OCCURRENCE OF PARACETAMOL IN WATER AND SEDIMENTS IN OGBA RIVER

BY

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FACULTY OF LIFE SCIENCES

UNIVERSITY OF BENIN

BENIN CITY

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A PROJECT SUBMITTED TO THE DEPARTMENT OF ANIMAL AND ENVIRONMENTAL BIOLOGY, IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE DEGREE (BSc. HONS) IN ANIMAL AND ENVIRONMENTAL BIOLOGY OF THE UNIVERSITY OF BENIN, BENIN CITY.

DECEMBER 2022

CERTIFICATION

We certify that project work was carried out by **DESMOND OSARUMWENSE IYAMU** with matriculation number **LSC1704927** of the Department of Animal and Environmental Biology, Faculty of life Science, University of Benin, Benin City, Edo State.

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DEDICATION

I want to dedicate this project work to the almighty God, the giver of life, and for his mercy and protection. I also want to dedicate this project work to my Parents (**MR & MRS IYAMU)** for the love, care and moral support.

ACKNOWLEDGEMENTS

All thanks to Almighty GOD**,** the giver of life for the successful completion of this project work.

I appreciate my parents (MR. FREEDOM IYAMU & MRS. PHILOMENA IYAMU) and also my siblings (DESTINY, DIVINE, PRINCESS) for their support, both prayerfully and financially which has been of immense help to me throughout my stay in school.

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ABSTRACT

Paracetamol is a widely used for relieving pain and reducing fever worldwide as a non-prescription drug. It is one of the most pharmaceutical products often detected in sewage treatment plant effluents, surface water, and drinking water, so it has emerged as an imperative aquatic environmental pollutant, originating from pharmaceutical industries and human use. The experiment was carried out at the University of Benin's forensic ecotoxicology lab. This research employed column chromatography methods to extract and analyze paracetamol, from the surface water of the Ogba River in Benin City, Edo State, Nigeria, as well as the river's physicochemical parameters. Paracetamol was detected in water as having a concentration with mean values of 0.17555ug/ml, 0.8056ug/ml, and 0.46776 ug/ml for Stations 1, 2, and 3 respectively. In sediments, Paracetamol was detected in concentration with mean values of 0.357995 ug/ml, 0.7553 ug/ml, and 1.9228 ug/ml for Stations 1, 2, and 3 respectively. The result of the water sample from the three stations sampled were observed to be high in the concentration of iron, with a mean value exceeding the WHO limit set for drinking water quality. Reduction of human exposure to pharmaceuticals through drinking-water can be achieved through a combination of preventive measures, such as regulations, public guidance and consumer education to encourage the proper disposal of unwanted pharmaceuticals and minimize the introduction of pharmaceuticals into the environment.

CHAPTER ONE

INTRODUCTION

OCCURRENCE OF PARACETAMOL IN WATER AND SEDIMENTS

Acetaminophen, generally known as paracetamol, is a popular fever reducer and pain medication (Martindale, 2009). According to, it is one of the most often found pharmaceutical chemicals in sewage treatment plant effluents, surface water, and drinking water (Kim, *et al.*, 2007). This substance is more difficult to detect in heavily populated areas, such as metropolitan areas, where drug usage is expected to be high (Luna*et al.*, 2012). Concerns have been raised concerning the potential effects of paracetamol on the environment and human health due to its prevalence in the aquatic environment and drinking water (Wu *et al.*, 2012).

According to (Sebastine and Wakeman 2003; Zhang *et al.*, 2008), global paracetamol use has increased. It is one of the top three drugs prescribed in the UK and one of the top 200 prescriptions in the US. It is recognized as one of the top ten medications produced locally and one of the top ten meds imported into Yemen (Edrees *et al.*, 2017). Furthermore, paracetamol was prescribed as a second medication in Kuwait in 2008. Alajmi (2014) Every year, around 3102 paracetamol pills are consumed in the United Kingdom, equal to an average of 55 tablets per person (Jones, 1998). Rates in certain developed countries approached 20g/person/year in the Nordic countries (Sheen,et al., 2002). The United States generated 3.6109g of paracetamol in 2002. (Bednar and Maccrehan, 2006). It is easily conserved in aquatic environments due to its high solubility and hydrophilicity and has been found in drinking water, surface water, and wastewater all over the world (Wu *et al.*, 2012).

Because of the abundance of this chemical in the aquatic environment, researchers are investigating its biodegradation and biotransformation by diverse microorganisms. Some bacteria breakdown and convert paracetamol to a non-toxic compound by using it as a carbon and energy source (Wu *et al*., 2012). The strategic pathway for paracetamol biotransformation by some microbes has been described (Fang *et al*., 2011; Wu *et al*., 2012; Zhang *et al*., 2013). The annual production of thousands of tons of paracetamol has recently gained a lot of attention because to the potential environmental and human health consequences. Long-term exposure to this chemical will raise its concentration in water sources.

1.1 JUSTIFICATION OF THE PROBLEM

The use of paracetamol products for animal and human reasons raises concerns about the environmental fate of these products and their metabolites throughout rivers, streams, seas, and oceans due to their insignificant removal through urine and feces (farre *et al*., 2008). However, because they are the result of human actions, they may serve as stratigraphic markers for the timing and assessment of anthropogenic environmental impacts, as pesticides and synthetic fiber have (water *et al*., 2016).

This study is justified in view of the potential dangers of paracetamol in the environment, as well as the need to collect data in order to access and date the environmental impact of anthropogenic activities.

1.2 AIM OF THE STUDY

This study intends to show the occurrence of paracetamol in waterand sediments of Ogba River in Benin City, Edo state with specific objectives to:

1. Determine the concentration of paracetamol occurrence in related sediments in ogba river in benin city, Edo state.
2. To summarize the knowledge about the possible pathway of paracetamol that reaches the aquatic environment from different sources. However, the presence of paracetamol concentration in drinking water, surface water, ground water, wastewater and sewage water around the world.

