100th of the present limit if based on the odour threshold of 0.001 mg L^{-1} [19].

2.3.2.2 Factors Affecting Taste and Odour

(1) Temperature: The growth rate of microorganisms is also positively associated with the temperature which leads to the development of bad-tasting metabolites. The odour of a substance is also temperature influenced because of the relationship between odour and vapour pressure, therefore odour measurement usually specifies temperature.

(2) pH: The presence of a high pH level can also affect the taste and odour of a substance, especially when it controls the equilibrium concentration of the neutral and ionized forms of a substance in solution. The average threshold increases from 0.075 to 0.450 mg L^{-1} as the pH increases from 5.0 to 9.0 [19].

(3) Residual Chlorine: A balance is also sought when it comes to the level of residual chlorine. This condition ensures that the water is free of harmful microorganisms and has a good taste.

(4) Total Dissolved Solids (TDS): Total dissolved solids (TDS) refer to the solid organic matter and inorganic salts that can be produced by various sources such as sewage, urban run-off, and natural carbonates, chlorides, sulphate, nitrate, sodium, potassium, calcium and magnesium. The major determinant of the TDS level in water is the geochemical characteristics of the ground it comes in contact with, for example, granite and silicon sands, and well-leached soils have TDS less than 360 mg L^{-1}, the palatability of drinking water according to its TDS level with rating was given as less than 500 mg L^{-1} as excellent level and greater than 1700 mg L^{-1} as unacceptable (Table 2.2) [19]. TDS is related to other water quality parameters like hardness, which may occur if the high TDS content is due to the presence of carbonates.

Table 2.2: Palatability of Drinking Water According to its TDS Level

Rating	TDS levels (mg L^{-1})
Excellent	<300
Good	300-600
Poor	600-900
Unacceptable	>1700

Source: Adapted from World Health Organisation[19]

(5) Turbidity: The presence of various microorganisms, such as silt, clay, colloidal particles, plankton, other microorganisms and suspended matter, in the water sample can cause a water's light scattering and absorbing properties to change[19]. Turbidity can be measured by either nephelometry or light scattering. When the water is affected by these factors, its colour can also change. The presence of these microorganisms can also affect the quality of water by promoting the growth of various microorganisms. It also affects the chemical quality of drinking water through the formation of complexes between the turbidity causing humic matter and heavy metals[19].

(6) Colour: The presence of organic compounds, such as humic, in drinking water can cause its colour to change. Usually, these substances are produced by the decay of vegetation. The red and blue colours of water are caused by the actions of bacteria, which oxidize the iron and manganese into their respective compounds. The colour of water is measured by comparing the sample with the platinum cabalt standards where one unit of colour is that produce by 1 mg L^{-1} platinum of chloraplatinate ion. A limit of 15 TCU is recommended in drinking water[19].

(7) Dissolved Oxygen: Dissolved oxygen is a measure of pollution that can be used to determine the quality of water. This indicator can also be used to determine the effectiveness of various water treatment processes. The recommended level of dissolved oxygen for drinking water is 8 mg L^{-19}. A lower level of contamination or corrosion can indicate that the water is unfit for consumption.

(8) Hardness: The hardness of water is caused by the presence of various ions, such as magnesium and calcium. These two substances commonly cause water to resist the action of soap by forming a hard and creamy consistency. Unlike when the anions are sulfates, chlorides, and nitrates, the carbonate anion, may be easily eliminated by boiling. Due to its strong solubilizing capacity, groundwater is frequently harder than surface water and can have concentrations up to several thousand mg L^{-1}, especially in the case of rocks containing gypsum, calcite, and dolomite. Sewage and soil runoff, particularly from limestone formations, building materials containing calcium oxide, and textile and paper products containing magnesium are further sources of hardness.

(9) Alkalinity: Alkalinity is an index of the buffering capacity of water produced anions of weak acids, like hydroxides, bicarbonates and carbonates. Loss of color is directly related to an increase in alkalinity in the water sample and is often near to its hardness value.

(10) Chloride: Contaminated groundwater is caused by the presence of chloride, which can be caused by various factors, such as the presence of brine in oil wells, sewage discharge, and refuse leachate. The recommended level of chloride in drinking water is 250 mg L^{-1} any higher value than 1000 mg L^{-1} is an indication of polluted water with chloride[19].

(11) Toxic Chemicals: Contaminated drinking water supplies can also be caused by the presence of other organic and chemical contaminants.

(12) Nitrates and Nitrites: They are considered together because conversion from one form to the other occurs in the environment and the health effects of nitrates are generally as a consequence of its ready conversion to nitrites in the body. The recommended levels for nitrates in drinking water are typically below 50 mg of nitrate-N per liter, levels above these are

indicative of polluted water that is unfit for consumption[19]. To reduce the levels of nitrate in the water, treatment by the oxidizing effects of chlorine can be applied.

(13) Others: Some of the toxic chemicals that can be found in drinking water supplies include ammonia, which is in the non-ionized form (NH_3) and ionized form (NH_4^+). Other chemicals that can pose a threat to human health include arsenic, chromium, and aluminum, fluoride, mercury and organic contaminants.

2.4 Heavy Metals

Heavy metals are defined as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids such as arsenic, that are able to induce toxicity at low level of exposure[19].

2.4.1 Lead

Although lead is a natural component of the Earth's crust, its concentration in drinking water is relatively low. This is because the water treatment process removes most of the lead from the water. However, it can still cause corrosion since the low pH level and softness of the water can affect the formation of lead deposits. The maximum intake of lead from food, air and water is 3 mg $week^{-1}$ (0.05 mg kg^{-1} of body weight) for adults[19]. This is because it can have negative effects on various organs. One of these is the nervous system, which is affected by prolonged exposure to lead. It can also lower the kidney's clearance and performance[20]. Even at low levels, lead poisoning can be a threat to children's health. It is associated with impairment of childhood cognitive function[21]. Exposure to high levels of lead during pregnancy can lead to various health conditions, such as birth defects, low birth weight and impaired neuro-development[22]. In addition to this, lead poisoning can also occur when the concentration of lead reaches between 100 and

140 micrograms per liter[23]. According to the international Agency for Research on cancer (IARC) inorganic lead is carcinogenic to human[24].

2.4.2 Iron

The most abundant element in the crust is iron, which can be found in water in its various states. Rock and mineral dissolution acid mine drainage, land fill leachates, sewage and iron related industries are causes of high iron levels in groundwater, lakes and reservoirs, particularly where reducing conditions are present[25]. It is an essential micronutrient as it plays a critical role in major biochemical activities, such as oxygen transport and electron transfer[26]. There are about 3-5 grams of iron (45-55 mg kg^{-1}) in human body; about 60–70% is utilized within hemoglobin in circulating red blood cells[27]. Although iron is very important it can be hazardous when exist in high concentration. Ingestion of excessive amounts of iron can irritate the gastrointestinal tract and cause various gastric discomfort symptoms such as nausea and vomiting. It can also cause severe damage to the gastrointestinal tract, which can lead to bleeding and a wall of the intestine being perforated[28].

Excess of iron disrupts the redox balance of the cell resulting in generation of chronic oxidative stress, which organized the signaling networks related to malignant transformation[29]. It has been known that high iron consumption can increase the risk of developing breast cancer[30]. The risk of accumulating iron in the body is higher than that of other heavy metals due to the high consumption of iron supplements and dietary iron. This can also lead to various health complications, such as severe gastrointestinal bleeding and necrotizing gastritis[31].

2.4.3 Cadmium (Cd)

Cadmium is a non-essential element which is soluble in the biological systems[32]. It is known to have a high toxicity and can affect the functioning of various organs in the body. It can also bioaccumulate and disrupt the functions of vital organs[33]. Both acute and chronic exposure to cadmium has a negative impact for human health. High levels of cadmium can cause blood pressure to rise and destroy red blood cells. It can also increase the risk of cancer. Studies have shown that prolonged exposure to low levels of cadmium can lead to an increased likelihood of developing cancer[34].

2.4.4 Nickel (Ni)

Exposure to nickel can cause various pathological effects. Oral exposure to large doses of nickel mainly targets the cardiovascular system[35]. One of the most common effects of this element is an allergic reaction that can occur in people who are sensitive to nickel[36]. Most of the toxicity of nickel might be attributed to its interference with the physiological processes of zinc and calcium[37]. According to the International Agency for Research on Cancer (IARC) and the United States Department of Health and Human Services, nickel compounds have been classified as human carcinogens. In studies, nickel compounds have been known to induce various types of tumors in animal systems[38]. A case of Ni toxicity was reported in a young child, who accidentally ingested a large amount of nickel sulfate crystals about 570 mg kg^{-1} of Ni. After a couple of hours, the child started to have cardiac arrest. He later died 8 hours following the exposure[39]. Some of the other symptoms of severe exposure to nickel compounds include vomiting and abdominal pain[40].

2.4.5 Chromium (Cr)

Chromium exists in two ionic forms, trivalent and hexavalent, the latter being toxic and is associated to human carcinogenesis and acute toxicity of aquatic organisms. Since its reduced form is also essential for animals, the recommended daily limit of chromium is 11 to 25 g day^{-1} for children and 30 to 35 g day^{-1} for adults[41,42].

2.4.6 Copper (Cu)

Copper has beneficial effects it can also have toxic effects when consumed at high levels. To minimize these effects, it's important to monitor the daily copper limit. For children and adults, the daily copper consumption should be around 900 and 340 micrograms per day, respectively[43].

2.4.7 Calcium (Ca)

The adult body contains 1,200 g of calcium. Calcium is in the hard structure of bone and teeth in most bodies. It plays an important role in several of the enzymatic steps involved in blood coagulation[44]. Deficiency of calcium results in rickets, which eventually results in the deformation of legs and other disfigurements which cannot be reconnected easily except by major surgery[45].

2.4.8 Magnesium (Mg)

Some of the most common rich sources of magnesium are vegetables, cereals, spices, and cocoa[46]. Green leafy vegetables such as spinach are also rich in magnesium[47]. In the UK, the daily recommended values for magnesium are 300 mg for men and 270 mg for women[48]. In the U.S. the Recommended Dietary Allowances (RDAs) are 400 mg for men ages 19–30 and 420 mg for older; for women 310 mg for ages 19–30 and 320 mg[49]. It's important to note that the

kidneys filter out excess magnesium before it enters the bloodstream, and this is why it's unlikely that an overdose would occur[50]. However, high doses of magnesium can cause severe hypermagnesemia and even death[51,52]. In the case of overdose, the most common symptom are nausea, vomiting, and diarrhea. Other symptoms such as confusion and a slow heart rate can also occur. Death from cardiac arrest is also usually caused by this condition[53].

2.4.9 Other Heavy Metals

Potassium (K), Phosphorus (P), Sodium (Na), Zinc (Zn), Chromium (Cr), Cobalt (Co) and Selenium (Se) have been reported to be found in drinking water. They are also known to have toxic effects when ingested at high levels. Due to their bioaccumulation in the body, these elements can disrupt the functioning of various organs, such as the liver, kidney, and brain[54]. Although some of these metals are essential, they can still pose a threat to health if they're present in higher concentrations[55].

2.5 Sources of Pollution

When the quality of water is reduced due to human activity to the point where it is no longer appropriate for its intended use, this is referred to as pollution[56]. Pollutants are any of the several foreign chemicals that have the potential to degrade the quality of water. They could be organic, inorganic, or biological. Pollution has several detrimental effects, including impairment to human health, restrictions on aquatic activities, and the incapacity of the water to support industrial, agricultural, and other associated economic operations. The use of aseptic tanks and latrines can also contribute to the contamination of groundwater supplies, increasing the levels of pathogens, inorganic chemicals, nitrate, and biochemical oxygen demand (BOD, COD). These

diseases are frequently seen in developing countries like Africa, Asia, and South America[56]. It was noted that the unhygienic methods of waste disposal, such as defecating in streams and dumping trash in pits, rivers, and drainage channels, which are common in most Nigerian urban populations, could be anticipated to have an impact on the quality of surface and groundwater[57].

The effectiveness of waste disposal techniques, the safety of land use patterns, the density of disposal systems in an area, the makeup of trash and soil, and a number of other site-specific factors will all affect the level of pollution (contamination). Well liming gets rid of contaminants, which raises the standard of the water[57]. The practice of dumping industrial waste effluents into streams, sanitary sewers, and open land has the potential to contaminate ground water. Other sources of pollution that can degrade water quality besides industrial waste disposal techniques include pipelines and mining operations. The production of oil and gas is frequently accompanied by significant brine discharges, which are disposed of in abandoned pits, evaporation ponds, and streams. These techniques run the risk of introducing brine pollution into aquifers, which would increase levels of sodium, calcium, ammonia, boron, chlorides, sulfates, trace metals, and significant amounts of total solids[57]. Agricultural sources of pollution include irrigation with significant groundwater recharge[58].

The possible effect on the ground water includes an increase in ground water salinity, due to inadequate drainage and direct evapotranspiration of irrigation return flow from soils whose salinity has been increased by salts from fertilizers[3,56]. Animal waste from slaughter houses and animal pens can also contribute to the issue. These animals are often confined for their meat and milk production and are often subjected to storm run-offs carrying significant amounts of nitrates, salts, organic loads and bacteria to surface and sub-surface water[4]. Agrochemicals such as fertilizer, pesticides and insecticides also pollute ground water. Nitrate based fertilizers are a

significant contribution to groundwater pollution. This is because nitrogen in solution is neither fully utilized by plants nor absorbed by the soils. Stock piles of solid materials from construction sites, individual's plants residue are potential groundwater pollutants when precipitation falls on these piles, causing a leaching of heavy metals, salts and other organic and inorganic constituents. The following considerations was given as a way of reducing groundwater contamination or pollution[9]:

1. A well should be sited uphill of a polluting source. This is with a view to diverting to drain from the well into a polluting source rather than converse.

2. The distance between a well and a polluting source should not less than 30 m (100 feet).

3. Well construction should start towards the end of the dry season.

2.6 Elemental Analysis

Various industries such as oil and gas, chemicals, and food and pharmaceutical companies require the use of various analytical techniques to determine the presence of certain elements in their samples. It is important that the laboratory uses the right technique for the job. One of the most common analytical techniques used for this purpose is the use of flame and graphite furnace absorption atomic spectroscopy, inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The technique used for the heavy metal analysis for this project was ICP-OES.

2.6.1 Inductively Coupled Plasma (ICP)

The inductively coupled plasma (ICP) is argon plasma maintained by the interaction of an RF field and ionized argon gas, the ICP reaches temperatures as high as 10,000 ^{o}K, with the sample

experiencing useful temperatures between 5,500 °K and 8,000 °K[59]. These temperatures allow complete atomization of the elements in a sample, minimizing chemical interference effects. The plasma is formed by a tangential stream of argon gas flowing between two quartz tubes. Radio-frequencies (RF) power is applied through the coil and an oscillating magnetic field is formed.

The plasma is created when the argon is made conductive by exposing it to an electrical discharge which creates seed electrons and ions. Inside the induced magnetic field, the charged particles (electrons and ions) are forced to flow in a closed annular path. As they couple with the RF field, heating takes place and additional ionization occurs[59]. The process occurs almost instantaneously and the plasma extents to its full dimensions. Viewed axially from the end, the plasma has a circular 'doughnut' shape. The sample is injected as an aerosol through the center of the doughnut. The characteristic of the ICP confines the sample to a narrow region and provides an optically thin emission source and a chemically inert atmosphere. This results in a wide dynamic range and a minimal chemical interaction in an analysis. Argon is also used as a carrier gas for the sample[59].

2.6.2 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP optical emission spectroscopy (ICP-OES) is the measurement of the light emitted by the elements in a sample introduced into the ICP source[60]. The measured emission intensities are hen compared to the intensities of standards of known concentration to obtain the elemental concentrations in the unknown sample[60]. There are two ways of viewing the light emitted from an ICP. In the classical ICP-OES configuration, the light across the plasma is viewed radially resulting in the highest upper linear ranges. By viewing the light emitted by the sample looking down the center of the torch or axially, the continuum background from the ICP itself is reduced

and the sample path is maximized[60]. Axial viewing provides better detection limits by as much as a factor of 10 than those obtained by radial viewing.

Most Perkin Elmer ICP-OES systems use a patented dual-viewing (DV) system, allowing the plasma to be viewed in either orientation in a single analysis by simply moving a mirror, providing the best detection capabilities and widest working ranges of any system[60]. The optical system used for ICP-OES consists of a monochromator that is used to separate individual wavelengths of light and focus the desired wavelengths onto the detector. In today's modern ICP-OES systems, solid-state detectors based on charge-coupled devices (CCD) are used, providing very flexible systems and eliminating the need for large numbers of single photomultiplier detectors. ICP-OES is the best overall multi-element atomic spectroscopy technique with excellent sample throughput and a very wide analytical range[60].

2.6.3 Operational Principle of ICP

When the torch is turned on, an intense magnetic field from the RF generator is turned on. The argon gas flowing through is ignited with a Tesla spark unit (typically a copper strip on the outside of the tube)[59]. The argon gas is ionized and this field flows in a particular rotationally symmetrical pattern toward the magnetic field of the RF coil. A stable high-temperature plasma of about 7000 K is then generated as the result of the inelastic collision created between the neutral argon atom and the charged particles[59]. A peristaltic pump delivers an aqueous sample into a nebulizer where it is atomized and introduced directly inside the plasma flame. The sample immediately collides with the electrons and other charged ions in the plasma and they are broken down into charged ions[59]. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma giving off the characteristic wavelengths

of the elements involved[59]. The light emitted by the atoms or ions in the ICP is converted into electrical signals by the PMT or CCD (photomultiplier tube) in the spectrometer. The intensity of the electron signal is compared to previous measured intensities of known concentration of the element and the concentration is computed. Each element will have many specific wavelengths in the spectrum which could be used for analysis[59].

2.6.4 ICP-OES: Uses, Benefits, Drawbacks

ICP-OES is regarded as suitable for the detection of most elements (73), with the exception of radioactive elements requiring analysis by gamma-ray spectroscopy, the halogen group, and trace contaminants found in the argon gas mixture that is used in the ICP-OES testing procedure[60]. Common areas of application include food and beverage, environmental, toxicology, photonics, agricultural testing, petrochemicals, and other areas of application where rapid elemental analysis is of great interest. ICP-OES efficiently measures 1 to 60 elements per minute[60]. Method development is relatively simple, and "analytical grade" solvents and reagents may be used for testing[60]. Running ICP-OES samples does not require the attention of a specialist: a method can be calibrated by a specialist and run by average laboratory personnel[60]. Medium sample volumes are best for ICP-OES. The biggest drawback is the high potential for spectral interference. Also, an ICP-OES system requires a high-volume gas installation in the laboratory[60].

Atomic absorption (AA) and inductively coupled plasma (ICP) techniques primarily differ in sensitivity and the number of elements/samples that can be routinely measured[60]. For analyzing a

few elements and a small number of samples at concentrations of 100 ppb or higher, then AA techniques are frequently more efficient and cost-effective[60]. If many elements and samples need to be analysed with detection limits of a few ppb or lower then ICP techniques are typically preferred. Where the selection is based on analyte detection limit, flame AA and ICP-OES are favored for moderate to high levels while graphite furnace AA and ICP-MS are favored for lower levels[60].