CHAPTER TWO

2.0LITERATURE REVIEW

2.1 THE OCCURRENCE OF PARACETAMOL IN DRINKING WATER:

Acetaminophen (paracetamol) is a contaminant found in drinking water that might be utilized as a source of drinking water. In places such as Atlanta, Minneapolis, New York City, Oklahoma City, and Minnesota City, paracetamol concentrations in drinking water ranged between 0.0003-0.298g/L. (Stackelberg *et al*., 2007, Kleywegt *et al*., 2011).

The first chemical found in finished drinking water was discovered in samples collected in Atlanta, Georgia (Frick et al., 2001). In the United States, paracetamol levels in drinking water samples were found to be more than 0.02g/L in Nevada (Westerhoff *et al*., 2005), 0.12g/L and 0.0003g/L in source and finished drinking water, respectively (Stackelberg *et al*., 2007), and 0.002g/L in 7% of drinking water samples (Intertox inc. 2015).

Furthermore, in France, paracetamol was measured at 0.211g/L. Drinking water in the Herault watershed (Rabiet, *et al*., 2006) in Marseille was 0.210g/L (Togola and Budzinski, 2008), and finished drinking water was 0.045g/L. (Vulliet, *et al*., 2011). In addition, paracetamol concentrations of 0.298g/L and 0.017g/L were found in source and drinking water, respectively. Canada's Ontario (Kleywegt *et al*., 2011). Furthermore, 0.260g/L and 0.010g/L were found in source and finished drinking water in Spain, respectively (Boledo, *et al*., 2011).

Acetaminophen (paracetamol) is a pollutant detected in Minnesota lakes that might be utilized as drinking water sources. The Minnesota Department of Health (MDH) created a health-based guideline value for acetaminophen in drinking water and believes that levels in drinking water would not damage Minnesotans based on this value.

Only untreated drinking water contained paracetamol at a quantity of 0.010 parts per billion (ppb). Only a few studies, however, have tested for acetaminophen in treated drinking water (Melinda et al., 2014). High dosages of acetaminophen may cause serious liver damage. Based on the quantities of acetaminophen identified in Minnesota lakes, drinking water exposure is likely to have minimal to no health hazards.

2.2 THE OCCURRENCE OF PARACETAMOL IN GROUND WATER:

The presence of paracetamol in ground water is caused by sewage effluent and surface water infiltration. It is either not adequately absorbed by soil particles throughout the soil passage or is biodegraded yet remains persistent (Heberer, 2002).

Paracetamol has been discovered in ground water used for drinking water sources in the United States. It was identified at 0.036g/L and 6.5g/L in public and private supply wells in Massachusetts (Zimmerman, 2005), 0.015g/L in ground water wells in Nebraska (Verstraeten,*et al*., 2005), 0.16g/L in distinct ground water samples (Focazio,*et al*., 2008), and 0.38g/L in ground water samples (Barnes *et al*., 2008). 1.89g/L in ground water samples from California (Fran MS and Belitz K. 2011), and 0.12g/L in ground water samples from Minnesota (Fran MS and Belitz K. 2011). (Erickson *et al*.,2014). However, it was found to be 0.034g/L in ground water wells in Spain (Radjenovic *et al*., 2008) and 0.010g/L (17%) in ground water in Rhône-Alpes, France (Vulliet and Cren-Olivé, 2011).

2.3 PARACETAMOL IN SURFACE WATER:

In the surface water such as lakes and rivers the presence of paracetamol is due to the uncontrolled discharge of wastewater effluent to an environment containing the substance. According to (Stackelberg *et al,*.2007), Acetaminophen is one of the most frequent pharmaceutical products in approximately 75% of natural water such as rivers and lakes.

In the USA surface water, acetaminophen was detected at range 0.026µg/L In Las Vegas wash water, Nevada and Arizona (Boyd and Furlong, 2002), between 1.95-10µg/L in streams (Kolpin *et al.,* 2002, Kolpin *et al.,* 2004), 0.110µg/L in surface water (Cahill, *et al.,* 2004), 0.009µg/L in surface water (Stackelberg *et al.,* 2004), 1.78µg/L in surface water (Glassmeyer and Shoemaker, 2005), 0.031µg/L in New Jersey stream water (Alvarez, *et al.,* 2005), 0.117µg/L in the Colorado river (Snyder *et al.,* 2007), and 0.012µg/L in 13.3% of surface and subsurface samples of Tennessee river (Conley *et al.,* 2008).

In Germany, paracetamol was found with concentration 0.065µg/L In Elbe river water (Wiegel *et al.,* 2004) and 1.99µg/L in the Leine river (Nödlera *et al.,* 2010). In Spain surface water, it was 0.250µg/L recorded in Ebro river basin water in Croatian (Gros, *et al.,* 2006), from 0.012 to 0.030µg/L in three river waters (Ebre, Llobregat, and Ter) (Pedrouzo *et al.,* 2007), 2.42µg/L in Llobregat river (Ginebreda *et al.,* 2009), 0.043µg/L in the Hanares-Jarama-Tajo river in Madrid (Fernandez *et al.,* 2010), 1.968µg/L in the Mediterranean rivers in the Castellon province (Gracia-Lor *et al.,* 2011), and 0.021µg/L in reservoir water, 0.243µg/L in Onyar river, and 0.023µg/L in the Mediterranean sea in Barcelona and Catalonia (Gros *et al.,* 2012).

In the United Kingdom, paracetamol was found between 0.112-0.555µg/L In surface water the south-east of England (Bound and Voulvoulis, 2006), 1.388µg/L in river Taff, in Wales, and

0.058µg/L in river Warta, Poland (Kasprzyk-Hordern *et al.,* 2009). Also, it was ranged between 0.0041-0.073µg/L in surface water in South Korea (Kim *et al.,* 2007), 0.0348µg/L in the Han river, North Korea (Choi *et al.,* 2008), and 0.10µg/L in the river water samples in Busan city, North Korea (Sim, *et al.,* 2010).