2.7 Human Exposure to Parabens

The industry estimated that adults used about 17.66 grams of paraben-containing cosmetics per day, while children used about 0.378 grams[61]. The anticipated total daily intake of parabens for adults and newborns, respectively, was calculated to be roughly 142.08 mg and 3.024 mg, depending on the allowable paraben concentration. The paraben dose is 2.368 mg kg^{-1} body weight (bw) day^{-1} for an adult weighing 60 kg. The average daily total personal paraben exposure estimated was lower and equaled to 76 mg (1.26 mg kg^{-1} bw day^{-1}), with cosmetics and personal care products (PCPs) accounting for 50 mg (0.833 mg kg^{-1} bw day^{-1}), pharmaceutical products for 25 mg (0.417 mg kg^{-1} bw day^{-1}), and food accounting approximately for 1 mg (10–13 µg kg^{-1} bw day^{-1})[62]. Six parabens' amounts in various commodities from China were recently determined[63]. The total paraben concentrations reached up to 2530 ng g^{-1} fresh weight, and the detection rate was 99%. (Mean: 39.3 ng g^{-1}). The value of human exposure to parabens from food products was very modest when compared to the daily exposure to parabens from personal

care products. It was calculated to be about 1 μg kg^{-1} bw day^{-1} (mean) and 3 μg kg^{-1} bw day^{-1} (95th percentile)[63].

2.8 Occurrence in Environment

Due to the widespread use of preservatives, such as parabens, in cosmetic products, their environmental occurrence has been increasing. They have been detected in various environmental matrices, such as surface water, air dust, and sewage sludge.

2.8.1 Naturally Occurring Parabens

Although most parabens used commercially are synthetic, some organisms can also naturally create them. It was reported that a marine bacterium biosynthesizes pHBA and its alkyl esters[64]. A4B-17, a strain of the bacterium belonging to the genus Microbulbifer, was found to produce remarkably large quantities of these compounds. This includes 10 mg L^{-1} of pHBA, 24 mg L^{-1} of butyl ester, 0.4 mg L^{-1} of heptyl ester and 6 mg L^{-1} of nonyl ester. The compounds produced by the bacterium can prevent the growth of various bacteria, such as Gram-positive bacteria and yeasts[64]. The observed exudation of β-carbolines along with methyl paraben in herbaceous plant: Oxalis tuberosa hairy roots was triggered upon fungal cell wall elicitation[65]. Methylparaben was also detected at a trace concentration (0.8 μg g^{-1}) in Andrographis paniculata herbs, but the origin of the compound in the plant tissue was not known[66].

2.8.2 Water Resources

Due to the widespread use and production of these compounds, their leaking into the environment can be caused by various factors. Surface waters are vulnerable to contamination because, among other things, they are found in the lowest points of the landscape. In addition to

runoff from non-point sources and the deposition of airborne particles, parabens can also enter the aquatic environment as a result of wastewater treatment outputs. The scant information that is currently available about the occurrence of parabens in various surface waters is displayed in Table 2.3. The species utilized in cosmetics, methyl- and/or propylparaben, had the highest concentration values and detection rates. Propylparaben and Methylparaben concentrations were identified in China's rivers at values of 1062 ng L^{-1} and 3142 ng L^{-1}, respectively[67].

In European rivers, the maximum concentrations detected were lower, up to 400 ng L^{-1} for MeP and 69 ng L^{-1} for PrP[68,69]. The presence of EtP and BuP in water samples was recorded less frequently. Measured concentrations of the compounds were relatively low in comparison with MeP and PrP, and equaled up to 147 ng L^{-1} (EtP) and 163 ng L^{-1} (BuP)[70,71].

There aren't many studies on BeP in surface waters, BeP was only infrequently found in water samples, where its maximum concentration was 4.4 ng L^{-1} [72]. Moreover, there is a wide range in the time of year when these pollutants are most frequently found in surface waters. Low flow conditions were connected with the highest observed paraben concentrations[73,74]. Seasons with low flows cause loads of released chemicals to dissolve in less water, increasing the concentrations of such compounds. However, the level of parabens was shockingly high during the high-flow season[75]. This occurred as a result of wastewater treatment plants' discharge of raw materials into rivers.

The capabilities of the WWTPs were surpassed during periods of severe rainfall, which led to the direct discharge of some of the untreated influents into the environment. When calculating the environmental impact of personal care products, paying close attention to local conditions, and using technical solutions, seasonal variations should be taken into consideration. The findings

regarding paraben levels in water are inconclusive. It was reported that the occurrence of the most commonly used methylparaben in tap water at concentrations of around 15 ng L^{-1} (17 ± 4 ng L^{-1}) [76]. While another investigation found no evidence of MeP in water filtration plant-treated drinking water[77].

Table 2.3: Concentration Ranges of Parabens Detected in Surface Waters (ng L^{-1})

	Sampling area (number of sites)	MeP	EtP	PrP	BuP	BeP	References
Riverine water	Pearl River Delta, South China (9 sites)	NQ-1062	-	NQ-3142	ND	-	67
	South Wales, UK (10 sites)	<0.3-400	<0.5-15	<0.2-24	<0.3-52	-	68
	Galicia, Spain (2 sites)	1.8-17.3	NQ-3.0	NQ—69	NQ-7.0	NQ-1.2	69
	North-eastern part of Switzerland (3 sites)	3.1-17	<0.3-1.6	<0.5-5.8	<0.2-2.8	<0.2-4.4	70
	Not specified	ND-NQ (LOD=17)	ND-NQ (LOD=8.8)	NQ-23.8 (LOD-4.0)	ND-54.1 (LOD=5.7)	-	78
	Southern India (29 sites)	ND-22.8	2.47-147	ND-57.0	NQ	-	70
	Urban streams in	25-676	<1.3-64	<0.8-207	<0.6-163	<0.2-2.3	71

	Tokushima and Osaka, Japan (12 sites)						
	Central Pacific region of Japan (4 sites)	2.1-5.4	NQ	4.9-25	NQ-12	-	79
	Greater Pittsburgh Area, USA (6 sites)	2.2-17.3	ND	ND-12	ND-0.2	-	101
Estuarine system	Ria de Aveiro area, Portugal (>50 sites)	<1.6-62	<0.3-6.7	<0.5-0.64	<0.2-42	0.2-0.3	80

NQ — detected but too low to be quantified; ND — not detected; LOD — limit of detection.

2.8.3 Soils, Sediments and Sludge

The solubility of these compounds and their octanol-water partition coefficient determining affinity to organic matter indicate that the accumulation of these compounds in sediments increases with the chain length of alkyl substituent. Some results showed that parabens, as well as their chlorinated derivatives preferentially partition into the suspended solid phase in river water. The concentrations of parabens and their chlorinated derivatives in the suspended solid phase are several times higher than those in the dissolved phase[79]. In Spain, a series of studies was carried out on the various types of compounds in agricultural and forestry soils and sediments[81]. The highest concentration of these compounds was found for the two most commonly used preservatives, MeP and PrP (the most often used preservatives in health care and

beauty products). The recorded values were up to 6.35, 5.10, 0.29, 4.03, 0.45, 0.71 ng g^{-1} dry weight (dw) for MeP, EtP, iPrP, PrP, BeP and BuP, respectively.

It is important to mention that, in general, in terms of the concentration of these compounds the highest concentrations were found in sediments[81]. This may arise from the fact that sediments typically contain a lot of organic fractions and may have continuous contact with pollutants dissolved in aqueous solution, which leads to paraben deposition. The presence of high levels of BuP (377 ng g^{-1} dw) in marine sediment samples was found from contaminated site in Tenerife[82]. It was also reported that the presence of several parabens in agricultural soils, soils amended with treated sewage sludge and industrial soils, with the higher concentration of MeP (up to 8.04 ng g^{-1} dw), followed by EtP (up to 1.23 ng g^{-1} dw) and two forms of BuP (about 1 ng g^{-1} dw each) [83]. PrP was found to be present in the garden soil at 1.5 ng g^{-1} dw[84]. Relatively high concentrations of parabens, up to 127 ng g^{-1} dw for MeP and up to 15–23 ng g^{-1} dw for EtP, PrP and BuP, were found in sediments and soils from Canada[85]. The effect of effluent discharges from wastewater treatment plants on water ecosystems is clearly visible when comparing concentrations of parabens in sediments from parts of the river situated below the dispersion plume of the wastewater effluents (19–56 ng g^{-1} dw), to sediments from a pristine mountain stream, where no Parabens were detected[85]. Several studies focused on occurrence of parabens in sewage sludge and biosolids[86,87,88,89]. Methylparaben and propylparaben were found in most of the WWTP samples, at levels between 5 – 202 ng g^{-1} dw and 4 – 44 ng g^{-1} dw, respectively[86,87,88].

The concentrations of MeP and PrP in municipal sludge cakes (biosolids) were similar, up to 91 ng d^{-1} dw and 8 ng d^{-1} dw, respectively. However, EtP and BuP were not detected[89]. The vegetables that were gathered from soil that had been fertilized with municipal biosolids showed no signs of any of the six parabens examined[90]. According to estimates, parabens discovered in

sewage sludge from WWTPs were present at levels that did not endanger individuals or the environment when the sludge was used as fertilizer or a soil amendment[91]. Nonetheless, additional research to determine the possibility for endocrine disruption would be advised.

2.8.4 Air and Dust

The presence of parabens in air and dust suggests that they came from the personal care products used by households[92,93]. Personal exposure to these compounds can be via inhalation and oral ingestion[92]. The concentrations of parabens found in indoor air were up to 21 ng m^{-3} for MeP, 4.0 ng m^{-3} for EtP and 3.2 ng m^{-3} for BuP[92]. The estimated daily mean breathing rates for adults (16–70 years) and children (0–2 years) are equal to 185 dm^3 kg^{-1} bw day^{-1} and 658 dm^3 kg^{-1} bw day^{-1}, respectively[94]. According to mean breathing rates and the assumption that the most frequently detected MeP (67%) is present in indoor air at a median concentration (2.9 ng m^{-3}), the daily intake of MeP through inhalation is equal to 0.547 ng kg^{-1} bw day^{-1} and 1.91 ng kg^{-1} bw day^{-1} for adults and children, respectively[93]. When maximal MeP concentration (21 ng m^{-3}) is used in the calculations, the estimated daily intake is equal to 3.89 ng kg^{-1} bw day^{-1} for adults and 13.8 ng kg^{-1} bw day^{-1} for children[93].

The values of paraben concentrations in indoor dust indicated significant regional and individual variation, likely as a result of varied per capita consumption of personal care products. The most prevalent parabens were methyl and propyl. The maximal measured concentrations were 14,300 ng g^{-1} for MeP, 3110 ng g^{-1} for EtP, 110,800 ng g^{-1} for PrP, 3920 ng g^{-1} for BuP and 190 ng g^{-1} for BeP[92,93,95,96,97]. However, when compared with the levels of these compounds in the sewage sludge, the concentrations of these compounds in dust were much higher. The following total geometric mean concentrations of six parabens in dust were found, in the decreasing order, in

Korea (2320 ng g^{-1}) > Japan (2300 ng g^{-1}) > USA (1390 ng g^{-1}) > China (418 ng g^{-1}), while the average concentration of the sum of four parabens in Europe (Spain) was 1399 ng g^{-1}. Methylparaben accounted for 42–73 % of the total paraben concentrations[92,93,95,96,97]. The mean estimated daily intakes (EDIs) of total parabens via dust ingestion were estimated to be high for infants (5.57 ng kg^{-1} bw day^{-1}) and toddlers (6.63 ng kg^{-1} bw day^{-1}). The mean EDIs for children were between 0.98 ng kg^{-1} bw day^{-1} to 5.42 ng kg^{-1} bw day^{-1}, depending on the region. The mean EDIs of parabens via dust ingestion were 5–10 times lower in adults than in children, 0.2–1.18 ng kg^{-1} bw day^{-1} [97].

2.8.5 Biota

The data concerning paraben presence in organisms are scarce. Parabens were detected in fish tissue (20 species) with great frequency[98,99]. Out of the 20 species analysed, MeP, PrP and BuP were found in over 90% of the samples, whereas EtP in about 70%. The highest concentration of MeP was found in fish tissue samples with a concentration of up to 3600 ng g^{-1}. The concentrations of three of the four compounds, namely EtP, PrP, and BuP, in fish were over 840 ng g^{-1}, 1100ng g^{-1}, and 70 ng g^{-1}, respectively. The values of total concentrations of parabens in adult fish (coral grouper) were over twice as high (4700 ng g^{-1}) as in juvenile form (2200 ng g^{-1}), which may indicate growth-dependent compound accumulation[99]. However, in fish tissue samples, the concentrations of these compounds were much lower and equaled maximally 84.69 ± 6.58 ng g^{-1} for methylparaben and 0.19 ± 0.04 ng g^{-1} for propylparaben[100]. Moreover, parabens were found to be absent in the fish brain tissue[101]. The estimated dietary human exposure to the four parabens in the Philippines through fish meat intake was 2 µg kg^{-1} day^{-1}, and was 5000-times lower than the acceptable daily intake (10 mg kg^{-1} day^{-1})[99].

2.9 Pathways and Sources

The global spread of the use of parabens has resulted in their widespread presence in the environment. The main sources of these compounds are wastewater treatment plants. Although the presence of these compounds in various forms of the environment is known to be associated with human exposure, the main sources of this chemical are pharmaceutical and personal care products. The fate of parabens in the environment as well as sources and pathways of human exposure are compiled in Figure 2.1.

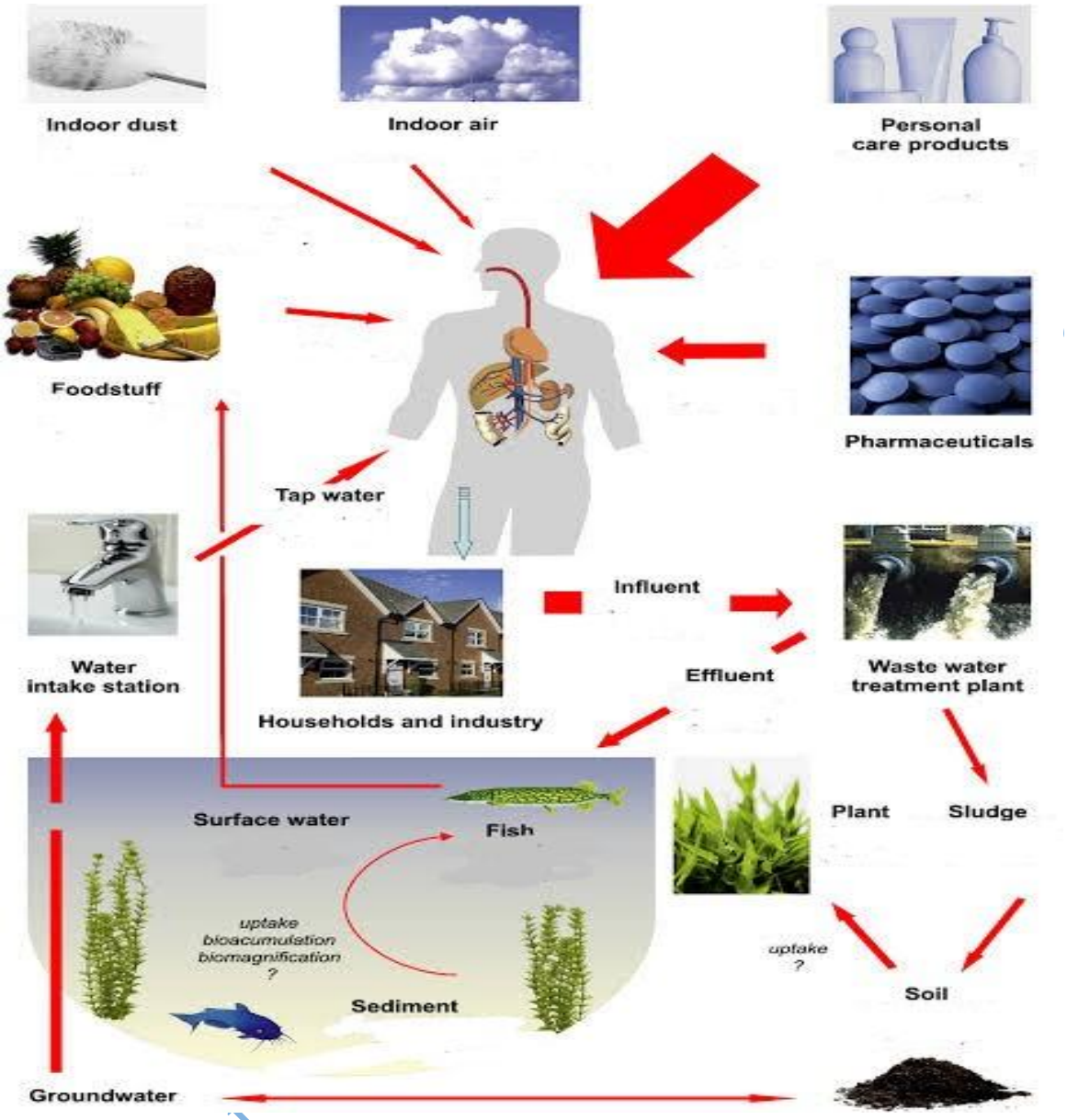

Figure 2.1: Sources, Fate and Pathways of Exposure to Parabens in the Environment

Source[64,65,66,67,68,69,70,71,72,73,74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90,91,92,93,94,95,96,97,98,99].

2.10 Occurrence of Parabens in Personal Care Products, Pharmaceuticals and Food

2.10.1 Occurrence in Personal Care Products (PCP)

Humans are exposed to parabens through the daily use of PCPs. The main contribution from the exposure is via the dermal route while smaller contribution comes from the exposure by ingestion and inhalation. In 215 cosmetic goods, parabens were used often, and MeP, EtP, and PrP detection rates were 98%, 32% and 38%, respectively[102]. The maximum concentrations of MeP and PrP were up to 3200 µg g^{-1} and EtP at 1900 µg g^{-1} [102]. Both BuP and BzP were present in 16% of products, at levels of 100–600 µg g^{-1} and 100–700 µg g^{-1}, respectively[102]. The average detection frequencies based on the more recent research articles, for MeP, EtP, PrP and BuP were 73%, 38%, 65%, and 25%, respectively[103,104,105,106,107]. These results suggest that parabens are still widely used in cosmetic goods, even if their direct comparability is complicated by potential variations in method detection limits (MDL). Depending on the type of PCP being used, paraben detection frequencies and concentrations vary greatly. Rinse-off and leave-on products can be used to categorize PCPs that include parabens. MeP, EtP, and PrP maximum and mean concentrations were found to be 8200, 1040, and 488 µg g^{-1} and 757, 94.5, and 47.2 µg g^{-1}, respectively, for rinse-off products like body wash in the United States[103].

In comparison to Chinese rinse-off products, these paraben concentrations were one to three orders of magnitude higher. The reported median amounts of MeP, EtP, and PrP in body wash (n = 6) in China were 7.23, 1.48, and 9.99 µg g^{-1}, which were comparable to prior results (the maximum concentrations were not indicated)[105,108]. Using a novel technique (ultrahigh-performance liquid chromatography-tandem mass spectrometry), the researchers examined 22 shower gel varieties offered for sale in Spain. MeP was discovered to be the most prevalent paraben, with maximum and median concentrations of 1209 µg^{-1} and 3.28 µg g^{-1}, respectively.