In France, paracetamol was reported between 0.0106-0.0723µg/L In surface water in Marseilles area (Togola and Budzinski, 2008), 0.071µg/L in surface water (Vulliet and Cren-Olivé, 2011). Also, it was ranged 0.078-0.610µg/L in 15% of river water samples in Serbia (Grujic, *et al.,* 2009), 3.35µg/L in Sindian river, 15.7µg/L in Dahan river, and 0.085µg/L in Gaoping river in Taiwan (Lin and Tsai, 2009), 0.01µg/L in Langat River dam in Selangor, Malaysia (Al-odaini, *et al.,* 2010), and up to 15µg/L in the Nairobi River, Kenya (Koreje *et al.,* 2012).

2.4 PARACETAMOL IN WASTEWATER:

Acetaminophen is one of the medications found in waste water at various amounts all around the globe. (Thomas *et al*., 2009; Gracia-Lor *et al*., 2012). It was measured between 1.746-43.223g/L in WWTP influent samples, 13.874-177.674g/L in Ulleval University effluent samples, and 5.421-1368.47g/L in Riskshospitalet waste water in Oslo, Norway (Thomas *et al*., 2007).

In the United Kingdom, paracetamol concentrations ranged from 5.529 to 69.57g/L in WWTP influent in Howdon (Roberts and Thomas, 2006), from 0.129 to 0.555g/L in WWTP effluent in England (Bound and Voulvoulis, 2006), and from 211.38g/L in influent and 0.353g/L in effluent of Coslech WWTP in South Wales (Kasprzyk-Hordern *et al*., 2009).

In Spain, paracetamol levels ranged from 0.5 to 29g/L in hospital wastewater in Almeria (Gomez et al., 2006), from 0.130 to 26.09g/L in WWTP influent (Radjenovic *et al*., 2007), from 16.72g/L in WWTP influent and 0.338g/L in effluent in Barcelona and Catalonia (Gros *et al*., 2012), from 1.13-201g/l

According to (Glassmeyer and Shoemaker, 2005), paracetamol was detected at levels of 1.06g/L in WWTP effluent, 0.96g/L in the Back River WWTP influent in Baltimore (Yu *et al*., 2006), 61g/L in WWTP influent and 0.86g/L in effluent in New York (Bentti and Brownawell, 2007), 140g/L in hospital WWTP influent in San Marcos, Texas ((Kostich *et al*., 2014). Furthermore, 1000g/L of WWTP influent was discovered in Wisconsin (Wilcox *et al*., 2009).

Acetaminophen levels in WWTP effluent in France ranged from 11.3g/L (Rabiet *et al*., 2006) to 0.108-11.308g/L (Togola and Budzinski, 2008). (Miege, *et al*., 2008). Furthermore, it was found to be 23.3g/L in waste water influent in Sydney, Australia (Al-Rifai *et al*., 2007) and 1.7g/L in WWTP influent in Japan (Okuda, *et al*., 2008). In South Korea, it was measured between 0-0.26g/L in influents and 0-0.16g/L in WWTP effluents (Han *et al*., 2006), between 0.0018-0.0019g/L in WWTP effluent (Kim *et al*., 2007), and 21.95g/L in WWTP influent and 0.017g/L ultra filtration effluents (Kim et al., 2007). (Snyder *et al*.,2007). However, in Western Greece, it was documented with 20.6g/L in influent and 0.9g/L in effluent of WWTP, as well as 9.3g/L in influent and 3.6g/L effluent of hospital WWTP (Kosma *et al*., 2010).

Acetaminophen levels in hospital WWTP influent and effluent in North Korea were found to be 41.9g/L and 6.75g/L, respectively. In addition, 6.80g/L was recorded in municipal WWTP influent (Sim *et al*., 2010) and 10.234g/L in Ulsan WWTP influent (Behera *et al*., 2011). In Taiwan, it was observed up to 186.5g/L in hospital wastewater influent and up to 417.5g/L in medicine manufacturing plant wastewater influent (Lin and Tsai, 2009), from 1.80-30.967g/L in six WWTP effluents (Lin *et al*., 2010), and 2.695g/L in influent and 0.33g/L in effluent of WWTP (Dutta *et al*., 2014).

In Italy, acetaminophen levels ranged from 246g/L in raw WWTP influent to 5.9g/L in two hospitals' waste water influents, as well as 1.2g/L in WWTP influent and 0.058g/L in effluent (Verlicchi *et al*., 2012). (Verlicchi *et al*., 2012). However, it was 107g/L in hospital wastewater influent in Switzerland (Kovalova et al., 2012), 150g/L in hospital wastewater in China (Wu *et al*., 2012), and up to 58.857g/L in hospital wastewater influent, 9.286g/L in WWTP influent, and 0.106g/L in effluent in Colmbra, Portugal (Santos *et al*., 2013).

Furthermore, acetaminophen was found in concentrations ranging from 57.5 to 77.4g/L in the WWTP influent and 90.2g/L in the hospital wastewater influent in Quebec, Canada (Ba *et al*., 2014). At Kuwait, paracetamol was found in the maximum concentrations of 2.086g/L in WWTP effluent samples and 0.0521g/L in WWTP effluent in 2011. (Alajmi 2014). In addition, 12g/L was recorded in hospital WWTP influent and 0.073g/L in WWTP effluent in Saudi Arabia (Al-Qarni *et al*., 2016).

2.5 PARACETAMOL IN SEWAGE WATER:

One of the most common medications found in sewage treatment plant effluents is paracetamol (Kim *et al*., 2007). According to (Ternes, 1998), the first incidence of acetaminophen was observed in the STP effluent in Germany at a concentration of 6g/L. It was 148g/L in Sydney and Australia in STP influent (Khan and Ongerth, 2005). It was also reported to be 1.9g/L in the final effluents of eight STPs in Atlantic Canada (Brun *et al*., 2006), 4.8g/L in STP influent, and 1g/L in activated sludge effluent in the South of England, UK (Jones *et al*., 2007).

The greatest concentrations of acetaminophen were observed in Almeria (Gomez *et al*., 2007), 37.458g/L in STP influent in Madrid (Rosal *et al*., 2010), and 19.850g/L in STP influent in Catalonia (Pedrouzo *et al*., 2007). It was also discovered to be at a level of 56.9g/L in STP influent in Seoul, North Korea (Choi *et al*., 2008), 84g/L in STP influent samples in Stockholm, Sweden (Ganiyat, 2013), and 0.07g/L in STP effluent in Selangor, Malaysia (Al-odaini *et al*., 2010).