EtP came in second with maximum and median concentrations of 10.6μ g g^{-1} and 9.29μ g g^{-1}, respectively, and PrP came in third with maximum and median concentrations of 7.96μ g g^{-1} and 7.04 μg g^{-1}, respectively[108]. In bodywash products (n = 18) available in China, a different investigation found slightly lower paraben concentrations: the maximum concentrations of MeP, EtP, and PrP were 2.8, 1.3, and 0.6 μg g^{-1}, respectively, while the mean concentrations were 0.5, 0.1, and 0.1 μg g^{-1}, respectively[104]. The paraben level in leave-on goods, like body or hand lotions and face creams, however, seems to be comparable between those sold in China and the United States, with far higher concentrations than those found in other items. Because leave-on PCPs have a larger lipid content than rinse-off PCPs, the latter need more preservatives to maintain the quality of the latter's goods, which is why the former contain higher levels of parabens[108]. It was showed that body or hand lotions (n = 18) and face creams (n = 11) contained the highest levels of MeP, EtP, and PrP, at 2830, 379, and 1540 μg g^{-1}, respectively, with the mean concentrations being 1120, 31.2, and 596 μg g^{-1}, respectively[104]. Among the body lotions (n = 12), creams (n = 23), and toners (n = 10) offered in China, similar quantities of parabens (mean values at 300-450 μg g^{-1}) were found[110].

The maximum reported MeP concentrations in the United States were 3540 μg g^{-1} in 21 face creams and 2880 μg g^{-1} in 23 skin lotions, which were in the same order of magnitude as the levels found in comparable products in China [103]. The levels of EtP and PrP in the PCPs were also comparable in the two countries' products. Another study examined 77 feminine hygiene items and discovered that bactericidal creams and solutions had the highest levels of total parabens among all the tested samples, with a range of 0.363 to 946 μg g^{-1} and a median value of 5.35 μg g^{-1} that was consistent with the paraben levels of other types of PCPs[106]. With maximum concentrations up to 2 mg g^{-1} (mean concentrations: 267, 109, 81.6, and 318 μg g^{-1}, respectively),

the highest BuP concentrations in the U.S. were found in face cleansers, skin lotions, face creams, and lipstick [103]. However, the values of BuP were much lower in other types of PCPs when compared to MeP, EtP, and PrP. Butylparaben levels (concentration range) were tens of micrograms per gram in several PCPs (face cream, face cleanser), which is comparable to the levels of EtP and PrP in China[110,104]. Spain was the lone exception, where PCP BuP levels ranged from 2.16-2.83 µg g-1 [108]. These findings suggest that BuP is also commonly utilized in several PCPs. In PCPs, BzP and p-HBA have been found less frequently. Baby sunscreen was found to contain a high amount of BzP (up to 8.18 µg g^{-1}, with a mean of 2.56 µg g^{-1}) [103].

Overall, it appears that China has significantly less parabens in PCPs than some other nations do (the U.S. and Spain). Meanwhile, low quantities of parabens may imply higher levels of other sorts of preservatives, such as methylchloroisothiazolinone and methylisothiazolinone used in body wash and shampoo, given that other types of additives and preservatives are also utilized in PCPs[104]. In addition to PCPs, parabens are added to other consumer products, including commercial dentifrices, sanitary wipes, tickets, newspapers, food cartons, and paper currency[107,111]. Because paper products are mainly made of organic materials, such as wood fiber, linen or cotton, parabens have been employed as preservatives in the prevention of mold growth on paper products. The concentrations of total parabens in most analysed paper products were in the order of a few tens to thousands of ng g^{-1}; one sample contained ~2.25 mg g^{-1} of MeP[111]. The concentrations of parabens in dentifrices were above milligrams per gram, and it was demonstrated that, after using toothpaste and mouthwash, micrograms of paraben residues remain in the oral cavity[107].

Pads, pantyliners, tampons, and wipes were among the 77 feminine hygiene goods that parabens were discovered in, though at lower amounts than in the other examined feminine hygiene

products. MeP, EtP, and PrP were the three most prevalent parabens, with detection frequencies of 50–100%[106]. Furthermore, parabens have been found in pantyhose and socks at concentrations ranging from ng g^{-1} to µg g^{-1} [112,113]. This implies that while if exposure to parabens through consumer items is less than that through PCPs, it is still a possibility and should not be disregarded.

2.10.2 Occurrence in Pharmaceuticals

Parabens are employed as excipients and preservatives in the pharmaceutical business to stop the growth or deterioration of drugs. According to a U.S. study, liquid medicines had the greatest paraben occurrence rate (44%), and the highest total paraben content was 2689 µg g^{-1} [114]. Methyparaben and Propylparaben were the parabens found in medicinal items the most frequently, as was to be expected. Interestingly, substantial concentrations of p-HBA in the range of 0–128 µg g^{-1} were also discovered. This finding suggests that the presence of p-HBA should be included in future studies on the effects of PCPs and pharmaceuticals. Compared to solid formulations and soft gels, liquid pharmaceuticals have low concentrations of parabens, which is because they are unlikely to cause any issues with the growth of microorganisms. Aside from the U.S., p-HBA was also detected in various pharmaceutical formulations made in other countries, such as Japan, Italy, and Spain[114]. Although the exact source of p-HBA was not known, it was found that the frequency of its presence exceeded that of other major parabens (MeP and PrP) compounds[112].

A study conducted in China revealed that the detection frequency of every major paraben exceeded the detection frequency of the respective parabens in the pharmaceuticals sold in the U.S. [115]. A study conducted in China also revealed that the detection rate of various major

paraben compounds exceeded that of the other compounds. The daily intake of pharmaceuticals, which is computed based on the estimated daily consumption, was lower than that of food and PCPs. This suggests that the pharmaceutical industry is not a major source of paraben for humans. However, in certain cases, the use of liquid formulations that contain high levels of parabens can be considered a concern. This is because of the possible effects of the compounds on the health of susceptible individuals, such as pregnant women.

2.10.3 Occurrence in Food

Since parabens are allowed as preservatives in food products, it is not surprising that studies have shown high levels of these compounds in various food items. Some of the different types of food products that contain these parabens include processed food. Among the different types of parabens, the compounds that are commonly used in food products are MeP, PrP, and EtP, while BuP and BzP are less used. With the exception of Saudi Arabia, where ready-to-eat food contained paraben levels of up to mg g^{-1} of total parabens114, paraben levels in food products are typically lower in food products, ranging from g g^{-1} to below ng g^{-1} levels, despite the fact that the detection rate of parabens in food products is comparable to that of PCPs[116]. It was noted that at least one of the six parabens examined was present in 282 food samples from 13 food categories, including cereals, meat, fish, and seafood, eggs, dairy products, bean products, fruits, vegetables, cookies, beverages, cooking oils, and condiments, which were gathered from nine Chinese cities[117].

The total paraben concentrations ranged from of 0–2.53 µg g^{-1} fresh weight. MeP was found in vegetables at a maximum concentration of 2.17 µg g^{-1}. Nevertheless, condiments had the highest levels of EtP and PrP, which were 1.14 and 0.547 µg g^{-1}, respectively. Although there were

varying levels of parabens found in different food products, the levels of these compounds were not significantly different between the analysed categories[118]. In the US, 267 samples totaling beverages, dairy products, fats and oils, fish and shellfish, cereals, meat, fruits, and vegetables were examined for parabens[118]. Although the concentration range was different (0-0.409 µg g^{-1} fresh weight), with the highest detected concentration being around six times lower than in the samples from China, it was discovered that the rate of paraben detection in food was comparable to that of samples taken in China. However, there was no discernible difference in the overall concentrations of parabens among dietary groups. In Slovenia and China, the levels of these compounds were not significantly different from those in the U.S, which contained parabens at ng L^{-1}, however, the surprising finding was in one of the tincture samples, which had a concentration of 2.22 mg L^{-1} [119,120]. The latter was unexpected because it exceeded ADI[121].

It is important to talk about that the detection rate of the total parabens that are present in food items sold in China and the U.S. was approximately 90%, which is significantly higher compared to the food items analysed in Saudi Arabia[117,116]. However, in Saudi Arabia, the levels of parabens in processed food were three orders of magnitude higher when compared to the concentrations in the U.S[116,117,118]. A total of 215 ready-to-eat food products were analysed for the study, and the levels of these compounds were found in different food categories such as vegetables, fruits, dairy products, and cereals, meat, fish, cookies and snacks, beverages, condiments and others. Almost all of the samples analysed had parabens with varying levels of total paraben of 0-1113 µg g^{-1} [116]. The highest concentrations were found in cereals and condiments, where the measured MeP at ~495.7 µg g^{-1} was the highest concentration in all analysed samples and at the same level as in Personal Care Products. Compared to other food products, the levels of parabens were found to be low in baby food products food (n = 112,

including meat, fish, fruit, vegetable, and cheese) from Italy, which is believed to be due to the country's strict regulations regarding the use of preservatives in baby food products[122].

However, surprisingly p-HBA which is the major metabolite of parabens was also found in all the samples. The presence of p-HBA was also found in various food such as fish and fish products, pet food, and beverages[119,120,123,124,125,126]. It is not clear if the presence of this compound in fruits and vegetables is due to the degradation of the parabens or if it is natural. Products such as foods that are not processed and do not contain preservatives, such as seafood and fish, are also known to contain high levels of parabens with MeP, EtP and PrP as dominant parabens. The concentration range of these substances according to a study on five fish species was 0.26 to 1.71 ng g^{-1} wet weight in Taihu Lake from 2009 to 2017[127]. High quantities of MeP, PrP, and EtP were present in every sample, and 77% of the samples also included BzP. There were no appreciable variations in the paraben concentrations among the five fish species.

Studies of a similar nature were also carried out in China and the US, where the maximum levels of MeP in fish were determined to be 4.79 ng g^{-1} and 12.2 ng g^{-1}, respectively.[117,118] In the meantime, the highest concentrations of MeP in fish and shrimp were found in Taiwan, China, at 18.5 ng g-1; in Milan, Italy, the concentrations of MeP in fish and bivalves ranged from 0.8 to 32 ng g-1; and in the UK, the highest concentrations of MeP in fish and shrimp were found at 2.8 ng g^{-1} [124,125,128]. In fish and seafood, Europe and North Africa had the highest levels of PrP (0.65 ng g^{-1})[123]. These findings suggested paraben contamination in the environment. MeP was the most frequently found type of paraben in fish samples across studies, despite having the lowest potential for bioaccumulation among the commonly used parabens. This raises concerns about the environmental concentrations of parabens and whether MeP is present at the highest levels compared to other parabens.

The chemicals were detected in greater concentrations in PCPs, cosmetics, and liquid medications than in food products, according to an assessment of the data gathered regarding their prevalence in various food, pharmaceutical, and personal care goods. The median paraben concentrations in PCPs have been found to be at g g^{-1} level, with the highest concentration value reaching hundreds of µg g^{-1}, several orders of magnitude higher than the paraben levels found in food, despite the fact that liquid pharmaceuticals typically contain ng g^{-1} levels of parabens. Despite the fact that parabens are present in food products at high exposure levels, it is crucial to remember that this exposure is still much higher than that of pharmaceuticals. Although the three most common types of parabens (MeP, EtP and PrP) were found in both food and personal care products, their relative prevalence was different in different categories. While EtP is the second most commonly used paraben in food, followed by PrP, in PCPs, cosmetics and pharmaceuticals, PrP was the second highest occuring paraben after MeP. Studies also indicated that the use of both PrP and MeP in combination was common. For instance, it was demonstrated that the concentrations of MeP and PrP had a significant linear correlation (r=0.74) in cosmetics[104]. It is believed that the use of mixtures of these two compounds allows for the reduction of their overall levels while increasing the effectiveness of the preservative activity.

2.11 Human Exposure and Health Effects

A human's exposure to different ambient chemicals can result from a number of different things, including inhalation, nutritional intake, and skin absorption. According to research, the primary human source of parabens is dermal PCP application.[104]. Parabens are partially degraded to p-HBA and partially transported into the bloodstream after cutaneous absorption to keratinocytes, where they then undergo metabolic transformation[129]. In general, parabens do not accumulate in the tissues since they are digested by the body. Certain parabens have a short half-life; therefore,

their metabolites can be employed as biomarkers to gauge human exposure[130]. Since 1984, reports on the impact of parabens on women's estrogenic qualities have surfaced[131]. Much research has been done on the relationship between exposure to these chemicals and numerous endocrine-related disorders, particularly in sensitive individuals including children and pregnant women. Several recent research on the amounts of these compounds in children and pregnant women have been evaluated due to the growing concerns about the negative effects of parabens. In order to discover potential patterns and elements that would merit additional research, these studies were then contrasted with the levels seen in the general population.

2.11.1 Susceptible Population - Pregnant Women

Due to the importance of the endocrine system particularly in pregnant women, it is important that the system is regularly monitored because slight disruption in its functioning may lead to complications during pregnancy. Therefore, these subjects are particularly vulnerable to endocrine disruption. Epidemiological and toxicological studies have shown that exposure to various parabens can cause various health conditions. For example, in China, the exposure levels of urinary parabens during early pregnancy were conducted in relation to gestational diabetes mellitus (GDM) [132]. They found that the levels of EtP in the urine of these pregnant women with GDM were higher than those of the women who did not have gestational diabetes. There was also no evidence indicating that the levels of EtP or PrP in the urine of pregnant women were linked to the development of gestational diabetes.

The researchers concluded that the higher levels of EtP could be associated with an increased risk of GDM in women who were older or obese before conceiving. Other studies also indicated that the levels of PrP and BuP in the urine of pregnant women were associated with lower

inflammation and higher levels of oxidative stress biomarkers[133]. Furthermore, it was discovered that the amounts of EtP in the urine associated favorably with oxidative stress indicators including malondialdehyde and 8-hydroxydeoxyguanosine, indicating that EtP exposure may contribute to oxidative stress[134]. This is noteworthy in light of research showing that oxidative stressor exposure during pregnancy and early childhood may affect adult health[135]. It is important that the levels of EtP in the urine of pregnant women are regularly monitored. Data collected from various sources such as the breast milk, serum, and placenta of pregnant women showed that the levels of parabens were detected in various components of their bodies during the period 2013 to 2020 the results also showed that pregnant women in the U.S. had the highest concentration of paraben in their urine, which was over 1000 µg L^{-1}, and that the median concentrations in more than ten nations, including the U.S., were more than 100 µg L^{-1} for MeP and 20 µg L^{-1} for PrP (Figure 2) [133,136,137,138,139,140,141,142,143].

The levels of several parabens were higher in Greece than they had been in other investigations. For instance, MeP and PrP were found at the maximum concentrations of 67,461 and 28,182 µg L^{-1}, respectively[144]. The concentration distribution was uneven, with just a few significantly higher concentrations, as indicated by the median concentrations being lower than 100 µg L^{-1}. The next greatest concentrations were discovered in the U.S., where MeP and PrP had maximum values of ~12,598 µg L^{-1} and ~2028 µg L^{-1} respectively, and average values of 687 µg L^{-1} and 142 µg L^{-1} [145]. Pregnant women's urine samples were shown to have lower concentrations of these substances, according to other studies carried out in this nation. These were higher than those discovered in other nations despite the lower amounts of these substances[145]. MeP and PrP median concentrations in pregnant women's urine in China were 16 and 0.83 µg L^{-1}, 4.25 and 0.3

μg L^{-1}, and 19.37 and 1.83 μg L^{-1}, respectively. These values were 10 times lower than those in other nations[146,147,148].

Similar patterns were observed in the paraben concentrations measured in indoor dust samples, which were likewise lower in the samples from China than in those from other nations. The higher per capita usage of cosmetics and PCPs in the U.S., Japan, Korea, and France compared to China may be the cause of the higher levels of parabens discovered in the dust and human samples from these nations. Except for samples from Korea, where the median amounts of EtP were 4–9 times higher than those in other countries, the levels of EtP in the urine of pregnant women were typically low or undetectable[134]. Nonetheless, the maximum concentration of these compounds was high in several nations, including Japan, China, and the United States 2022, 2929 and 653 μg L^{-1}, respectively. Although the levels of BuP were generally lower in the urine samples of pregnant women, a study conducted in the U.S. revealed that the chemical was found in a high concentration at a level of ~146.61 μg L^{-1} [145].

These findings are similar to previous studies from 2010 to 2013 summarized in a review[134,142,149,150,151,152,153,154]. Both according to the review and the data reviewed herein (Figure 2.2) the majority of the total paraben concentrations found in the urine of pregnant women were composed of MeP and PrP, which accounted for ~90% of the total paraben concentrations. The levels of PrP were also associated with the presence of MeP in the urine samples of pregnant women. This was expected since the common use of both PrP and MeP in various products had been known to increase the exposure of these chemicals to pregnant women[134]. As was predicted, there are significant geographic differences in the prevalence and levels of parabens in pregnant women, which are probably caused by variations in the paraben content of PCPs, food, and environmental matrices among nations.

It was impossible to identify a clear trend in the amounts of these compounds over time because of the scant information concerning their presence in urine samples from pregnant women. Therefore, it is still unknown whether the susceptible populations' exposure is rising or falling over time. In addition to the presence of these chemicals in the urine samples, they were also found in other body fluids, such as the breast milk, amniotic fluid, and serum; the latter implying that parabens can cross the placental barrier and affect the development of the fetus[139,153,155,156,157,158,159]. Despite the various precautionary measures that women can take to avoid exposure to harmful chemicals, they still continue to ignore the effects of PCPs. The high levels of PCPs in pregnant women could be due to the increased metabolism of these women. This is because their bodies can easily absorb these chemicals, which could be one of the reasons for the high paraben levels in pregnant women.

2.11.2 Susceptible Population – Children

Studies on children's exposure to parabens have just lately started to emerge and are very restricted, despite the fact that children are more vulnerable than adults to some environmental stressors like EDCs. It has been known that exposure to certain chemicals, such as parabens, can cause DNA damage in children. They have also been linked to an increased risk of developing asthma and aeroallergen sensitization[134,160,161,162]. In addition, exposure to EtP can also cause respiratory health issues[163]. In studies conducted on children's urine samples from various countries, the detection frequencies and paraben concentrations, including MeP, were found to exceed 86%., and EtP and PrP were found in over 60% of samples.

The data collected from various countries revealed that the median concentrations of MeP decreased following the descending order: Korea (79.6 μg L^{-1})[134] > Albany, the U.S. (51.8 μg L^{-}

^{1})[164] > Brazil (38.8 µg L^{-1})[160] > California, the U.S. (38.6 µg L^{-1})[138] > Greece (17.1 µg L^{-1})[144] > Germany (14.5 µg L^{-1})[164] > Greece (11.5 µg L^{-1})[166] (Figure 2.3). The data collected from various countries revealed that the median level of MeP in the urine samples of children was below 10 micrograms per liter, including Sweden, India, China[164,167,168,169]. Methylparaben levels ranged from 2.25 µg $L^{-1}$and 79.6 µg L^{-1}, which was higher than the values for PrP (0.5–3.4 µg L^{-1}) and for EtP (0.15–2.8 µg L^{-1}) at the minimum and maximum, respectively. A study on kindergarten and primary school students found that older children had higher levels of parabens in their urine samples, indicating that older children are exposed to larger quantities of parabens[169].

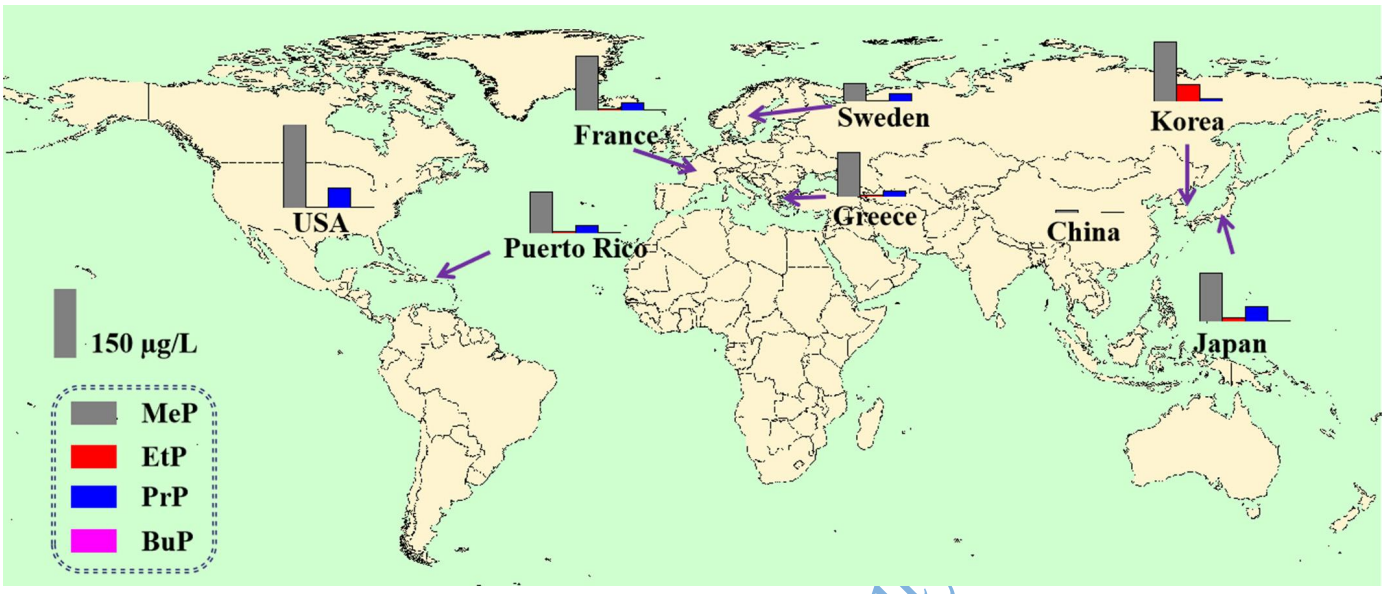

Figure 2.2: Concentrations of Parabens in the Urine of Pregnant Women in Different Countries

The bar graphs show the median concentrations of MeP, EtP, PrP and BuP (µg L^{-1}) measured in urine samples collected from pregnant women in the respective countries. (n-number of samples analysed). [USA (n=481); Puerto Rico (n=602); France (n=520); Sweden (n=98); Greece (n=239); Korea (n=46); China (n=209); Japan (n=111)].

Source[136,137,138,139,140,141,142,143]

A comparable study conducted in Brazil examined the levels of MeP and PrP in the urine of children between the ages of 6 and 14 as well as between male and female children. It discovered that older female children had higher levels of MeP and PrP in their urine than younger female children[160]. Increasing usage of PCPs, paraben-containing processed foods, and cosmetics by older kids may be the cause of this. However, other research likewise revealed no difference in paraben concentrations in different gender groups of children in the U.S. and China, despite the fact that there were variations in the two age groups examined in the latter study[164]. However, they noted that the levels of these chemicals were higher in Korean infants. This suggests that their mothers may have been exposed to high levels of these chemicals as South Korea is a known consumer of cosmetics and personal care products[134,170]. Generally, compared to pregnant women, children had decreased but still significant paraben levels. (Figures 2.2 and 2.3).

2.11.3 General Population

The scientific literature has continued to expand regarding the effects of parabens on humans. In addition, studies have shown that these chemicals can cause various health effects, such as reproductive damage, developmental impairment, metabolic disorders and cancer, has been rapidly increasing. In epidemiological studies, it has been shown that the levels of urinary paraben especially BuP in the urine can affect the length of a woman's menstrual cycle[171]. This relationship was also observed in women with high levels of EtP and MeP, which can lead to reduced fecundity[172]. Another research has revealed a substantial dose-response association between paraben exposure levels and type 2 diabetes mellitus (T2DM)[173]. In vitro migration and invasion of human breast cancer cells were induced by exposure to parabens at levels that produced the maximum proliferative response, and PrP inhibited apoptosis in cancer cells by activating Akt kinases[174,175].

It has been shown that individual parabens or their combinations can increase proliferation of human breast cancer cells at the concentrations detected in breast cancer tissue by comparing the established paraben concentrations which cause the maximum growth of human breast cancer cells in vitro to the measured paraben concentrations in breast tissue[176]. In 2004, it was discovered that these substances were present in human breast cancer tissue; later, it was determined that these substances were also present in all areas of the human breast, with median concentrations of 168 ng g^{-1} for PrP, 16.6 ng g^{-1} for MeP, and 85.5 ng g^{-1} for total parabens[177,178].

These findings emphasize the value of keeping an eye on human exposure levels to parabens. The highest median values have been found in Japan, with female urine samples for MeP and PrP measuring ~273 µg $L^{-1}$and ~8.4 µg L^{-1}, respectively, and male populations measuring 43.8 and 1.49 µg L^{-1}, respectively[179]. These two countries appear to have much greater paraben exposure levels than other countries when combined with the paraben levels measured in Korea, which were 166 µg L-1 for MeP and 15.5 µg L-1 for PrP[180]. Comparing urinary paraben levels across nations indicated that, on average, persons in developed nations are exposed to far lower levels of parabens than people in the U.S., the E.U., Japan, and South Korea (Figs. 2.3 - 2.4), indicating regional diversity in product usage and paraben content. For instance, in Saudi Arabia, patients with type 2 diabetes mellitus had a greater concentration of parabens than the control group without T2DM[173]. This suggests that the country's food products are also more contaminated with these chemicals compared to other regions[116]. However, the exact relationship between these two observations is still being studied. Overall, the data collected from the literature suggest that the levels of these chemicals in the urine are different in different demographic groups (Figure 2.3).

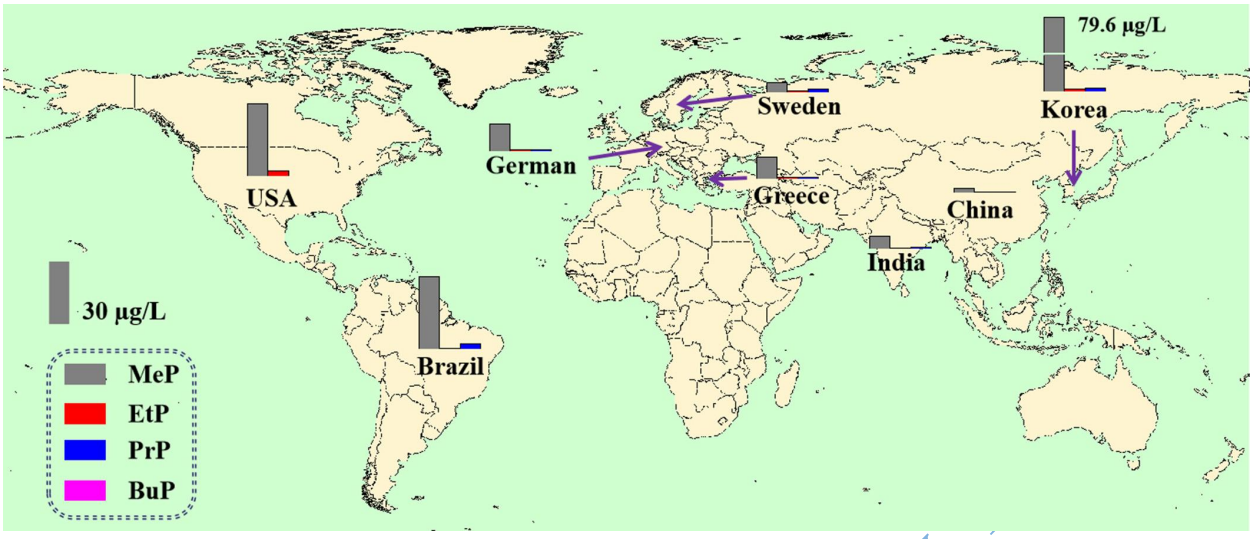

Figure 2.3: Concentrations of Parabens in the Urine of Children (2–14 years old) in Different Countries

The bar graphs show the median concentration of MeP, EtP, PrP and BuP (µg L^{-1}) measured in urine samples collected from children in the respective countries. (n– number of samples analysed). [USA (n=40); Brazil (n=300); German (n=59); Sweden (n=98); Greece (n=500); Korea (n=46); China (n=255); Indian (n=76)].

Source[134,144,160,164,165,167,168,169]

For example, a comparison of the female and male groups revealed that, between 2005 and 2009 in the United States, the median urine MeP concentrations in females (60 µg g-1) were roughly 10 times higher than in males (6.37 µg g-1), which was consistent with the findings from earlier studies[171,172,179,181,182,183,184]. To compare the amounts of each paraben in the three population categories, data on the levels of urine parabens in pregnant women, children, and the general population were examined across numerous nations worldwide. According to the investigation, pregnant women had levels of MeP and PrP (median values: 122 and 22.8 µg L^{-1}, respectively) that were 6–10 times greater than those of children (MeP: 14.5 µg L^{-1}, PrP: 0.945 µg L^{-1}) and the general population (MeP: 20.7 µg L^{-1}, PrP: 2.3 µg L^{-1}.

The findings show that pregnant women are more exposed to parabens than the general population or children are (particularly for MeP and PrP), perhaps putting this vulnerable demographic group at greater risk. The fact that the median EtP levels in the three demographic groups were not significantly different may be related to the fact that all groups had far lower overall EtP body burdens than MeP and PrP levels. The median concentration of EtP was 1.895 µg L^{-1}in pregnant women, 0.66 µg L^{-1}in children and 1.608 µg L^{-1}in the general population, which were one to two orders of magnitude lower than the levels of MeP and PrPIn all the demographic groups, the level of BuP was, as was to be predicted, the lowest of the four parabens. BuP was infrequently found in urine samples from children, which differed noticeably from the amounts in pregnant women and the general population. In pregnant women, the median BuP concentration (0.25 µg L^{-1}) was highest. Low BuP concentrations found in human samples are in line with the low BuP levels found in food and PCPs.in food and PCPs.

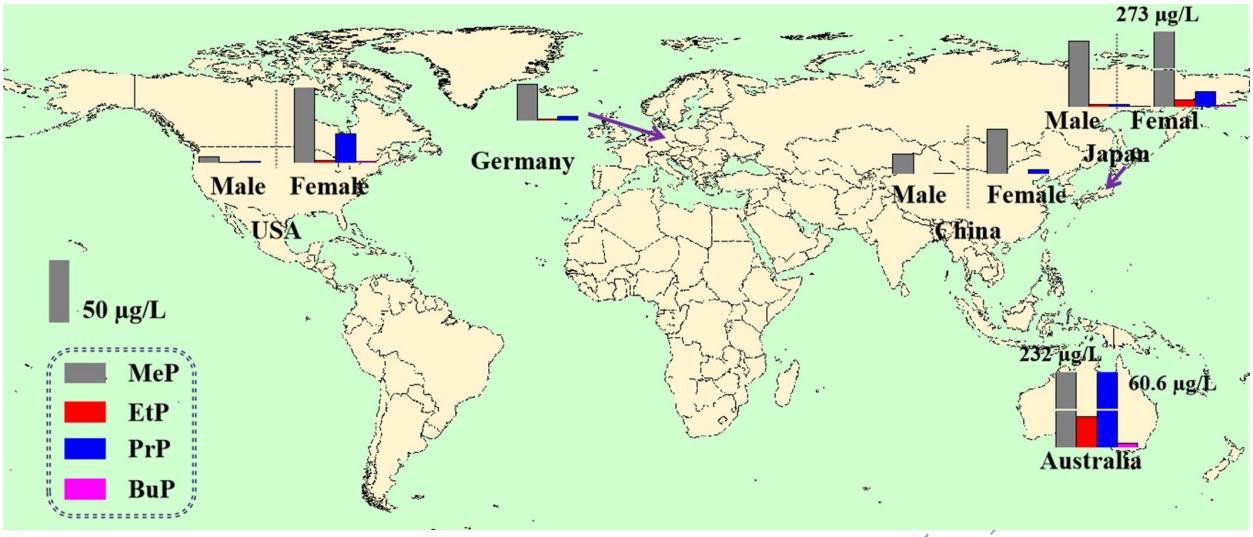

Figure 2.4: Concentrations of Parabens in the Urine of the General Population in Different Countries

The bar graphs show the median concentration of MeP, EtP, PrP and BuP (µg L^{-1}) measured in urine samples collect from general population in the respective countries. [USA (women, n=470, men, n=439); Germany (n=60); Japan (women, n= 128, men n=42); China (women, n=50, men n=50); Australia (n=2400)]

Source[116,171,172,173,179,180,181,182,183,184]

2.12 Paraben Analysis

2.12.1 Solid Phase Extraction (SPE)

Solid phase extraction (SPE) is a sample preparation technique often used by chromatographers prior to analysis. Solid phase extraction (SPE) is most often used to remove interfering compounds from a sample, although it can also be used to enrich/concentrate analytes of interest in the sample. Solid phase extraction (SPE) makes use of a solid phase material (there are many to choose from) that functions to retain the interfering substances, while solvents elute the sample, which is collected and analysed.

2.12.2 The Basic Principles and Methods of Solid Phase Extraction

SPE technology is based on liquid-solid phase chromatography theory. It uses selective adsorption and selective elution to enrich, separate and purify samples. It is a physical extraction process that includes both solid and solid phases. It can also be approximated. Think of it as a simple chromatographic process. Solid phase extraction (SPE) is a separation principle using liquid chromatography using selective adsorption and selective elution. The more common method is to pass a liquid sample through an adsorbent, retain the substance to be tested, and then use an appropriate strength solvent to wash away the impurities, and then elute the test substance with a small amount of good solvent, thereby achieving the purpose of rapid separation, purification and concentration. It is also possible to selectively adsorb the interfering impurities and let the measured substance flow out; or simultaneously adsorb the impurities and the north side substance, and then selectively elute the test substance with a suitable solvent.

2.12.3 High-Performance Liquid Chromatography (HPLC-UV)

High-performance liquid chromatography (HPLC) is a technique used to separate molecules based on size and surface charge among other properties. The incorporation of ultra-violet (UV) spectroscopy with HPLC allows the concentration of molecules to be determined following separation. High-performance liquid chromatography has been used for manufacturing (e.g., during the production process of pharmaceutical and biological products), legal (e.g., detecting performance enhancement drugs in urine), research (e.g., separating the components of a complex biological sample, or of similar synthetic chemicals from each other), and medical (e.g., detecting vitamin D levels in blood serum) purposes[185].

Chromatography can be described as a mass transfer process involving adsorption. High-performance liquid chromatography relies on pumps to pass a pressurized liquid and a sample mixture through a column filled with adsorbent, leading to the separation of the sample components. The active component of the column, the adsorbent, is typically a granular material made of solid particles (e.g., silica, polymers, etc.), 2–50 µm in size. The components of the sample mixture are separated from each other due to their different degrees of interaction with the adsorbent particles. The pressurized liquid is typically a mixture of solvents (e.g., water, acetonitrile and/or methanol) and is referred to as a "mobile phase". Its composition and temperature play a major role in the separation process by influencing the interactions taking place between sample components and adsorbent. These interactions are physical in nature, such as hydrophobic (dispersive), dipole–dipole and ionic, most often a combination.

High-performance liquid chromatography is distinguished from traditional ("low pressure") liquid chromatography because operational pressures are significantly higher (50–350 bar), while

ordinary liquid chromatography typically relies on the force of gravity to pass the mobile phase through the column. Due to the small sample amount separated in analytical HPLC, typical column dimensions are 2.1–4.6 mm diameter, and 30–250 mm length. Also, HPLC columns are made with smaller adsorbent particles (2–50 μm in average particle size). This gives HPLC superior resolving power (the ability to distinguish between compounds) when separating mixtures, which makes it a popular chromatographic technique. The schematic of an HPLC instrument typically includes a degasser, sampler, pumps, and a detector. The sampler brings the sample mixture into the mobile phase stream which carries it into the column. The pumps deliver the desired flow and composition of the mobile phase through the column. The detector generates a signal proportional to the amount of sample component emerging from the column, hence allowing for quantitative analysis of the sample components. A digital microprocessor and user software control the HPLC instrument and provide data analysis.

Some models of mechanical pumps in an HPLC instrument can mix multiple solvents together in ratios changing in time, generating a composition gradient in the mobile phase. Various detectors are in common use, such as UV/Vis, photodiode array (PDA) or based on mass spectrometry. Most HPLC instruments also have a column oven that allows for adjusting the temperature at which the separation is performed. The sample mixture to be separated and analysed is introduced, in a discrete small volume (typically microliters), into the stream of mobile phase percolating through the column. The components of the sample move through the column at different velocities, which are a function of specific physical interactions with the adsorbent (also called stationary phase). The velocity of each component depends on its chemical nature, on the nature of the stationary phase (column) and on the composition of the mobile phase. The time at which a specific analyte elutes (emerges from the column) is called its retention time. The

retention time measured under particular conditions is an identifying characteristic of a given analyte. Many different types of columns are available, filled with adsorbents varying in particle size, porosity, and surface chemistry. The use of smaller particle size packing materials requires the use of higher operational pressure ("backpressure") and typically improves chromatographic resolution (the degree of peak separation between consecutive analytes emerging from the column). Sorbent particles may be hydrophobic or polar in nature. Common mobile phases used include any miscible combination of water with various organic solvents (the most common are acetonitrile and methanol).

Some HPLC techniques use water-free mobile phases (see normal-phase chromatography below). The aqueous component of the mobile phase may contain acids (such as formic, phosphoric or trifluoroacetic acid) or salts to assist in the separation of the sample components. The composition of the mobile phase may be kept constant ("isocratic elution mode") or varied ("gradient elution mode") during the chromatographic analysis. Isocratic elution is typically effective in the separation of sample components that are very different in their affinity for the stationary phase. In gradient elution the composition of the mobile phase is varied typically from low to high eluting strength. The eluting strength of the mobile phase is reflected by analyte retention times with high eluting strength producing fast elution (=short retention times).

A typical gradient profile in reversed phase chromatography might start at 5% acetonitrile (in water or aqueous buffer) and progress linearly to 95% acetonitrile over 5–25 minutes. Periods of constant mobile phase composition may be part of any gradient profile. For example, the mobile phase composition may be kept constant at 5% acetonitrile for 1–3 min, followed by a linear change up to 95% acetonitrile. The chosen composition of the mobile phase depends on the intensity of interactions between various sample components ("analytes") and stationary phase

(e.g., hydrophobic interactions in reversed-phase HPLC). Depending on their affinity for the stationary and mobile phases, analytes partition between the two during the separation process taking place in the column. This partitioning process is similar to that which occurs during a liquid–liquid extraction but is continuous, not step-wise. In this example, using a water/acetonitrile gradient, more hydrophobic components will elute (come off the column) late, once the mobile phase gets more concentrated in acetonitrile (i.e., in a mobile phase of higher eluting strength). The choice of mobile phase components, additives (such as salts or acids) and gradient conditions depends on the nature of the column and sample components. Often a series of trial runs is performed with the sample in order to find the HPLC method which gives adequate separation.