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 STUDY AREA

Research Area and Water Sampling: The Ogba River, which is situated in Benin City, Edo State, was sampled for paracetamol levels as part of this study. The experiment was conducted at the University of Benin's forensic ecotoxicology lab, Department of Animal and Environmental Biology, and water samples were taken as directed. For sample collection, amber glass bottles that had already been washed with distilled water were utilized. Within 24 hours, the samples were sent to the lab in a cooler with ice packs. Within one week after the date of collection, samples were promptly pre-treated and kept in a refrigerator (- 20 °C) until analysis.

Three stations were selected along the Ogba river and they are seen in fig 3.1below

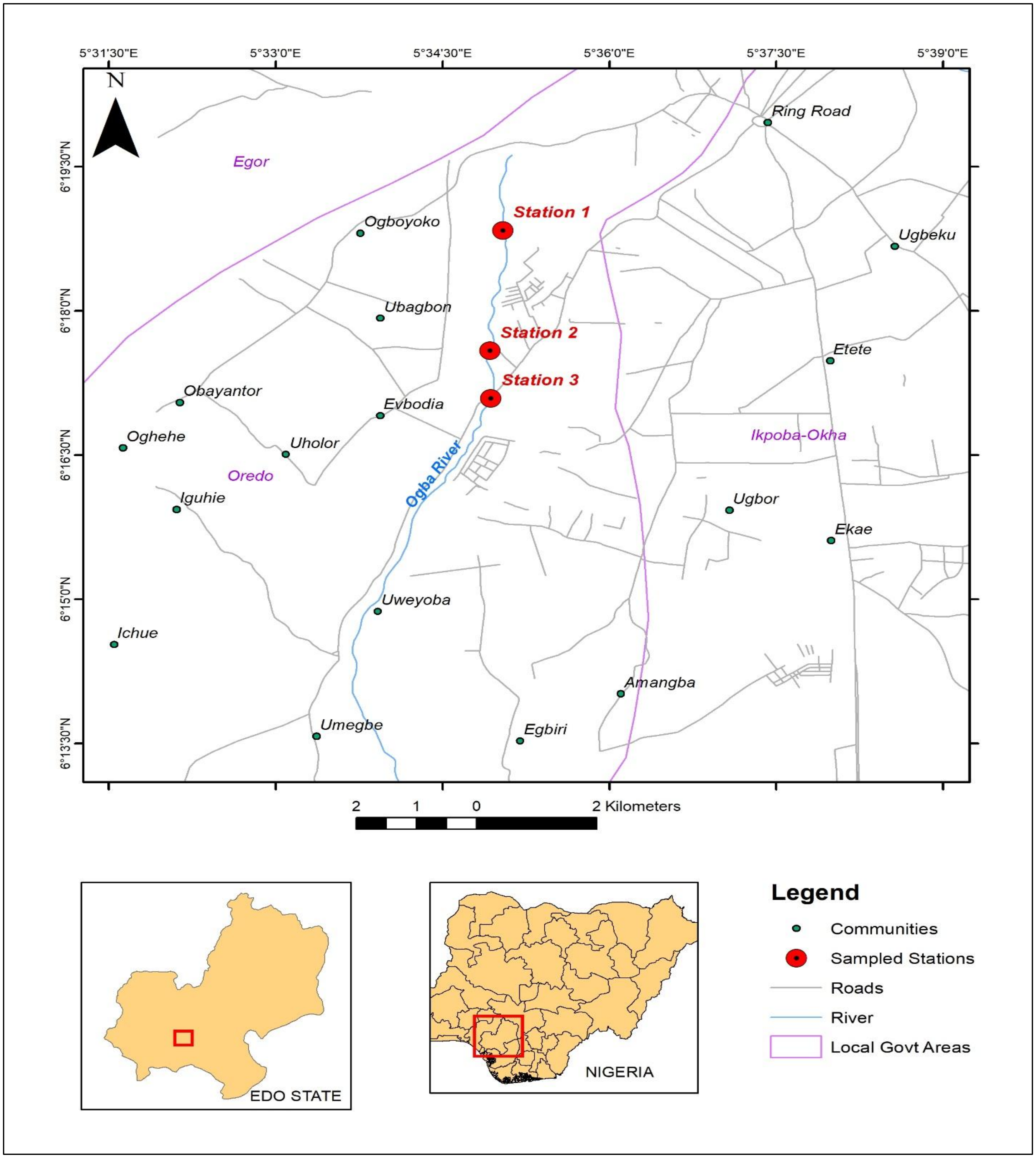

Figure 3.1: MAP OF STUDY AREA

3.2 Geology

The studied region is characterized by the Benin formation which is formed of coarse sand intermingled with lignite and areas of lateritic sand clay. The Benin formation extends to roughly 762.5 meters thick and is placed on top of the Agbodo formation which in turn is stratigraphically above the Akpata formation (Olomukoro, 1983). (Olomukoro, 1983).

3.3 Climate

Benin has two different seasons: rainy and dry. From April until October, the wet season lasts. The wet season lasts from November to March the following year. There was no rainfall reported at the start of the research period (January-March 2007), but little rainfall was recorded in April-May, and considerable rainfall was recorded between June and August**.**

3.4 Vegetation and land use

At the area of study, houses are located near the river banks which are inhabited by villagers. The main occupation of these villagers are farming and hunting. Fishing seems to be practically non-existent and is prohibited. The river serves as a source of drinking water and other domestic activities. Human activities around the river are mainly bathing and laundry.

3.5 Human activities

Benin City is an ancient city and has a considerable population with the majority involved in artisanal trading and commercial transportation. Subsistence farming is also widespread around the city. A number of breweries, small-scale pharmaceutical companies, a petroleum depot, some furniture factories, battery assembly factories, and metal works exist within the city. These forms of human activities are potentially waste generating, and wastes are usually disposed of in an indiscriminate manner.

3.6 Sampling Methods

Three sampling stations were chosen in plate 1, 2 and 3. Sampling was carried out once every month between the month of January and August.