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Chapter Three

Methodology

3.1 Description of the Study Area

The study area is located around the boundary between Oyo and Ogun States which is located in South West Nigeria. Oyo State covers approximately an area of 28,454 square kilometers while Ogun State has a land area of 16,762 km^2 [1,2]. Oyo state lies between coordinates 8°00 N and 4°00 E while Ogun state lies between latitude 6.2 °N and 7.8 °N and longitude 3.0 °E and 5.0 °E. The climate of both states is equatorial, notably with dry and wet seasons with relatively high humidity. The dry season lasts from November to March while the wet season starts in April and ends in October. Ogun state's yearly average daily temperature is 29.34 °C, the state receives about 141 mm of precipitation and has 224.18 rainy days annually. Likewise, the average annual temperature in Oyo State is 25.9 °C and it receives about 1467 mm of precipitation falls annually.

Observation of these sites showed the potential of these contaminants (parabens and heavy metals) seeping into the groundwater in these communities. In some sampling sites, dumpsites, poor sanitation, inadequate wastewater treatment, and poultry activities which can result in significant levels of contamination of the groundwater were observed. The coordinates of the sampling points for the study are presented in Table 3.1 and Figure 3.1 represent the map of the study area.

Table 3.1. Coordinates for the Sampling Sites

Sample	Coordinates
S1	7°9'15"N, 3°47'29"E
S2	7°8'51"N, 3°47'6"E
S3	7°8'42"N, 3°47'3"E
S4	7°9'4"N, 3°47'10"E
S5	7°9'21"N, 3°47'4"E
S6	7°9'9"N, 3°47'9"E
S7	7°8'49"N, 3°47'30"E
S8	7°11'24"N, 3°49'19"E
S9	7°12'35"N, 3°49'52"E
S10	7°13'33"N, 3°50'16"E

Source: Author's Analysis, 2023

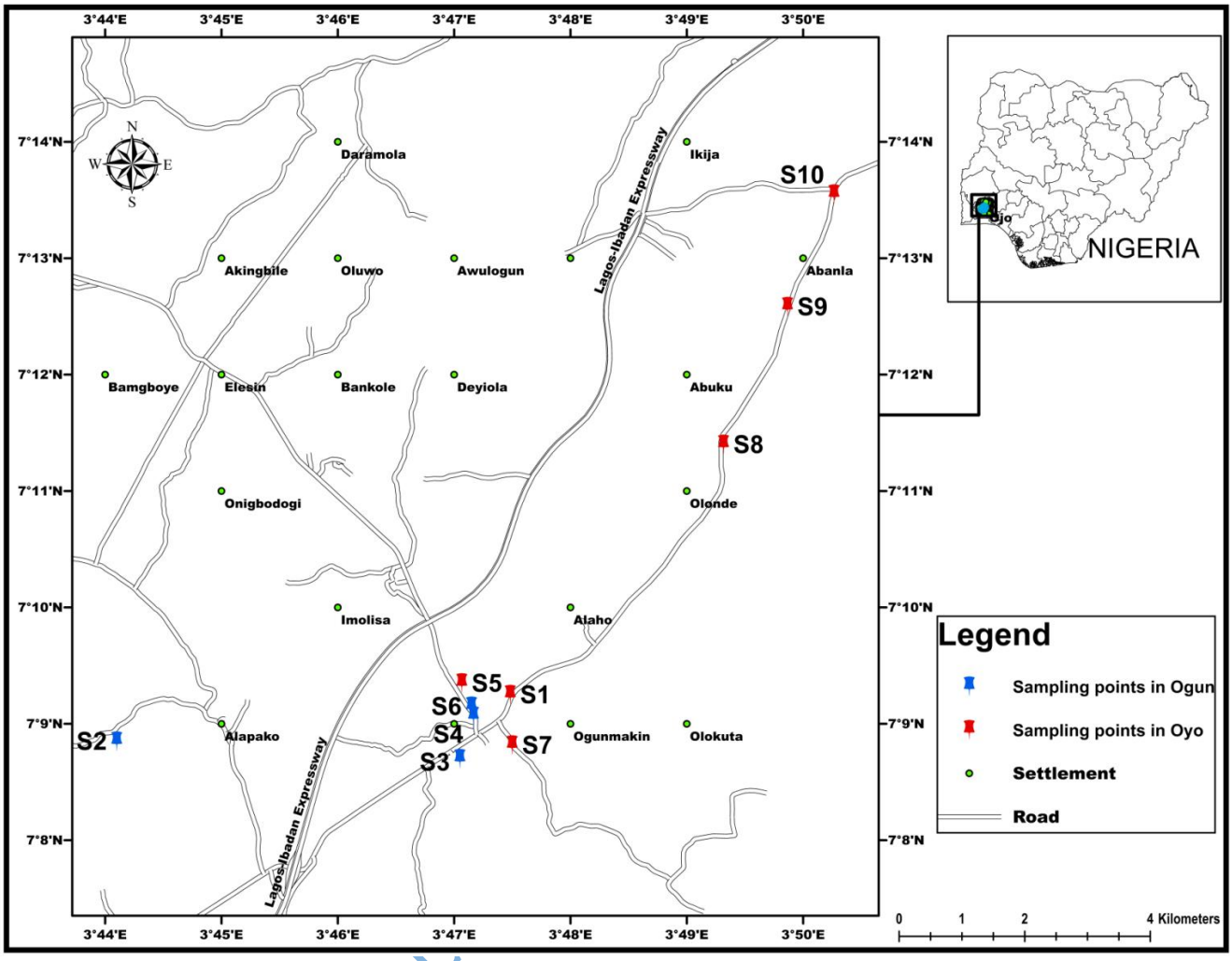

Figure 3.1 Location of the Sampling Points Within the Study Area
Source: Author's Analysis, 2023

3.2 Sample Collection

3.2.1 Sample Collection and Preservation

Grab groundwater samples were collected randomly from ten (10) hand-dug wells from two rural communities in Oyo and Ogun State, Nigeria. Sampling sites and their coordinates are shown in Table 4.1. Samples were collected in 500 mL amber bottles which were pre-washed in the laboratory and rinsed on-site with sample water before usage. These samples were all transported to the laboratory in a Styrofoam cooler and stored at 4 °C in the laboratory refrigerator until extraction. Samples for heavy metals would be stored in plastic bottles and preserved with 5 ml concentrated HNO_3 and kept in the refrigerator for further analysis while the physicochemical parameters were determined on site.

3.3 Determination of Physicochemical Parameters

Five important parameters were selected for physicochemical analysis of the groundwater samples: dissolved oxygen concentration (DO), temperature, pH, total dissolved solids (TDS) and conductivity. These physicochemical parameters were instrumentally measured on site using HANNA meter (HI 9124N model).

3.4 Sample Preparation

3.4.1 Extraction of Parabens

200 mL of each sample was spiked with a known concentration (200 µg L^{-1}) of the mixed analytes (methyl-, ethyl-, propyl-, butyl- and chlorinated methylparaben). A blank sample containing no analyte was also prepared with ultrapure water. The Solid Phase Extraction (SPE) cartridges (Oasis HLB, 500 mg, 12 mL) was conditioned with 3 mL of HPLC grade methanol followed by equilibration with 3 mL of ultrapure water. 200 mL of samples was passed through

the cartridges at a flow rate of between 5-8 mL min^{-1}. Washing was done by passing 3 mL of ultrapure water through the cartridges. The cartridges were dried in the vacuum oven for 5 min and elution was done with 3 mL of HPLC grade methanol, followed by 3 mL of HPLC grade acetonitrile. The eluate was evaporated to dryness in the vacuum oven and reconstituted with 0.5 mL of HPLC grade methanol.

3.4.2 Digestion

100 mL of the well-mixed water sample was acidified with 5 mL concentrated HNO_3 and 5 mL concentrated H_2SO_4. The mixture was then heated until the volume reduced to about 15-20 mL. The digested samples were allowed to cool to room temperature. They were then filtered through Whatman 0.45µm filter paper and the final volume adjusted to 100 mL with distilled water and stored for further analysis[1]. Instrumental analysis was carried out using Perkin Elmer Inductively Coupled Plasma-Optical Emission Spectrometry optima 8000 (ICP-OES), Shimadzu.

3.5 Instrumentation

All analyses were carried out on LC-UV system comprised of Agilent Series 1100 LC system (Agilent Technologies, Germany). Separation of analytes was done on LC C18 column (5 µm particle size, 250 × 4.6 mm i. d) and all injections were done automatically by an autosampler. The chromatographic conditions were as follows: mobile phase, isocratic elution of water/methanol (30/70, v/v); flow rate, 0.7 mL min^{-1}; injection volume, 40 µL; column temperature, 20 °C and detector wavelength, 254 nm.

3.6 Standards and Reagents

Acetonitrile and methanol of HPLC grade and Oasis HLB SPE cartridges (500 mg, 12 mL) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ultrapure water was obtained with Milli-Q Direct 8/16 System. The standard stock solutions of each analyte (200 mg L^{-1}) were prepared singly in methanol and stored at 4 °C. Working solutions (2 mg L^{-1}) of mixed parabens were prepared by dilution of stock solution with ultrapure water fresh before use. A spike solution of 200 µg L^{-1} containing the mixed paraben will be prepared from the working solution by dilution.

3.7 Quality Control/Quality Assurance Protocol

All sampling bottles was cleaned thoroughly and rinsed with ultra-pure water. All chemicals were of analytical reagent grade. Ultra-pure water was used throughout the experiments for parabens analysis. Analytical standards (99%) were used for parabens analysis. The accuracy of the analytical procedure was authenticated by concurrent analysis of Certified Reference Materials (CRM) for elemental analysis[2,3]. Parameters such pH, DO, Temperature, TDS and Conductivity were determined on-site.

For parabens, procedural blanks were carried out for each extraction batch (8) to monitor for contamination introduced through the solvents and materials used in the extraction processes. Also, trip blank was carried out to check for the introduction of target analytes to and from sampling sites. None of the target analytes were detected in the trip blanks while butylparaben was detected in two of the procedural blanks, which was subtracted from the concentrations measured in the samples. Methanol blank and midpoint calibration standard was injected after each batch analysis to check for drift in instrumental response and also for carry-over of target analytes from prior injections. Quantification of analytes was carried out using external standards,

calibration curve was constructed by analysing aqueous solutions containing the analytes ranging from concentration of 10 to 1000 µg $L^{-1.}$ The results showed excellent coefficient of determination (r^2) of > 0.999. The limit of detection (LOD) was calculated as three times the ratio of signal to noise, using the standard deviation of the seven-point calibration intercepts divided by the slope. The limit of quantification (LOQ) was calculated as ten times the ratio. The LOD was between 8 to 16 µg L^{-1}. The regression coefficient, LOD and LOQ are presented in appendix 1. The recovery of target analytes was between 73.73% and 96.77% while the relative standard deviation (RSD) was less than 20%.

3.8 Health Risk Assessment

3.8.1 Health Risk Assessment for Parabens

Several studies have shown that parabens are toxic to aquatic organisms[4,5,6]. The risk to aquatic organisms was assessed, the risk quotient (RQ) was computed for algae, daphnia and fish. The risk quotient was calculated based on the parabens concentration that was recorded for this study in groundwater using the formula:

$$RQ = MEC/PNEC \quad \text{---------- (Equation 1)}$$

Where MEC is the measured environmental concentration in groundwater

PNEC is the predicted no-effect concentration.

The PNEC will be calculated for both acute and chronic tests using the EC_{50}/LC_{50} and NOEC respectively, divided by an assessment factor (AF)[6].

$PNEC_{acute}$ = (EC_{50}/LC_{50} of three acute toxicity tests)/AF_{acute}

$PNEC_{chronic}$ = (NOEC in chronic tests) /$Af_{chronic}$

Where EC_{50}/LC_{50} is the median effect/lethal concentration

NOEC is the no observed effect concentration.

An assessment factor of 100 will be used for the acute tests while an assessment factor of 10 will be used for chronic tests for algae and daphnia only[6].

The risk quotient is classified as: High risk (RQ ≥ 1); medium risk (1 < RQ ≤ 0.1); and low risk (RQ < 0.1) [7].

3.8.2 Health Risk Assessment for Heavy Metals

This risk will be evaluated via the ingestion pathway using the lifetime average daily dose (LADD) [8]. The chronic risk will be determined using chronic daily intake (CDI) and hazard quotient (HQ) index, based on the modified equation using[9,10,11,12]:

CDI = (C X DI)/BW---------- (Equation 2)

where CDI is the human exposure risk through the drinking water pathway (mg/kg/day),

C is the concentration of heavy metal in drinking water in mg L^{-1}

DI average daily intake rate (2.0 L Day^{-1} $person^{-1}$)

BW is the body weight (15 kg and 72 kg for children and adults, respectively)[8]. International oral reference dose values for the heavy metals RfD (mg kg^{-1} day^{-1}) used in this study were; 0.02 for Cr (VI); 0.14 for Mn; 0.02 for Ni; 0.001 for Cu; 0.001 for Cd and 0.004 for Pb. The reference

values stated by FAO/WHO (Codex Alimentarius Commission), US EPA 2015 and other published materials, were used in this study[13,14,15,16].

3.8.3 The Non-Carcinogenic Hazard Evaluation

The non-carcinogenic hazard will be evaluated through the HQ

$$HQ = CDI/RfD \quad \text{(Equation 3)}$$

Where RfD is the oral reference dose (mg/kg/day) for individual heavy metals that humans can be exposed to.

If the value of HQ is less than 1, it is considered safe for human health, while if the value of HQ exceeds 1, there is an unacceptable risk of adverse non-carcinogenic effects on human health[17].

3.8.4 Cancer Risk Estimation

The lifetime exposure to the incremental risk of an individual developing cancer will be evaluated using the lifetime target carcinogenic risk (TCR).

$$TCR = SF \times CDI \quad \text{(Equation 4)}$$

Where, CSF is the oral carcinogenic slope factor of 0.0085 (mg kg^{-1} day^{-1}) for Pb set by California environmental protection agency (OEHHA), EDI is the estimated daily intake of heavy metals. Acceptable risk levels for carcinogens range from 1 x 10^{-4} (risk of developing cancer over a human lifetime is 1 in 10,000) to 1 x 10^{-6} (risk of developing cancer over a human lifetime is 1 in 1,000,000)[18,19].

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Chapter Four

Results and Discussion of Findings

4.1 Physicochemical Analysis in Groundwater Samples

The water samples from the studied groundwater from the selected two communities varied in appearance from colourless to slightly brown and the temperature of the water samples was within acceptable limits for groundwater quality. Table 4.1 summarized the result of the physicochemical analysis such as DO, temperature, pH, TDS and conductivity of water samples collected from ten (10) groundwater samples from two communities located within the boundary between Oyo and Ogun States. The DO values for the groundwater samples ranged between < LOD and 0.04 mg L^{-1} which might be due to the depth and high temperature observed in the aquifers. In the case where these groundwater sources serve as a major source of drinking water to these communities, these DO values are very low as healthy water should have DO concentrations between 6.5 and 8.0 mg L^{-1} [1]. A high DO level in drinking water makes it taste better. Also, for aquatic organisms, when DO levels fall below 8 or 9 some oxygen-sensitive aquatic population such as fish becomes highly stressed and any DO level below 6 mg L^{-1} will not support aquatic life.

The pH ranged from 6.34 to 7.57, indicating that groundwater samples in this study were mostly neutral in nature and fall within the WHO permissible range (6.5 to 8.5) limit[2]. Similarly, the TDS values varied between 0.04 and 0.39 ppt showing that the TDS of the groundwater samples is below the permissible limits of 0.5 to 1.5 ppt set by WHO[3,4]. The presence of a high concentration of TDS in groundwater might be caused by the leaching of salts from the soil and the percolation of domestic sewage.

Table 4.1 Physicochemical Analysis in Groundwater Samples

	DO (mg L^{-1})	Temp (^{O}C)	pH	TDS (ppt)	Conductivity (mS)
S1	0.04 ± 0.03^{a}	30.27 ± 0.33^{a}	6.53 ± 0.02^{a}	0.04 ± 0.01^{a}	0.08 ± 0.00^{a}
S2	< LOD	30.13 ± 0.41^{a}	7.27 ± 0.01^{a}	0.37 ± 0.00^{b}	0.74 ± 0.00^{b}
S3	< LOD	29.60 ± 0.08^{a}	6.34 ± 0.02^{a}	0.10 ± 0.01^{a}	0.18 ± 0.02^{a}
S4	< LOD	30.47 ± 0.09^{a}	6.99 ± 0.03^{a}	0.39 ± 0.00^{b}	0.77 ± 0.01^{b}
S5	0.01 ± 0.00^{a}	31.70 ± 0.25^{a}	7.21 ± 0.01^{a}	0.27 ± 0.00^{b}	0.56 ± 0.01^{b}
S6	< LOD	31.67 ± 0.39^{a}	6.92 ± 0.02^{a}	0.21 ± 0.01^{b}	0.42 ± 0.01^{b}
S7	< LOD	30.23 ± 0.13^{a}	6.72 ± 0.02^{a}	0.09 ± 0.01^{a}	0.19 ± 0.01^{a}
S8	< LOD	30.60 ± 0.08^{a}	6.96 ± 0.01^{a}	0.24 ± 0.00^{b}	0.49 ± 0.01^{b}
S9	< LOD	31.13 ± 0.05^{a}	7.57 ± 0.01^{a}	0.39 ± 0.01^{b}	0.78 ± 0.01^{b}
S10	< LOD	31.27 ± 0.05^{a}	7.07 ± 0.01^{a}	0.20 ± 0.01^{ab}	**40.67 ± 0.47^{c}**
WHO*	4		6.5-8.5	500	2.5

Values in (Mean ± SD); DO; Dissolved Oxygen. Values are in mg L^{-1}. Different superscript letters in the same column indicate mean separations by Tukey's post hoc tests at the 5% level. *World Health Organization (WHO, 2022). Bold figures indicate values greater than WHO limit.
Source: Author's Analysis, 2023

Also, the conductivity values for the studied groundwater samples ranged from 0.08 (S1) to 40.67 mS (S10). All the conductivity values were within the acceptable conductivity limit in drinking water of 0.2 to 0.8 mS except for the conductivity value of 40.67 mS at S10. The high conductivity observed in S10 (40.67 mS) indicated the enrichment of salts in the aquifer while the low conductivity observed in S1 (0.08 mS) might be due to the presence of organic compounds such as oil. In all, the physico-chemical characteristics were not significantly different ($p > 0.05$) across the two communities, indicating similarities in their physico-chemical profile and influencing factors except for conductivity at S10 (40.7 ± 0.58) which was significantly different.

4.2 Heavy Metal Concentrations in Groundwater Samples

Table 4.2 summarized the concentrations of heavy metals in groundwater samples. Generally, the average concentrations of the studied heavy metals within the two communities were found to be in decreasing order Ca > Mg > Na > K > Co > Al > Fe > Cr > Mn > Zn > Cd > Ni > Pb > B > Cu > Se. The concentration values for Mn were all below the WHO permissible limit except in S2 (0.99 mg L^{-1}). The average concentrations of Fe, Al, Co, Cr and Pb were observed to be higher than the WHO permissible limits in all the samples at all the sampling locations. Consuming water from these aquifers may lead to an unwarranted build-up of these heavy metals in the body, due to their non-biodegradable nature.