3.6.1 STATION 1

This is located upstream. The flow rate at this station is minimal and the bank is flanked by medium sized trees which shielded a portion of the river from sunlight in the early hours of the day. It was located at N-06.19324 and E-005.35004. Water and Air temperature are 29 and 34 respectively.

PLATE 3.5.1: SHOWING SAMPLING STATION 1

3.6.2 STATION 2

This station is located about 100m from station 1. The substratum is covered with stone and the bank region is rocky. Human activities i.e. bathing and laundry was more in this station. The water current is fast compare to station 1. Water is clear and it is exposed to sunlight compared to station 1. It was located at N-06.29313 and E-005.58206. Water and Air temperature are 29 and 36 respectively.

PLATE 3.6.2: SHOWING SAMPLING STATION 2

3.6.3 STATION 3

This station is about 100m from station 2. The substratum is sandy. The dominant vegetation along the bank are tall and few grasses. The water current is high and no human activity was recorded here throughout the study period. It is located at N-06.28489 and E-005.58223. Water and Air temperature are 28 and 32 respectively.

PLATE 3.6.3: SHOWING SAMPLING STATION 3

3.7 Determination of Physicochemical Properties

Physicochemical properties will be analysed according to the methods described by APHA (2011).

3.6.1 Hydrogen Concentration (pH)

Hydrogen concentration of the water sample will be determined in-situ using a battery-powered pH meter and reported to the nearest 0.1 pH unit.

3.6.2 Electrical Conductivity (µS/cm)

A conductivity meter (HACH 44600-00) was used to measure the conductivity of water samples in μScm^{-1}. The probe was dipped into the container of the samples until a stable reading was obtained and recorded in micro-siemens per centimeter (µs/cm). Care was taken to ensure that the terminals of the meter were not in contact with the wall of the beaker while the reading was being taken (APHA, 2005).

3.6.3 Alkalinity

Pipette 50ml of the water then, add 3 drops of 0.25% phenolphthalein indicator. If a pink color is obtained, titrate with 0.025M H_2SO_4 until colorless. To the colorless solution from the titration or to the original solution (if no color is produced on adding phenolphthalein), add 3 drops of 0.1% Methyl orange endpoint. The solution may be reserved for chloride determination.

Run Blank Determination with the reagents and CO_2- free water with corrections made if found necessary.

3.6.4 Hardness

Pour 50 ml of the sample into a conical flask. 1 spatula full of Murexide indicator and 1ml NaOH Fill the burette with E.D.T.A, note the beginning titre value, then titrate until the endpoint is purple. Take note of the final titre values.

3.6.5Temperature

A calibrated mercury thermometer will be used to determine the temperature at the sampling site by suspending the thermometer 10 cm below the surface of water for about 2 mins before the readings are taken (Al-Bayatti et al., 2012). Temperature determination will be done at the point of collection.

3.6.6 Dissolved Oxygen (DO) (mg/L)

It was determined using the Winkler method. Samples were collected in the field using 250ml DO glass bottles with stoppers. The bottles were filled and stopped below the water's surface. This was done to avoid air bubbles from entering the water samples. The samples were fixed by adding 1ml of Winkler A solution manganese (ii) sulphate ($MnSO_4$) and 1ml of Winkler B solution (alkaline-iodide-azide) each, forming a precipitate. Placing firmly the stopper, the samples were shaken mechanically. In the laboratory, 2 ml of concentrated sulphuric acid (H_2SO_4) was added to the sample to dissolve the precipitate. Thereafter, an aliquot of 100ml was measured into a 250ml conical flask and two drops of the freshly prepared starch indicator were added and thoroughly shaken. The solution was titrated against 0.025M sodium thiosulphate solution ($NaS_2O_3.5H_2O$) until it becomes colorless. The volume of sodium thiosulphate used is equal to the amount of dissolved oxygen (DO) in mg/L in the sample (APHA, 2005; Ogbeibu and Ogiesoba-Eguakun, 2019).

3.6.7 Turbidity

Turbidity will be measured in the laboratory using a turbidimeter.

3.6.8 Nitrate

Nitrate will be determined in the laboratory using the cadmium reaction method and the optical density will be read at 410 nm in a spectrophotometer.

3.6.9 Phosphate

This will be determined using the ascorbic method with optical density read at 890 nm in a spectrophotometer.

3.6.10Transparency

This is the level of the clearness of a water measured with the aid of a secchi disc.

3.6.11 Sulphate

This will be determined following the turbidimetric method and reading the optical density at 450 nm in a spectrophotometer.

3.6.12 Heavy Metals

Total Suspended Solids (TSS)

TSS will be determined using the methods as described by APHA (2005).

Total Dissolved Solids

Total dissolved solids are regularly dissolved in water making it unhealthy for use. This will be calculated thus:

Total dissolved solids (mg/l) = ((W1 – W2)) x 1000

Where: W1 represents weight of total solids

W2 represents weight of total suspended solids

3.6.13Biological Oxygen Demand (BOD5) (mg/L)

Water samples for BOD_5 determination were collected in amber-colored reagent bottles, by immersing the bottle into the water and corking it below the water surface, to prevent air bubbles. The bottles were further tied in black polythene bags to prevent light penetration. The samples were then incubated at 20ºC for 5 days in the laboratory. The dissolved oxygen was determined at the beginning and end of the incubation period using Winkler's method (APHA, 2005; Ogbeibu and Ogiesoba-Eguakun, 2019).

$$BOD_5\ (mg/L) = DO1 - DO5$$

Where BOD5 = Biological oxygen demand at day five

DO_1 = dissolved oxygen on day one

DO_5 = dissolved oxygen at day five

3.7 Extraction Phase

3.7.1 Solid Phase Extraction:

Solid Phase Extraction was used to extract paracetamol from water samples.The Solid Phase Extraction cartridges were purchased from SiliCycle Inc., Quebec, Canada. Extraction of the analyte followed the procedures of Olaitan,*et al*. (2014). The extraction was carried out in batches using a vacuum under the flow of N2 and then brought to 1 ml by adding 900 µL of aqueous high performance liquid chromatography mobile phase (Cahill,*et al*., 2004, Olaitan,*et al*., 2014). SPE manifold, which accommodated twelve C18 cartridges. Each of the cartridges was preconditioned using 5 ml of Acetonitrile. Thereafter, 500 ml of the filtrate from the water samples were loaded on the cartridge. The extracted target analyte adsorbed to the sorbents were desorbed with acidified methanol. These compounds were slowly reduced to 100 µL.