Chromium has been found to be toxic, consuming water with high Cr concentration may cause headache, diarrhoea, nausea, and vomiting[5]. Lead is a toxic metal and high dosages of Pb can damage the central nervous system and the kidneys[6]. For this study, Cd was not detected in the groundwater samples except in S10 with a concentration of 2 mg L^{-1} which is much higher than

the WHO limit of 0.005 mg L^{-1}. High dosages of Cd may cause Kidney damage, renal disorder and they are also known to be human carcinogens[5]. In addition, the results showed a significant variation ($p > 0.05$) of Ca, Mg, K, Na and Mn across all the sampling sites. However, Fe, Cu, Zn, Al, B, Cd, Co, Cr, Ni, Pb and Se were not significantly different ($p > 0.05$) across the two communities, indicating similarities in their influencing factors.

4.3 Comparison of Heavy Metal Concentrations in the Two Communities

Figures 4.1 and 4.2 showed the levels of concentrations of heavy metals in sites S1 to S10 in comparison to WHO limits. Oyo State comprises S1, S7, S8, S9 and S10 while Ogun state comprises sites S2 to S6. It was observed that Fe, Co and Cr concentrations were all higher than the WHO limits across the two communities. Selenium was not detected in Oyo state but it was detected in two sites (S2 and S5) in Ogun state with the concentration of 0.03 mg L^{-1} each which is higher than the WHO permissible limits. In terms of Zn and Mn, the two communities are almost similar except in S2 where Mn has the highest concentration of 0.99 mg L^{-1}. The concentrations of Fe and Cu also ranged from 0.84 to 3.19 mg L^{-1} and 0.02 to 0.20 mg L^{-1} with Oyo state having slightly higher concentrations than Ogun state. Also, Co and Cr also had similar concentration range with Oyo state having slightly higher concentration levels.

Fig. 4.3 shows the concentrations of non-essential elements in the groundwater samples across all sites. Non-essential elements are those elements that are readily synthesized in the body and are needed in small amounts. It was observed that the average concentrations of Al and Pb all exceeded the WHO permissible limits of 0.2 and 0.01 mg L^{-1} respectively. Cadmium was only detected in S10 with concentration of 2.00 mg L^{-1} which is way higher than the WHO limit of

0.005 mg L^{-1} while Ni concentrations was observed to exceed the WHO permissible limits in S3, S6, S7, S8 and S10.

Table 4.2: Elemental Concentrations of Groundwater Samples

	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	WHO[2]
Ca	9.14[a]	52.8[d]	15.3[ab]	36.5[c]	43.4[c]	26.9[b]	10.9[a]	13.5[a]	39.2[c]	19.3[b]	200
Mg	2.44[a]	12.0[b]	3.92[a]	23.5[d]	8.26[b]	14.0[c]	5.77[a]	14.0[c]	27.6[c]	9.05[b]	200
K	4.39[ab]	35.8[c]	1.29[a]	3.26[a]	6.40[b]	4.11[a]	2.41[a]	5.25[b]	3.54[a]	4.68[ab]	30.0
Na	2.24[a]	10.2[bc]	3.61[a]	13.3[bc]	8.39[b]	8.07[b]	3.77[a]	9.20[b]	13.1[bc]	6.62[b]	50.0
Mn	*0.07*[a]	**0.99**[c]	*0.09*[a]	*0.07*[a]	0.04[a]	**0.11**[a]	**0.11**[a]	**0.47**[b]	*0.07*[a]	**0.33**[b]	0.08
Fe	**1.68**[a]	**2.86**[b]	**1.39**[a]	**0.84**[a]	**1.10**[a]	**0.91**[a]	**3.16**[b]	**3.19**[b]	**1.64**[a]	**2.20**[b]	0.30
Cu	0.03[a]	0.02[a]	0.03[a]	0.03[a]	0.02[a]	0.03[a]	0.20[b]	0.03[a]	0.05[a]	0.07[ab]	2.00
Zn	**0.30**[a]	**0.24**[a]	**0.29**[ab]	**0.16**[a]	**0.13**[a]	**0.12**[a]	**0.18**[a]	**0.14**[a]	**0.20**[a]	**0.30**[ab]	0.05
Al	**1.53**[a]	**3.52**[b]	**1.23**[a]	**0.99**[a]	**1.08**[a]	**0.98**[a]	**3.11**[b]	**4.21**[b]	**2.16**[b]	**2.40**[b]	0.20
B	0.21[b]	0.05[a]	0.06[a]	0.13[a]	<LOD	0.25[b]	<LOD	0.08[a]	<LOD	0.18[a]	2.40
Cd	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	**2.00**[a]	0.003
Co	**5.38**[b]	**5.38**[b]	**2.67**[a]	**5.38**[b]	**2.67**[a]	**2.67**[a]	**5.38**[b]	**2.67**[a]	**5.38**[b]	**5.38**[b]	0.01
Cr	**0.72**[b]	**1.18**[b]	**0.60**[a]	**0.45**[a]	**0.59**[a]	**0.45**[a]	**1.12**[b]	**1.40**[b]	**0.96**[b]	**0.88**[b]	0.05
Ni	***0.08***[a]	***0.08***[a]	**0.24**[b]	***0.08***[a]	***0.08***[a]	**0.16**[ab]	**0.24**[b]	**0.16**[ab]	***0.08***[a]	**0.16**[ab]	0.07
Pb	**0.14**[b]	**0.14**[b]	**0.07**[a]	**0.14**[b]	**0.07**[a]	**0.07**[a]	**0.14**[b]	**0.07**[a]	**0.14**[b]	**0.14**[b]	0.01
Se	<LOD	<LOD	*0.03*[a]	<LOD	*0.03*[a]	<LOD	<LOD	<LOD	<LOD	<LOD	0.04

*Values are in mg L^{-1}. Different superscript letters in the same row indicate mean separations by Tukey's post hoc tests at the 5% level. *World Health Organization (WHO, 2022). Bold figures indicate values greater than WHO limit.*

Source: Author's Analysis, 2023

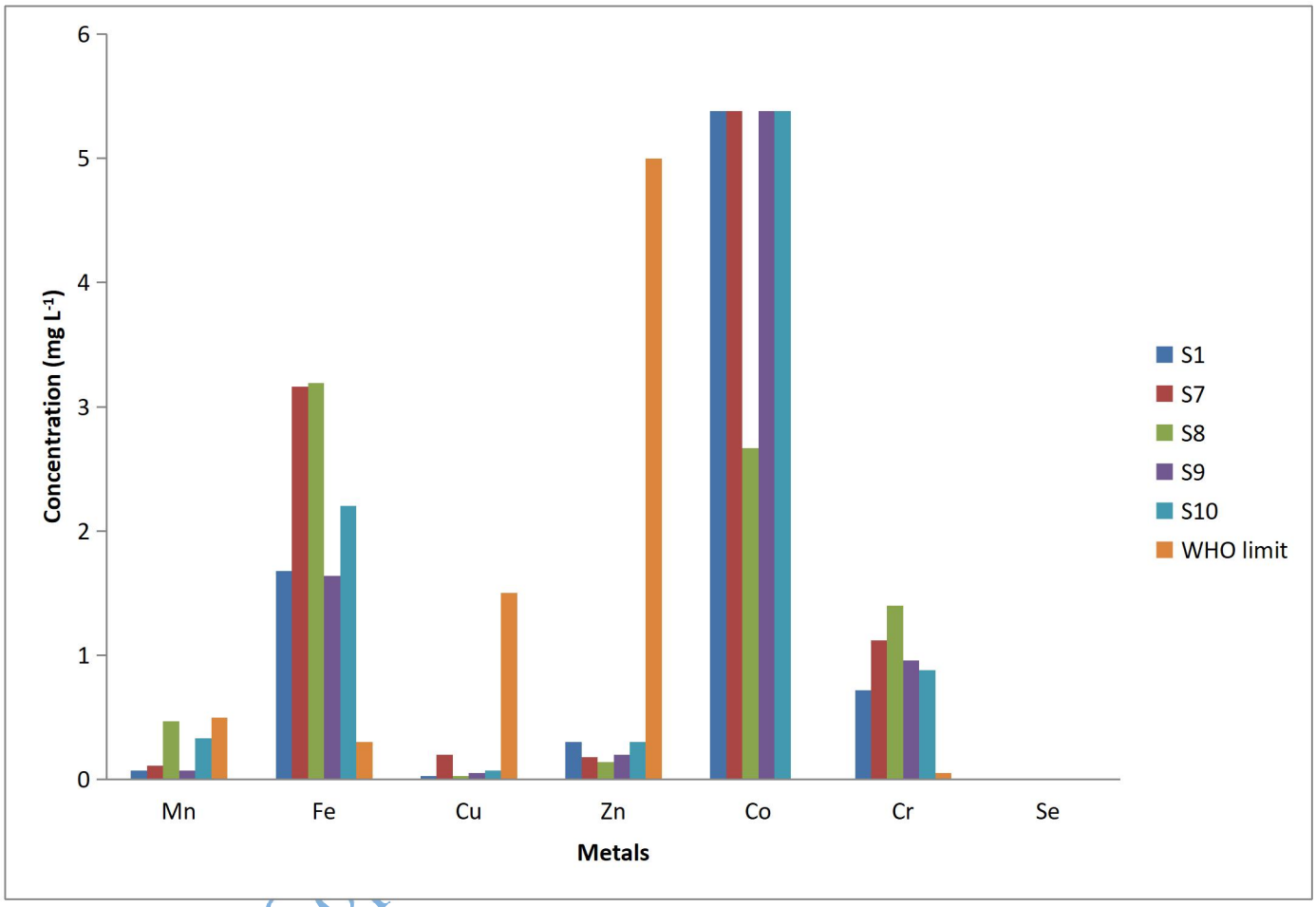

Figure 4.1: Concentration of Heavy Metals in Oyo Community in Comparison to WHO Limit

Source: Author's Analysis, 2023

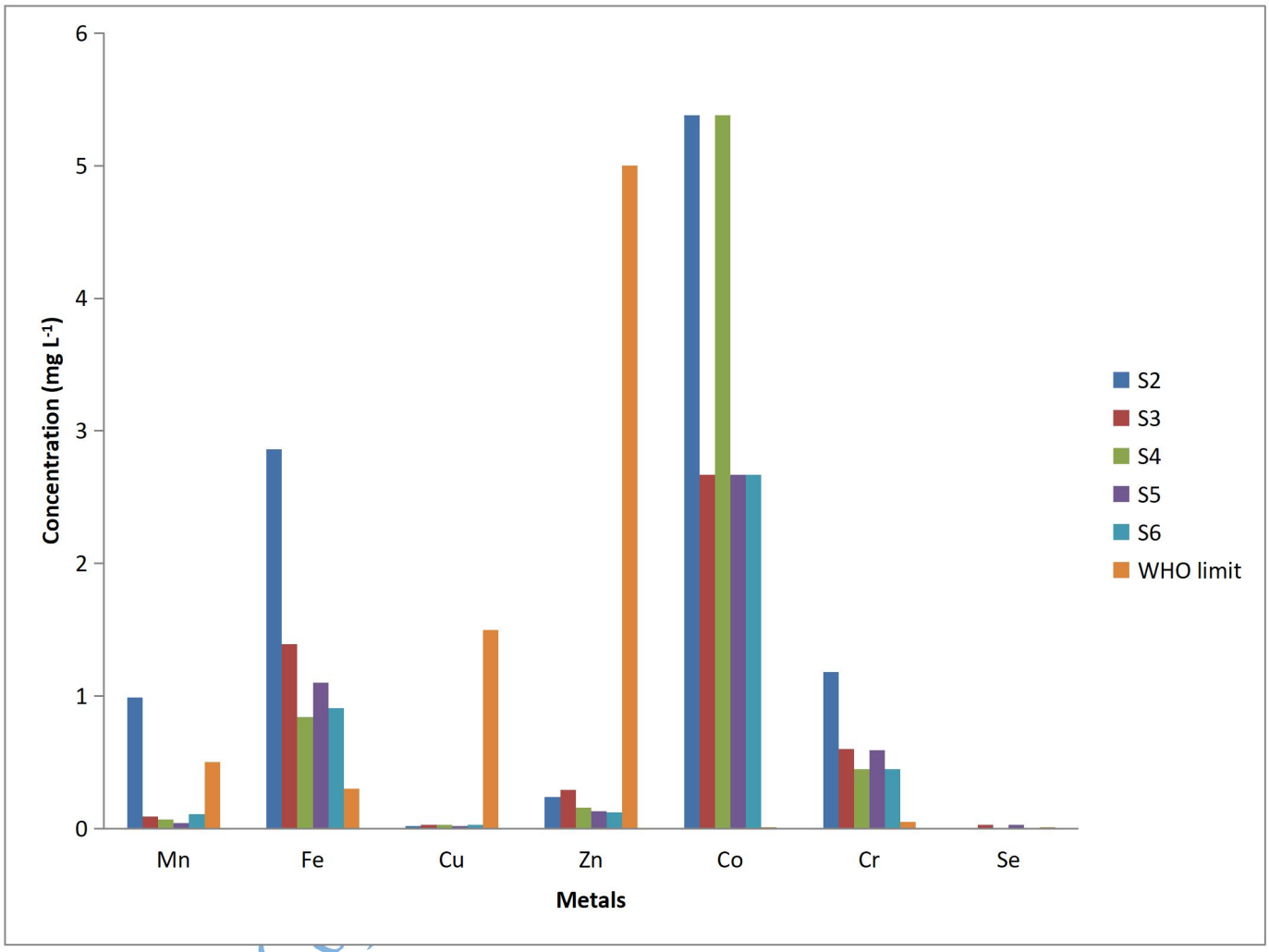

Figure 4.2: Concentration of Heavy Metals in Ogun Community in Comparison to WHO Limits

Source: Author's Analysis, 2023

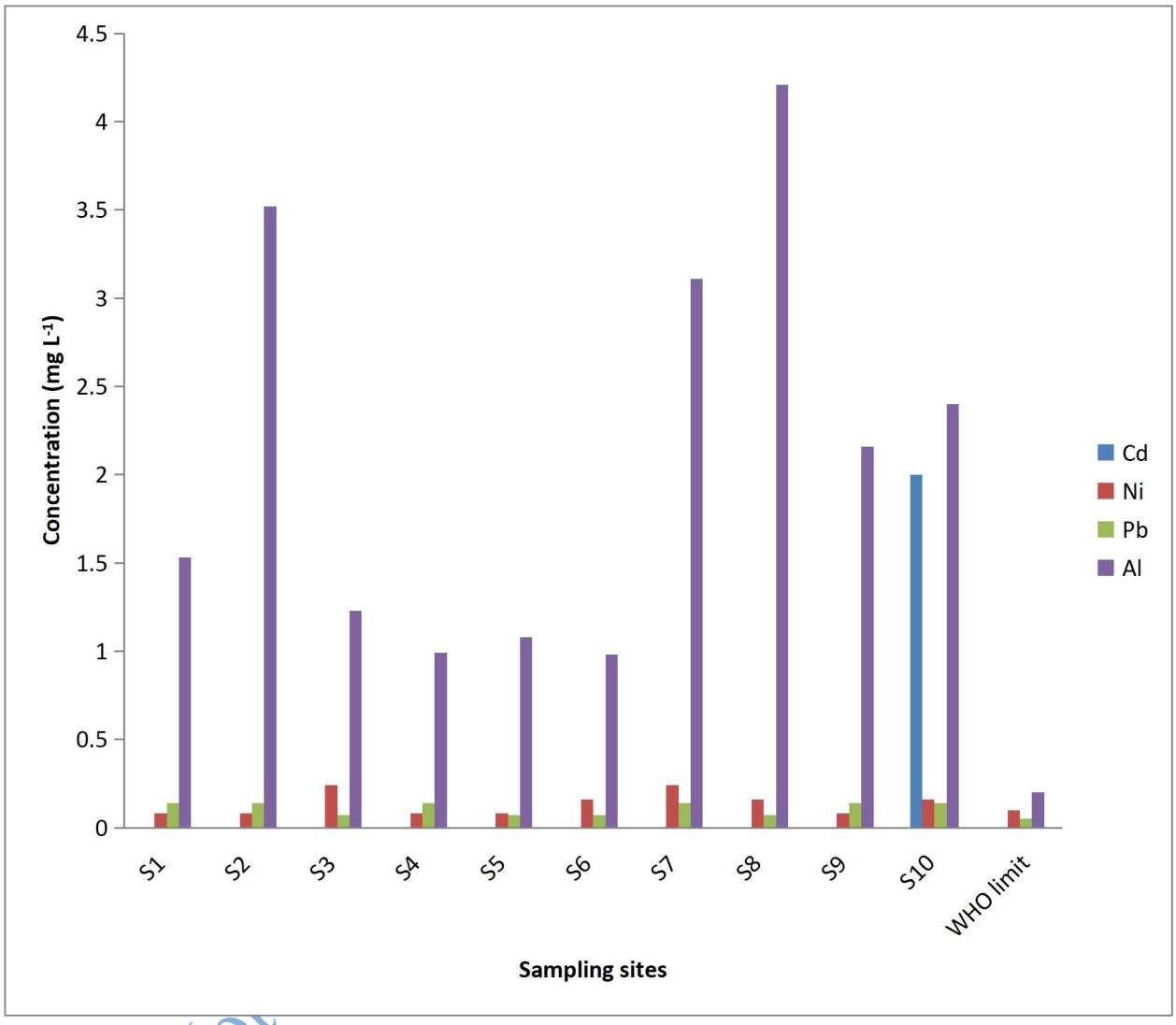

Figure 4.3: Concentrations of Non-Essential Elements in Groundwater Samples

Source: Author's Analysis, 2023

4.4 Correlation Matrix for Concentration of Essential Elements in Groundwater Samples

Significant correlation was observed between Na and Mg (r = 0.9), Mn and K (r = 0.9) and Na and Ca (r = 0.7) which indicated that their presence in the groundwater might be linked to same source. Potassium, Manganese and Chromium showed no correlation (r = 0.0) with Mg and also no correlation was observed between Zn and Cu, this means there is no relationship between these metals. Observation of negative correlation between metals such as Fe and Ca (r = -0.3) indicated that they have inverse relationship which means they might not be linked to the same source.

4.5 Correlation Matrix for the Concentration of Non-Essential Elements in Groundwater Samples

Table 4.4 shows the correlation between non-essential elements. A weak correlation ranging from 0.0 – 0.3 was observed between the metals which means there is hardly any association between them and they might not be linked to the same source. Cadmium and Aluminium showed no correlation (r = 0.0) which means there is no association between the metals. A negative correlation was observed between Pb and Ni (r = -0.3) which means they have an inverse relationship.

Table 4.3: Correlation Matrix for the Concentration of Essential Elements in Groundwater

	Ca	Mg	K	Na	Mn	Fe	Cu	Zn	Co	Cr	Se
Ca	1										
Mg	0.5	1									
K	0.6	0.0	1								
Na	**0.7**	**0.9**	0.2	1							
Mn	0.4	0.0	**0.9**	0.2	1						
Fe	-0.3	-0.2	0.4	-0.2	0.6	1					
Cu	-0.4	-0.2	-0.3	-0.4	-0.2	0.5	1				
Zn	-0.3	-0.4	0.1	-0.5	0.2	0.1	0.0	1			
Co	0.1	0.2	0.2	0.1	0.2	0.2	0.4	0.4	1		
Cr	-0.1	0.0	0.4	0.0	0.6	1.0	0.3	0.1	0.2	1	
Se	0.1	-0.4	-0.2	-0.3	-0.3	-0.4	-0.3	0.0	-0.6	-0.4	1

Correlations significant at $P \leq 0.05$

Source: Author's Analysis, 2023

Table 4.4: Correlation Matrix for Concentration of Non-Essential Elements in Groundwater Samples

	Al	Cd	Ni	Pb
Al	1			
Cd	0.0	1		
Ni	0.2	0.1	1	
Pb	0.2	0.3	-0.3	1

Correlations significant at $P \leq 0.05$.