3.7.2 High Pressure Liquid Chromatography:

Analysis of water samples using high-performance liquid chromatography (HPLC) was carried out according to the method described by Olaitan,*et al*. (2014). Analyses of the extracted compound were carried out using an Agilent 1100 LC System with a UV detector.All chemicals and reagents were of analytical grade supplied by Sigma-Aldrich. They include HPLC grades of methanol, acetonitrile, triflouroacetic acid (TFA), standard paracetamol (BP), diclofenac sodium (BP), amoxicillin (BP) and methylparaben.Measurements of the analytes were in microgram per litre (ug/L).

3.7.3 Extraction of active ingredient.

Use a pestle to crush the samples until it is homogenise.Weigh 2 gram of the homoegnise sample into a conical vial bottle.Add 5 ml of methanol or acetonitrile. Cap the conical vial bottle and thoroughly mix by shaking.Loosen the cap at least once during the processs to release any presure built up in the vial.

Carefully use pasteur pippette to transfer only the liquid phase to a centrifuge tube. Centrifuge at 4000 rpm for 5 mins. Add a second portion of the solvent to the conical vial and repeat the shaking process. After the solid materials have settled transfer the liquid phase to the centrifuge tube containing the first extract. Place the centrifuge tube in the centrifuge that is properly balanced and centrifuge the mixture for three minutes. Transfer the supernatant liquid with a pasteur pipette to a small tube.

3.7.4 Column chromatograph:

A silical gel column is prepared by inserting a small cotton into the top of the column and carefully push it down onto the neck of the pipette. Add silical gel to the column and pack it. Clap the pipette on a vertical position so the liquid can drain from the column into a 5 ml conical vial. Add 2 ml of the solvent to the top of the column and allow it to drain until the level of the solvent reaches the top of the silica gel. Collect the liquid that passes through the column into a 5 ml conical vial. When all the liguid has passed through the column, add an additional 1 ml of methanol to the column and allow it to drain. This ensures that all the analyte of interest has been eluted from the column.

CHAPTER FOUR

4.0 RESULTS

4.1 WATER PHYSICOCHEMICAL ANALYSIS IN OGBA RIVER

Throughout the duration of this survey, the occurrence of paracetamol in water and sediments was determined. Samples were collected from three stations at Ogba River that use conventional extraction processes.

4.1.1 ALKALINITY (mg/l)

The spatial and temporal variation in the alkalinity of the sample stations are represented in Table 4.1. The alkalinity of the various samples stations measured throughout the investigation period ranged from 20 – 8.2 mg/l in station 1, 20 – 20.2 mg/l in station 2, 54 – 54 mg/l in station 3. Station 3 reported the highest alkalinity of 54.0 mg/l, while station 1 recorded the lowest alkalinity of 8.2 mg/l. No significance difference ($p<0.05$).

4.1.2 HYDROGEN CONCENTRATION (pH)

The spatial and seasonal comparison in the value of pH for the water are proven in Table 4.1. the pH values measured during the research period for the 3 sample stations varied from 6.60 – 7.20 in station 1 with a mean value of 6.9, 6.30 – 6.50 in station 2 with a mean value of 6.40, 6.30 – 6.70 in station 3 with a mean value of 6.5. The stations 1, 2, and 3 recorded the maximum pH of 7.20 and station 2 recorded the lowest pH of 6.30. No significance difference ($p > 0.05$).

4.1.3 ELECTRICAL CONDUCTIVITY (µS/cm)

The spatial and temporal variations in electrical conductivity values for water are proven in Table 4.1. The electrical conductivity values ranged from 6.00 – 4.20 µS/cm in station 1 with a mean value of 5. 10 µS/cm, 5.00 – 7.00 µS/cm in station 2 with a mean value of 6.00 µS/cm, 120.00 – 120.00 µS/cm in station 3 with a mean value of 120.00 µS/cm. Station 1 recorded the lowest electrical conductivity value of 4.20 µS/cm and the greatest electrical conductivity value of 120.00 µS/cm. No significance difference ($p<0.05$).

4.1.4 TOTAL DISSOLVED SOLIDS (mg/l)

The spatial and temporal variations in the total dissolved solids value are shown in Table 4.1. The total dissolved solids value ranged between 31.8– 95.6mg/l in station 1 with a mean value of 63.7mg/l, 26.50 – 28.10mg/l in station 2 with a mean value of 27.30 mg/l, 63.60 – 64.40mg/l in station 3 with a mean value of 64.00mg/l. Station 1 recorded a maximum value of 95.60mg/l, while station 2 recorded the minimum value of 26.50 mg/l. No significance difference ($p<0.05$).

4.1.5 DISSOLVED OXYGEN (mg/l)

The dissolved oxygen recorded in the course of the duration of this research for the 3 stations as shown in Table 4.1 ranged between 2.80 – 4.60mg/l in station with a mean value of 3.70mg/l, 2.00 – 4.30mg/l in station 2 with a mean value of 3.15mg/l, 1.90 – 2.50mg/l in station 3 with a mean value of 2.20mg/l. Station 1 recorded the maximum dissolved oxygen value of 4.60mg/l, while station 3 recorded the lowest value of 1.90mg/l. No significance difference ($p > 0.05$).

4.1.6 BIOCHEMICAL OXYGEN DEMAND (mg/l)

The biochemical oxygen demand for the four station recorded during the course of this research as shown in Table 4.1 ranged among 1.50 – 2.00mg/l in station 1 with a mean value of 1.75mg/l, 0.20 – 0.5mg/l in station 2 with a mean value of 0.35mg/l, 0.2 – 0.4mg/l in station 3 with a mean value of 0.3mg/l. Station 1 recorded the greasiest biochemical oxygen demand of 2.00 mg/l, station 3 recorded the lowest biochemical oxygen demand of 0.20 mg/l. No significance difference (nil).