Source: Author's Analysis, 2023.

4.6 Non-Carcinogenic Risk (Hazard Quotient, HQ) and Overall Toxic Risk (Hazard Index, HI) for Children

Table 4.5 summarizes the non-carcinogenic human health risk assessment in children for the heavy metals in this study. The HQ for all the groundwater samples was all greater than 1 for Cr and Pb. The HQ values for Zn, Cu and Mn were all within acceptable limits. For Ni, all the calculated HQ values were >1 except at S3 and S7 with a value of 1.50. Chromium, Lead, and Nickel showed an unacceptable risk of non-carcinogenic effects in children. Elevated levels of Cr in the body have been linked to headache, diarrhea, nausea and vomiting[5]. High levels of Pb in the body might lead to health complications such as mental and physical retardation, memory lapses, and decreased alertness in children[7,8,9,10].

Similarly, elevated level of Ni has been linked to dermatitis, nausea, chronic asthma, coughing and cancer. The Hazard index HI which is the sum of individual metal HQ was calculated for each site. The HI values were all greater than 1. The observed results suggested an unacceptable risk of non-carcinogenic effects on the consumers of these groundwater sources[11]. The non-carcinogenic results showed that direct consumption of water containing these heavy metals by children living within this study site from these wells might lead to some potential health risks.

4.7 Non-Carcinogenic Risk (Hazard Quotient, HQ) and Overall Toxic Risk (Hazard Index, HI) for Adults

Table 4.6 summarizes the non-carcinogenic human health risk assessment in adults for the heavy metals in this study. The HQ for all Pb, Zn, Cu, Mn, and Ni were all < 1 which indicated an acceptable risk of a non-carcinogenic effect on human health in adults. The HQ values for Cr were all >1 which signified an unacceptable risk as high levels of Cr in the body have been

linked to headache, diarrhea, nausea and vomiting.[5] The cumulative HI was calculated and all values were >1 across all sampling sites with Cr as the dominant contaminant. This indicated unacceptable risks of non-carcinogenic effects on the health of people living within this study sites[11].

4.8 Carcinogenic Risk of the Elements in Groundwater Samples for Children (TCR)

The estimated target carcinogenic risk (TCR) values for the carcinogenic metals (Ni, Cr and Pb) observed in this study are summarized in Table 4.7 The TCR values were found to be in decreasing order of Ni > Cr > Pb and the values ranged from 9.0×10^{-5} to 9.5×10^{-2}. All of these values were above the USEPA recommended safe range of 1.0×10^{-6} to 1.0×10^{-4} except for Pb in S3, S5, S6 and S8[12]. In addition, the estimated TCR values for the three metals were all higher than the permissible limit of 1.0×10^{-4} which indicated a carcinogenic risk for the children in these communities.

Table 4.5: Non-Carcinogenic Risk (Hazard Quotient, HQ) and Overall Toxic Risk (Hazard Index, HI) for Children

HQ	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Cr	**33.33**	**53.33**	**26.66**	**20.00**	**26.66**	**20.00**	**50.00**	**63.33**	**43.33**	**40.00**
Pb	**5.56**	**5.56**	**2.78**	**5.56**	**2.78**	**2.78**	**5.56**	**2.78**	**5.56**	**5.56**
Zn	0.13	0.10	0.13	0.07	0.07	0.07	0.07	0.07	0.10	0.13
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.75	0.00	0.25	0.25
Mn	0.07	0.93	0.07	0.07	0.07	0.14	0.14	0.43	0.07	0.29
Ni	0.50	0.50	1.50	0.50	0.50	1.00	1.50	1.00	0.50	1.00
HI	**39.59**	**60.42**	**31.14**	**26.20**	**30.08**	**23.99**	**58.02**	**67.61**	**49.81**	**47.23**

Bold figures indicate values greater than 1.

Source: Author's Analysis, 2023

Table 4.6: Non-Carcinogenic Risk (Hazard Quotient, HQ) and Overall Toxic Risk (Hazard Index, HI) for Adults

HQ	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
Cr	**6.67**	**10.00**	**6.67**	**3.33**	**6.67**	**3.33**	**10.00**	**13.33**	**10.00**	**6.67**
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.03	0.03	0.03	0.00	0.00	0.00	0.03	0.00	0.03	0.03
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.25	0.00	0.00	0.00
Mn	0.00	0.21	0.00	0.00	0.00	0.00	0.00	0.07	0.00	0.07
Ni	0.00	0.00	0.50	0.00	0.00	0.00	0.50	0.00	0.00	0.00
HI	**6.70**	**10.24**	**7.20**	**3.33**	**6.67**	**3.33**	**10.78**	**13.40**	**10.03**	**6.67**

Bold figures indicate values greater than 1.

Source: Author's Analysis, 2023

Table 4.7: Carcinogenic Risk of the Elements in Groundwater Samples for Children (TCR)

	Cr	Pb	Ni	ΣTCR
S1	**5.0×10^{-2}**	**1.8×10^{-4}**	**1.7×10^{-2}**	**7.0×10^{-2}**
S2	**8.0×10^{-2}**	**1.8×10^{-4}**	**1.7×10^{-2}**	**1.0×10^{-1}**
S3	**4.0×10^{-2}**	9.0×10^{-5}	**5.1×10^{-2}**	**1.0×10^{-1}**
S4	**3.0×10^{-2}**	**1.8×10^{-4}**	**1.7×10^{-2}**	**5.0×10^{-2}**
S5	**4.0×10^{-2}**	9.0×10^{-5}	**1.7×10^{-2}**	**6.0×10^{-2}**
S6	**3.0×10^{-2}**	9.0×10^{-5}	**3.4×10^{-2}**	**6.0×10^{-2}**
S7	**7.5×10^{-2}**	**1.8×10^{-4}**	**5.1×10^{-2}**	**1.3×10^{-1}**
S8	**9.5×10^{-2}**	9.0×10^{-5}	**3.4×10^{-2}**	**1.3×10^{-1}**
S9	**6.5×10^{-2}**	**1.8×10^{-4}**	**1.7×10^{-2}**	**8.0×10^{-2}**
S10	**6.0×10^{-2}**	**1.8×10^{-4}**	**3.4×10^{-2}**	**9.0×10^{-2}**

Bold figures for TCR indicate values $>1.0 \times 10^{-4}$, ΣTCR = cumulative cancer risk.

Source: Author's Analysis, 2023

4.9 Carcinogenic Risk of the Elements in Groundwater Samples for Adults (TCR)

The estimated target carcinogenic risk (TCR) values for the metals (Ni, Cr and Pb) observed in this study are summarized in Table 4.8. The TCR values were found to be in decreasing order of Ni > Cr > Pb and the values ranged from to 0.00 to 5.0×10^{-3}. Some of these values were above the USEPA recommended safe range of 1.0×10^{-6} to 1.0×10^{-412}. The estimated cancer risk for Cr and Ni were all above the acceptable limit except in S3 and S7 for Ni. Pb values were all 0.00. In addition, the estimated TCR values for the three metals were all higher than the permissible limit of 1.0×10^{-4} which indicated a carcinogenic risk for the adults in these communities.

Table 4.8: Carcinogenic Risk of the Elements in Groundwater Samples for Adults (TCR)

	Cr	Pb	Ni	ΣTCR
S1	**1.0×10^{-2}**	0.00	0.00	**1.0×10^{-2}**
S2	**1.5×10^{-2}**	0.00	0.00	**1.5×10^{-2}**
S3	**1.0×10^{-2}**	0.00	**1.7×10^{-2}**	**2.7×10^{-2}**
S4	**5.0×10^{-3}**	0.00	0.00	**5.0×10^{-3}**
S5	**1.0×10^{-2}**	0.00	0.00	**1.0×10^{-2}**
S6	**5.0×10^{-3}**	0.00	0.00	**5.0×10^{-3}**
S7	**1.5×10^{-2}**	0.00	**1.7×10^{-2}**	**3.2×10^{-2}**
S8	**2.0×10^{-2}**	0.00	0.00	**2.0×10^{-2}**
S9	**1.5×10^{-2}**	0.00	0.00	**1.5×10^{-2}**
S10	**1.0×10^{-2}**	0.00	0.00	**1.0×10^{-2}**

Bold figures for TCR indicate values $>1.0 \times 10^{-4}$, ΣTCR = cumulative cancer risk.

Source: Author's Analysis, 2023

4.10 Comparison of (Recommended Dietary Allowance (RDA) and Tolerable Upper Intake Level (UL)) of Elements for Individuals to the Average Concentration of Elements in Groundwater in Oyo Community

The elemental distribution in the groundwater samples studied was compared to the Dietary Reference Intake (DRIs) (Table 4.9). It was observed from the results that the groundwater can have a significant contribution to the health and nutritional needs of individuals for some elements. The consumption of 2 liters of water which is the average daily intake contributed between 18.61 – 79.75% towards the RDA for Fe in both adults and children. It was also observed that all the groundwater sources observed in Oyo community contributed significantly to RDA for Fe. Iron is the second most abundant element in the earth's crust and its presence in water is caused by dissolved iron from the soil and rock formation through the seeping, percolation and draining of rainwater down the soil and rocks.

Magnesium is an essential element which helps in the formation of bones, development of strong teeth, regulation of muscles and blood pressure regulator. However, Mg only showed significant contribution in S9 (17.84 - 17.28%) and S10 (54.88 - 24.39%). Significant contribution was also observed for Mn in S8 (58.13 - 40.44%) and S10 (40.63 - 28.26%) and Cu only in S7 (44.44%). Ca, Zn, Se and Cr showed no significant contribution.

Table 4.9: Comparison of (Recommended Dietary Allowance (RDA) and Tolerable Upper Intake Level (UL)) of elements for individuals to the average concentration of elements in groundwater in Oyo

	Ca	Cu	Fe	Mg	Mn	Zn	Se	Cr
S1 (mg/2L)[x]	18.28	0.06	3.35	4.87	0.15	0.59	ND	1.44
RDA	1000-1300	0.9	8- 18	310-320	1.6-2.3	8 - 11	40-55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	1.83-1.41	6.67	41.88-18.61	1.57-1.52	9.38-6.52	7.38-5.36	ND	5.76-4.11
S7 (mg/2L)[x]	21.77	0.4	6.31	11.53	0.22	0.36	ND	2.24
RDA	1000-1300	0.9	8- 18	310-320	1.6-2.3	8 - 11	40-55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	2.18-1.68	44.44	78.88-35.06	3.72-3.60	13.75-9.57	4.5-3.27	ND	8.96-6.4
S8 (mg/2L)[x]	27.04	0.06	6.38	27.9	0.93	0.28	ND	2.8
RDA	1000-1300	0.9	8- 18	310-320	1.6-2.3	8 - 11	40-55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	2.70-2.08	6.67	79.75-35.44	9.58-9.28	58.13-40.44	3.5-2.55	ND	11.2-8
S9 (mg/2L)[x]	78.49	0.1	3.28	55.3	0.15	0.4	ND	1.92
RDA	1000-1300	0.9	8- 18	310-320	1.6-2.3	8 - 11	40-55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	7.85-6.04	11.11	41.18-22	17.84-17.28	9.38-6.52	5-3.64	ND	7.68-5.49
S10(mg/2L)[x]	38.54	0.15	4.39	18.1	0.65	0.59	ND	1.76
RDA	1000-1300	0.9	8- 18	310-320	1.6-2.3	8 - 11	40-55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	3.85-2.97	16.67	54.88-24.39	54.88-24.39	40.63-28.26	7.38-5.36	ND	7.04-5.03

All values are mg/ day, x = Average concentration (mg/2L), RDA (%) = Estimated contribution to diet for each element. ND = Not determinable

Source: Author's Analysis, 2023

4.11 Comparison of (Recommended Dietary Allowance (RDA) and Tolerable Upper Intake Level (UL)) of Elements for Individuals to the Average Concentration of Elements in Groundwater in Ogun Community

The elemental distribution in the groundwater samples studied was compared to the Dietary Reference Intake (DRIs) (Table 4.10). It was observed from the results that the groundwater can have a significant contribution to the health and nutritional needs of individuals for some elements. The consumption of 2 liters of water which is the average daily intake contributed between 10.06-71.38% towards the RDA for Fe in both adults and children. It was also observed that all the groundwater sources observed in Ogun community contributed significantly to RDA for Fe.

Magnesium is an essential element which helps in the formation of bones, development of strong teeth, regulation of muscles and blood pressure regulator. However, it only showed significant contribution in S4 (15.15-14.68%). Significant contribution was also observed for Mn in S2 (123.75-86.09%) and S3 (11.88-8.26%). The high percentage contribution of Mn observed in S2 might lead to health issues such as loss of appetite, slowed growth, reproductive issues and it may also cause anaemia Ca, Cu, Zn, Se and Cr showed no significant contribution.

Table 4.10: Comparison of (Recommended Dietary Allowance (RDA) and Tolerable Upper Intake Level (UL)) of Elements for Individuals to the Average Concentration of Elements in Groundwater in Ogun Community

	Ca	Cu	Fe	Mg	Mn	Zn	Se	Cr
S2 (mg/2L) x	105.69	0.03	5.71	23.92	1.98	0.47	ND	2.36
RDA	1000-1300	0.9	8 – 18	310-320	1.6-2.3	8 - 11	40 – 45	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	10.57-8.1	3.33	71.38-31.72	7.72-7.48	123.75-86.09	5.88-4.27	ND	9.44-6.74
S3 (mg/2L) x	30.56	0.06	2.77	7.83	0.19	0.58	0.06	1.2
RDA	1000-1300	0.9	8 – 18	310-320	1.6-2.3	8 – 11	40 – 55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	3.06-2.35	6.67	34.63-15.39	2.53-2.45	11.88-8.26	7.25-5.27	0.13-0.11	4.8-3.43
S4 (mg/2L) x	72.95	0.06	1.68	46.97	0.15	0.32	ND	0.9
RDA	1000-1300	0.9	8 – 18	310-320	1.6-2.3	8 – 11	40 – 55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	7.30-5.61	6.67	21-9.33	15.15-14.68	9.38-6.52	4-2.91	ND	3.6-2.57
S5	86.86	0.03	2.19	16.53	0.07	0.26	0.06	1.18
RDA	1000-1300	0.9	8-18	310-320	1.6-2.3	8-11	40-55	25-35
UL	2500	1	45	350	11	40	ND	ND
RDA%	8.69-6.86	3.33	27.38-12.17	5.33-5.17	4.38-3.04	3.25-2.36	0.13-0.11	4.72-3.37
S6 (mg/2L) x	53.79	0.06	1.81	28.09	0.22	0.23	ND	0.9
RDA	1000-1300	0.9	8 – 18	310-320	1.6-2.3	8 - 11	40 – 55	25-35
UL	2500	1	45	350	11	40	0.4	ND
RDA%	5.38-4.14	6.67	22.63-10.06	9.06-8.78	13.75-9.57	2.88-2.09	ND	3.6-2.57

All values are mg/ day, x = Average concentration (mg/2L), RDA (%) = Estimated contribution to diet for each element. ND = Not determinable

Source: Author's Analysis, 2023

4.12 Concentrations of Parabens in Groundwater Samples (µg L^{-1})

A total of 10 groundwater samples were tested for four target parabens (Table 4.11), the concentrations ranged from 30.14µg L^{-1} to 400.08µg L^{-1}. Butylparaben was detected in three sites S2, S4 and S9 with the concentrations of 207.36 µg L^{-1}, 30.14 µg L^{-1} and 400.08 µg L^{-1} respectively. Propylparaben was detected in two sites S6 and S7 with concentrations of 298.61µg L^{-1} and 114.91µg L^{-1}. Ethylparaben was only detected in S7 with a concentration of 295.39 µg L^{-1} and MeP was detected in sites S6 and S7 with concentrations of 341.53µg L^{-1} and 244.95µg L^{-1} respectively.

The trend of total concentrations of parabens is EtP<PrP<MeP<BuP. Sites S6 and S7 were the most contaminated with these parabens with the presence of MeP and PrP in S6 which could be due to the closeness of the well to a dumpsite while MeP, EtP and PrP were all detected in S7 which might result from closeness of the wells to a septic tank, dumpsite or poultry activities. The parabens concentration in this study were all considerably higher than those reported in other countries but closer to values from the study conducted in Osun state, Nigeria (Table 4.12): Egypt (MeP: 1.78 µg L^{-1}, PtP: 0.59 µg L^{-1}, BuP: 6.38 µg L^{-1}), Colombia (MeP: 0.08 µg L^{-1}, BuP: 0.007 µg L^{-1}), Spain (MeP: 0.018 µg L^{-1}, PrP: 0.017 µg L^{-1}), Nigeria (MeP: n.d.–212 µg L^{-1}, EtP: n.d.–210 µg L^{-1}, PrP: n.d.–217 µg L^{-1}, BuP: n.d.–293 µg L^{-1})[13,14,15,16]. The high concentration of parabens observed in Nigeria might be a result of the percolation of parabens into water aquifers from septic systems, uncontrolled hazardous waste release, landfills and rain run-off[14].