4.1.7 SULPHATE

The nutrient value primarily based on Sulphates for the 3 stations recorded throughout the length of the research as shown in Table 4.1 ranged among 4.00 – 3.00mg/l in station 1 with am mean value of 3.50mg/l, 5.00 – 8.00mg/l in station 2 with a mean value of 6.50mg/l, 6.00 – 6.00mg/l in station 3 with a mean value of 6.00mg/l . The lowest value of 3.00 mg/l was recorded at station 1, while station 2 recorded the highest sulphate value of 8.00 mg/l on October 2021. No significance difference ($p > 0.05$).

4.1.8 NITRATES (mg/l)

The nitrates content during the length of research as shown in Table 4.1 ranged among 0.517 – 0.240mg/l in station 1 with a mean value of 0.360mg/l, 0.578 – 0.589mg/l in station 2 with a mean value of 0.5835mg/l, 0.345 – 0.360mg/l in station 3 with a mean value of 0.3525mg/l. The highest nitrate value of 0.589 mg/l was recorded at station 2 in January, 2022 and lowest value of 0.240 mg/l was recorded at station 1. Analysis of Variance (ANOVA) results indicated that the study stations mean values did not differ significantly (nil).

4.1.9 AMMONIUM-N (mg/l)

The nutrient values based on Ammonium-N for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.443 – 0.226 mg/l in station 1 with a mean value of 0.3345 mg/l, 0.520– 0.560 mg/l in station 2 with a mean value of 0.540 mg/l, 0.557 – 0.568 mg/l in station 3 with a mean value of 0.5625 mg/l. In January 2022, station 3 recorded the highest ammonium value of 0.568mg/l while station 1 recorded the lowest value of 0.226 mg/l. No significance difference ($p > 0.05$).

4.1.10 PHOSPHATE (mg/l)

The nutrient values based on phosphate for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.111 – 0.069mg/l in station 1 with a mean value of 0.09 mg/l, 0.115 – 0.118 mg/l in station 2 with a mean value of 0.074 mg/l, 0.074 – 0.089 mg/l in station 3 with a mean value of 0.0815 mg/l. The highest phosphate value of 0.118 mg/l was recorded at station 2 and lowest value of 0.069mg/l was recorded at station 1. No significance difference.

4.1.11 CHLORIDE (mg/l)

The nutrient values based on chloride for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 14.12 – 7.06mg/l in station 1 with a mean value of 10.59mg/l, 14.12 – 14.18mg/l in station 2 with a mean value of 14.18mg/l, 14.12– 14.17 mg/l in station 3 with a mean value of 14.145 mg/l, 14.18 mg/l and 7.06 mg/l of chloride were measured at the highest and lowest sampling locations respectively. No significance difference ($p > 0.05$).

4.1.12 TURBIDITY (NTU)

The turbidity values recorded for the 4 sample stations during the period of investigation as seen in Table 4.1 ranged between 5.00 – 14.00 NTU in station 1 with a mean value of 9.50 NTU, 8.00 – 11.00 NTU in station 2 with a mean value of 9.50 NTU, 17.00 – 17.40 NTU in station 3 with a mean value of 17.20 NTU. The lowest value of 5.00 NTU was recorded at station 1 and the highest turbidity value of 17.40 NTU was reported at station 3. No significance difference ($p > 0.05$).

4.1.13 IRON (mg/l)

The nutrient values based on iron for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.842 – 0.654 mg/l in station 1 with a mean value of 0.748 mg/l, 0.411 – 0.419 mg/l in station 2 with a mean value of 0.415 mg/l, 0.532 – 0.540 mg/l in station 3 with a mean value of 0.536 mg/l. Station 1 reported the highest iron value 0.842 mg/l, while station 2 recorded the lowest value of 0.411 mg/l. No significance difference ($p > 0.05$).

4.1.14 ZINC (mg/l)

The nutrient values based on zinc for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.388 – 0.240 mg/l in station 1 with a mean value of 0.314 mg/l, 0.187 – 0.190 mg/l in station 2 with a mean value of 0.1885 mg/l, 0.203– 0.208 mg/l in station 3 with a mean value of 0.2055 mg/l, station 1 reported the highest zinc value of 0.388 mg/l, while station 2 recorded the lowest value of 0.187 mg/l. No significance difference (nil).

4.1.15 COPPER (mg/l)

The nutrient values based on copper for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.107 – 0.182 mg/l in station 1 with a mean value of 0.0265 mg/l, 0.105 – 0.116 mg/l in station 2 with a mean value of 0.1105 mg/l, 0.136 – 0.140 mg/l in station 3 with a mean value of 0.138 mg/l. Station 1 reported the highest zinc value of 0.182 mg/l, while station 2 recorded the lowest value of 0.105 mg/l. No significance difference (nil).

4.1.16 MANGANESE (mg/l)

The nutrient values based on manganese for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.038 – 0.050 mg/l in station 1 with a mean value of 0.044 mg/l, 0.042 – 0.047 mg/l in station 2 with a mean value of 0.0445 mg/l, 0.021 – 0.025 mg/l in station 3 with a mean value of 0.023 mg/l. Station 1 reported the highest manganese value of 0.050 mg/l while stations 3 recorded the lowest value of 0.021 mg/l respectively. No significance difference (nil).

4.1.17 MAGNESIUM (mg/l)

The nutrient values based on chromium for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 – 4.2 respectively and represented in Fig. 4.22 ranged between 4.38 – 3.20 mg/l in station 1 with a mean value of 3.79 mg/l, 1.95 – 2.50 mg/l in station 2 with a mean value of 2.255 mg/l, 5.83 – 5.90 mg/l in station 3 with a mean value of 5.865 mg/l. The stations 3 recorded the highest magnesium value of 5.90 mg/l. Whereas the station 2 recorded the lowest value of 1.95 mg/l. No significance difference ($p > 0.05$).