Table 4.11: Concentrations of Parabens in Groundwater Samples (µg L^{-1})

Sampling Sites	MeP	EtP	PrP	BuP
S1	<LOD	<LOD	<LOD	<LOD
S2	<LOD	<LOD	<LOD	207.36 ± 12.17
S3	<LOD	<LOD	<LOD	<LOD
S4	<LOD	<LOD	<LOD	30.14 ± 13.06
S5	<LOD	<LOD	<LOD	<LOD
S6	341.53 ± 11.36	<LOD	298.61 ± 2.13	<LOD
S7	244.95 ± 4.04	295.39 ± 7.33	114.91 ± 20.23	<LOD
S8	<LOD	<LOD	<LOD	<LOD
S9	<LOD	<LOD	<LOD	400.08 ± 3.63
S10	<LOD	<LOD	<LOD	<LOD

LOD: limit of detection

Source: Author's Analysis, 2023

Table 4.12: Comparison of Concentrations of Paraben with Previous Studies (µg L^{-1})

Country	Sample matrix	MeP	EtP	PrP	BuP	References
Egypt	Groundwater	1.78	-	0.59	6.38	15
Colombia	Groundwater	0.08	ND	-	0.007	16
Spain	Groundwater	0.018	-	0.017	-	17
Nigeria	Groundwater	ND – 212	ND – 210	ND – 217	ND – 293	13
Nigeria	Groundwater	ND - 341.53	ND - 295.39	ND - 298.61	ND - 400.08	This study

ND: not detected

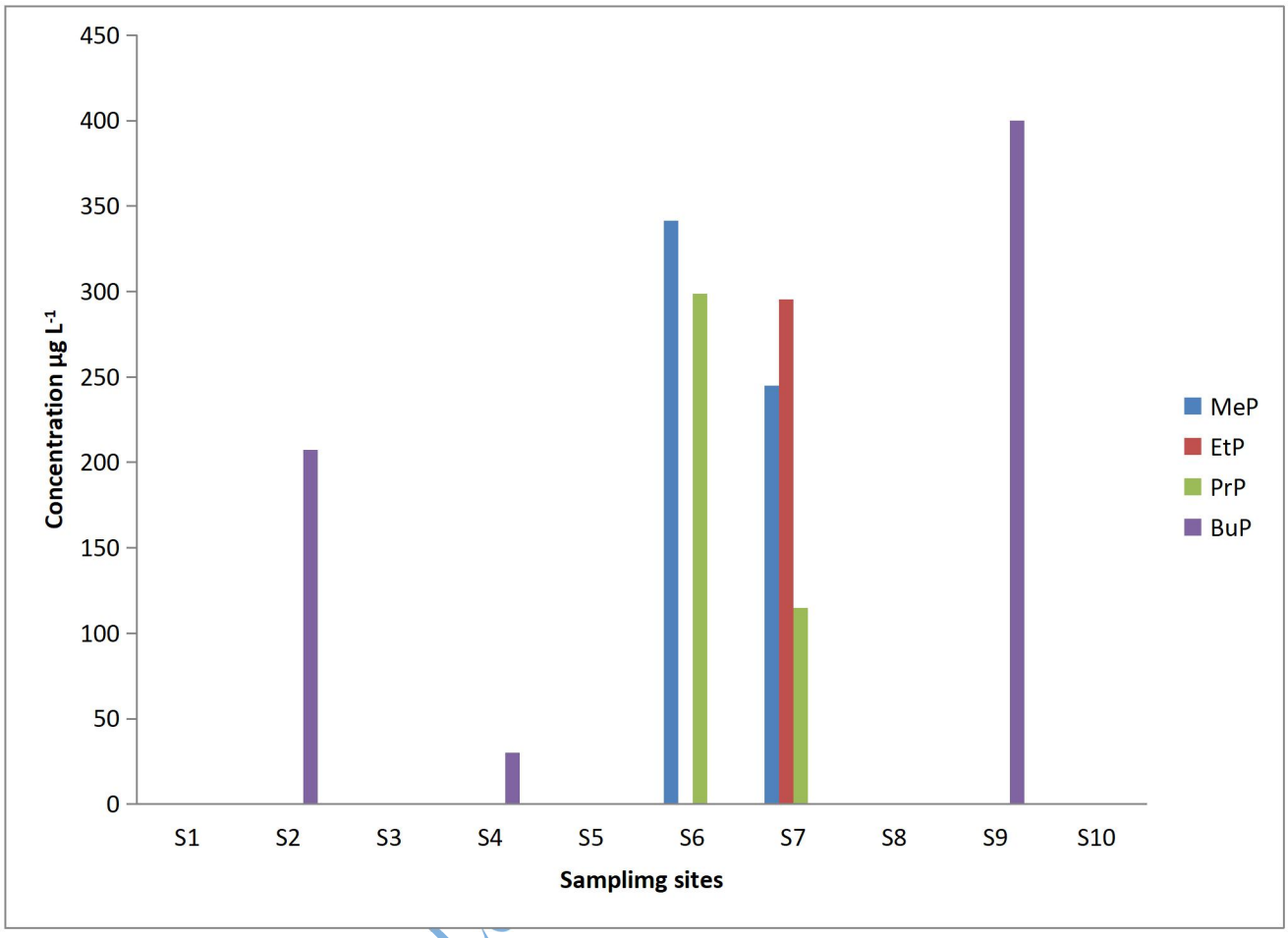

Figure. 4.4 Concentrations of Parabens in Groundwater Samples

Source: Author's Analysis, 2023.

4.13 Correlation Matrix for Concentrations of Parabens in Groundwater Samples

A significant correlation was observed among the concentrations of MeP and EtP (0.52) and also MeP and PrP showed a very strong correlation (0.96) indicating that their presence in groundwater can be linked to similar sources (Table 4.13). The significant correlation observed might also be because EtP, PrP can biodegrade to MeP which makes MeP ubiquitous in nature[18]. BuP showed a negative correlation with MeP, EtP and PrP which indicated that the source of BuP is different from the source of other parabens.

Table 4.13: Correlation Matrix for Concentrations of Parabens in Groundwater Samples

	MeP	EtP	PrP	BuP
MeP	1			
EtP	0.52	1		
PrP	**0.96**	0.25	1	
BuP	-0.25	-0.17	-0.26	1

Correlation is significant at $P \leq 0.01$

Source: Author's Analysis, 2023.

4.14 Acute and Chronic Risk Quotient of Target Analyte in Groundwater Samples

The ecological risk assessment MeP, EtP, PrP and BuP computed based on the risk quotient for average measured environmental concentrations obtained from this study are presented in table 4.14. Acute and chronic risk of the four parabens to algae, daphnia and fish was calculated for groundwater samples. All the parabens in groundwater samples (except BuP) posed a medium risk to algae at concentrations ranging from 0.12 - 0.83 for both acute and chronic risks. The BuP risk quotient (RQ) values for algae in S2 and S9 were as high as 2.18 (acute), 2.59 (chronic) and 4.21 (acute) 5.00 (chronic) which showed high risk to algae with RQ>1. The RQ values of MeP (acute and chronic) for daphnia were all ≥1 (high risk) except in S7 with value of 0.72 which indicated medium risk.

The highest RQ (acute) value was recorded in S9 with the concentration of 21.06 (BuP) which posed a very high risk to daphnia. Also, fish are susceptible to these parabens with the RQ (acute and chronic) values which were remarkably high an all the groundwater samples except in RQ (acute) for S6, S7 and S4 with the values of 0.54, 0.39 and 0.97 respectively. The highest RQ (chronic) value was recorded in S9 with the highest concentrations of 13.34 (BuP) which posed a high risk to fish. The potential risks to these organisms were in the order algae < fish < daphnia with BuP showing the highest risk and MeP posing lowest risk. Previous studies have revealed that parabens toxicity could increase with increasing alkyl chain length and that MeP was observed to be least acutely toxic[19,20].

The toxicity of paraben observed from this study was in the order BuP > PrP > EtP > MeP which agreed with a previous study[21]. The high concentrations of parabens recorded in this study resulted in the high risk observed and by extension, could have an impact on the environment and human health. In this study, the risk quotient for individual parabens was calculated but it is

important to note that concurrent occurrence of these parabens in the environment could lead to an increase in the risk quotient. Previous study has shown that toxicity was stronger in the presence of mixed parabens than single parabens[22].

4.15 Correlation Matrix between Parabens Concentrations and Physicochemical Parameters Values in Groundwater Samples

A significant correlation was observed between BuP and pH (r = 0.7) and also between BuP and temperature (r = 0.6) which indicated a strong association between these parameters (Table 4.15). EtP and DO show a weak negative correlation between all physicochemical parameters which means they have an inverse relationship. A significant correlation (r = 0.6) occurred between pH and temperature while pH showed a strong association (r = 0.8) with TDS.

Table 4.14: Acute and Chronic Risk Quotient of Target Analyte in Groundwater Samples

Sites	Analytes	Taxonomic group	$PNEC_{acute}$ (µg L^{-1})	$PNEC_{chronic}$ (µg L^{-1})	MEC (µg L^{-1})	RQ_{acute}	$RQ_{chronic}$
S6	MeP	Algae	800	2100	341.53	0.43	0.16
		Daphnia	340	240		1.00	1.42
		Fish	630	160		0.54	2.14
S7	MeP	Algae	800	2100	244.95	0.31	0.12
		Daphnia	340	240		0.72	1.02
		Fish	630	160		0.39	1.53
S7	EtP	Algae	520	1800	295.39	0.57	0.16
		Daphnia	74	160		3.99	1.85
		Fish	140	80		2.11	3.69
S6	PrP	Algae	360	740	298.61	0.83	0.40
		Daphnia	20	110		14.93	2.72
		Fish	49	40		6.09	7.47
S7	PrP	Algae	360	740	114.91	0.32	0.16
		Daphnia	20	110		5.75	1.05
		Fish	49	40		2.35	2.87
S2	BuP	Algae	95	80	207.36	2.18	2.59
		Daphnia	19	80		10.91	2.59
		Fish	31	30		6.69	6.91
S4	BuP	Algae	95	80	30.14	0.32	0.38
		Daphnia	19	80		1.59	0.38
		Fish	31	30		0.97	1.01
S9	BuP	Algae	95	80	400.08	4.21	5.00
		Daphnia	19	80		21.06	5.00
		Fish	31	30		12.91	13.34

Source: Author's Analysis, 2023

Table 4.15: Correlation Matrix between Parabens Concentrations and Physicochemical Parameters Values in Groundwater Samples

	MeP	EtP	PrP	BuP	DO	Temp	pH	TDS (ppt)	Conductivity
MeP	1								
EtP	0.5	1							
PrP	0.9	0.3	1						
BuP	-0.3	-0.2	-0.3	1					
DO	-0.2	-0.1	-0.2	-0.2	1				
Temp	0.3	-0.2	0.4	0.1	-0.1	1			
pH	-0.2	-0.2	-0.3	0.7	-0.4	0.6	1		
TDS	-0.3	-0.4	-0.3	0.6	-0.5	0.3	0.8	1	
Conductivity	-0.2	-0.1	-0.2	-0.2	-0.2	0.3	0.1	-0.1	1

Correlations significant at $P \leq 0.05$

Source: Author's Analysis, 2023

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Chapter Five

Conclusion

5.1 Summary of Findings

In summary, the physicochemical analysis results showed that the DO values are very low (<LOD – 0.04 mg L^{-1}) as healthy drinking water should have DO concentrations above 6.5 – 8.0 mg L^{-1}. The pH levels observed in the groundwater samples varied from 6.34 to 7.57 which clearly showed that the groundwater samples in this study are mostly neutral in nature and are within the WHO permissible limits. The TDS values varied between a minimum of 0.04 mS and a maximum of 0.39 mS which implied that the groundwater samples were within the permissible limits. The measured conductivity levels in S2 – S9 were all in permissible range. Low conductivity was observed in S1 (0.08 mS) and high conductivity was observed in S10 (40.67 mS) which indicated the enrichment of salts in the aquifer.

The concentrations of heavy metals across all sites were found to be in decreasing order Ca > Mg > Na > K > Co > Al > Fe > Cr > Mn > Zn > Cd > Ni > Pb > B > Cu > Se. The concentration values for Mn were all below the WHO permissible limit except in S2 with the value of 0.99 mg L^{-1}. The concentration values of Fe, Al, Co, Cr and Pb were observed to be higher than the permissible limits in all the samples. The cumulative HI calculated were >1 across all sampling sites with Cr as the dominant contaminant. This indicated unacceptable risks of non-carcinogenic effects on the health of people living within this study sites. In addition, the estimated TCR values for the three metals (Ni, Cr and Pb) were all higher than the permissible limit of 1.0×10^{-4} which indicated a carcinogenic risk for the children and adults in these communities.

Finally, the trend of total concentrations of parabens is EtP < PrP < MeP < BuP and Sites S6 and S7 were the most contaminated. The toxicity of paraben to aquatic organisms observed from this study was in the order BuP > PrP > EtP > MeP and were in the trend of algae < fish < daphnia with BuP showing the highest risk and MeP posing lowest risk.

5.2 Conclusion

This study showed that the groundwater sources in these communities in Nigeria contain high levels of parabens and some heavy metals such as Cr and Pb. Consuming water from these aquifers may lead to the unwarranted build-up of these contaminants in the body which may result to harmful consequences both to man and animals. The elemental non-carcinogenic and carcinogenic health risk assessment suggests that these groundwater sources are not safe for consumption for the children and adults in these communities.

5.3 Recommendations

Based on the outcome of this study, the following are hereby recommended:

1. More research should be conducted on occurrence of parabens in groundwater sources in Nigeria.
2. The government should make funds readily available to support research especially in the aspect of instrumental analysis.
3. People should be sensitized on cleanliness and against siting of wells close to septic tanks and dumpsites.
4. Other alternatives should be used as preservatives in personal care products instead of parabens.

5.4 Contribution to Knowledge

The findings from this study could be utilised for further research because information on parabens levels in groundwater sources in rural arears are scarce. This study has provided a new set of data on presence of parabens in groundwater.

5.5 Suggested Areas for Further Research

Future studies investigating the complications and implications of parabens are warranted. More data is needed on presence of parabens in groundwater in rural arears and the use of less toxic preservatives should be developed.

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Appendix I

Linear range, regression coefficient, limit of detection (LOD), limit of quantification (LOQ), recovery and relative standard deviation (RSD) for analysis of parabens in water samples.

						Intra-day		Inter-day	
Analytes	**Linear range ($\mu g\ L^{-1}$)**	**r^2**	**LOD ($\mu g\ L^{-1}$)**	**LOQ ($\mu g\ L^{-1}$)**	**Spiked conc. ($\mu g\ L^{-1}$)**	**Recovery (%) ± SD**	**RSD (%) n=6**	**Recovery (%) ± SD**	**RSD (%) n=18**
MeP	10-1000	0.9998	16	53	200	73.73 ± 1.02	1.14	82.58 ± 9.52	9.46
					400	91.55 ± 1.35	0.81	96.77 ± 16.83	9.59
					600	89.44 ± 2.05	0.85	85.25 ± 12.50	5.46
EtP	10-500	0.9998	9	29	200	81.98 ± 1.82	2.16	78.78 ± 10.69	13.21
					400	87.64 ± 1.04	0.69	91.44 ± 16.21	10.34
					600	88.10 ± 1.50	0.68	84.12 ± 9.68	4.63
PrP	25-500	0.9999	8	26	200	91.87 ± 1.35	1.62	87.43 ± 10.99	13.89
					400	92.15 ± 1.64	1.08	93.79 ± 13.44	8.69
					600	90.69 ± 2.13	0.98	86.68 ± 11.98	5.76

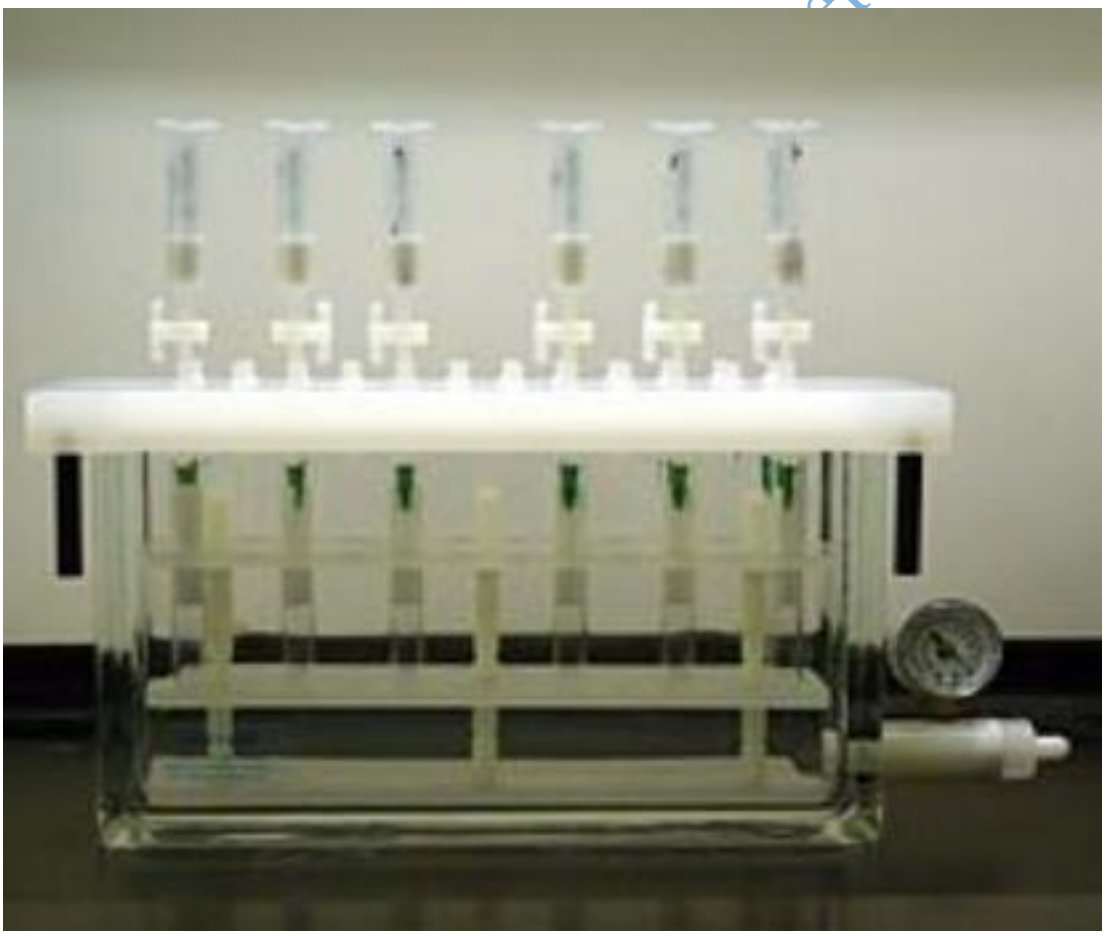
					200	92.63 ± 0.71	0.97	89.88 ± 14.29	19.95
BuP	10-1000	0.9999	10	34	400	93.44 ± 1.54	1.13	95.07 ± 13.42	9.69
					600	92.34 ± 3.32	1.65	88.04 ± 15.10	7.88

Appendix II

Picture of one of the sampling sites

Source: Author's Fieldwork, 2023

Appendix III



Picture of Solid Phase Extraction process carried out in the Laboratory

Source: Author's Analysis, 2023

Appendix IV

High-Performance Liquid Chromatography–Ultra Violet Detection HPLC-UV Used for this Research.

Source: Author's Analysis, 2023

Appendix V

Perkin Elmer®Optima™ 8000V Inductively Coupled Plasma Optical Emission Spectrometry ICP-OES Used for this Research.

Source: Author's Analysis, 2023

Bio-data

A. PERSONAL DATA

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Place of Birth	Ibadan
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Next of Kin	Miss Akintobi Oluwatobiloba
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B. EDUCATION BACKGROUND

Educational Institutions Attended with Dates and Qualifications

- Lead City University {**MSc. Environmental /Analytical Chemistry}** 2021- till date
- Lead City University {**BSc. Chemistry}** 2018-2020
- Federal University of Technology, Akure. {B. Tech Industrial Chemistry} 2010 – 2015
- YINBOL College, Orogun, Ibadan.
  (**Senior Secondary School Certificate**) 2006 – 2008
- Saint Annes Secondary School, Molete, Ibadan. 2002 - 2006
- Community Primary School, Sasa, Ibadan.
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C. WORK EXPERIENCE WITH DATES

- Lead City University, Ibadan. (Graduate Assistant) 2022 - till date
- Lead City University, Ibadan. (Laboratory Technologist) 2021 - 2022
- AMPAK Nigeria Limited. (Safety Officer) 2021
- Federal College of Education, (Technical) 2016 - 2017
  Asaba, Delta State. (Chemistry Instructor) (NYSC).
- Department of African Arts, University of Texas (Research Assistant) 2013 - till date
- ROM Oil Mills Limited, Ibadan, Oyo State. (Intern) 2014

D. AWARDS AND FELLOWSHIP

Best graduating Chemistry student

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1. Elemental distribution and health risk assessment of some herbal preparations.
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…… ……

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The University Compliance Certification

This is to certify that this Thesis was written by **Oluwakemi Abiola, AKINTOBI with Matric Number LCU/PG/002351** of the Department of Chemical Sciences, Faculty of Natural and Applied Sciences, Lead City University, Ibadan and it is in full compliance with the approved University format and style.

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Signature **Date**