Table 4.1: Showing the spatial variation of physical-chemical parameters in Ogba River, Benin city, Edo state

PARAMETERS	STATION 1	STATION 2	STATION 3	P-VALUES
	Mean ± SE (Min - Max)	**Mean ± SE (Min - Max)**	**Mean ± SE (Min - Max)**	
Hydrogen conc (pH)	6.9±0.42 (6.6-7.2)	6.4±0141 (6.3-6.5)	6.5±0.282 (6.3-6.7)	*P* >0.05
Electrical conductivity	5.1±1.27 (4.2-6)	6±1.414 (5-7)	120±0 (120-120)	*P* <0.05
Total dissolve solids(mg/l)	6.3±45.11 (31.8-95.6)	27.3±1.13 (26.5-28.1)	64±0.565 (63.6-64.4)	*P* <0.05
Suspended solids(mg/l)	8.5±0.707 (8-9)	11.1±1.55 (10-12.2)	17.2±0.28 (17-17.4)	*P* >0.05
Turbidity(NTU)	9.5±6.363 (5-14)	9.5±2.12 (8-11)	2.2±0.424 (1.9-2.5)	*P* >0.05
Dissolved oxygen(mg/l)	3.7±1.27 (2.8-4.6)	3.15±1.62 (2-4.3)	0.3±0.141 (0.2-0.4)	*P* >0.05
Alkalinity(mg/l)	14.1±8.34 (8.2-20)	20.1±0.141 (20-20.2)	68.2±0.282 (68-68.4)	*P* <0.05
Hardness(mg/l)	24±11.35 (16-32)	20.25±0.353 (20-20.5)	6±6 (6-6)	*P* <0.05
Sulphate(mg/l)	3.5±0.707 (3-4)	6.5±2.121 (5-8)	0.3525±0.010 (0.345-0.36)	*P* >0.05
Ammonium-N(mg/l)	0.3345±0.153 (0.226-0.443)	0.5±0.02 (0.52-0.56)	0.0815±0.010 (0.074-0.089)	*P* >0.05
Chloride(mg/l)	10.59±4.99 (7.06-14.12)	14.15±0.042 (14.12-14.18)	17.575±0.091 (17.51-17.64)	*P* >0.05
Magnesium(mg/l)	3.79±0.83 (3.2-4.38)	2.225±0.388 (1.95-2.5)	0.536±0.005 (0.532-0.54)	*P* >0.05
Iron(mg/l)	0.748±0.132 (0.654-0.842)	0.415±0.005 (0.411-0.419)	0.205±0.003 (0.203-0.208)	*P* >0.05

NOTE: *P* >0.05= Not significant different, *P* <0.05= Significantly different

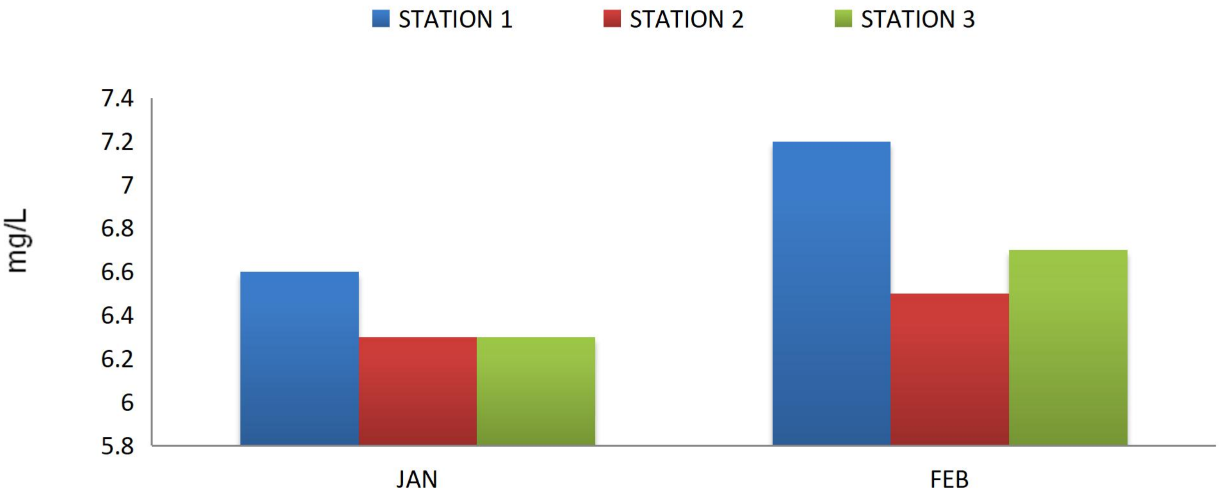

Figure 4.1: Spatial and temporal variation of Hydrogen concentration

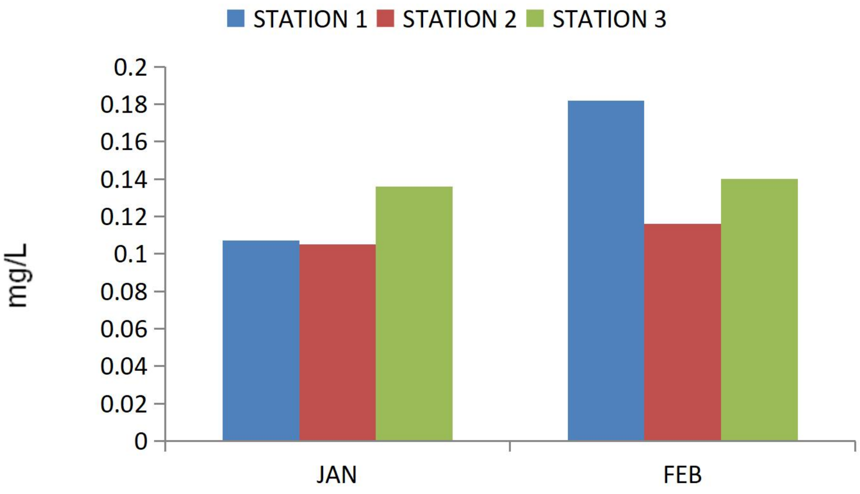

Figure4.2: Spatial and temporal variation Electrical Conductivity

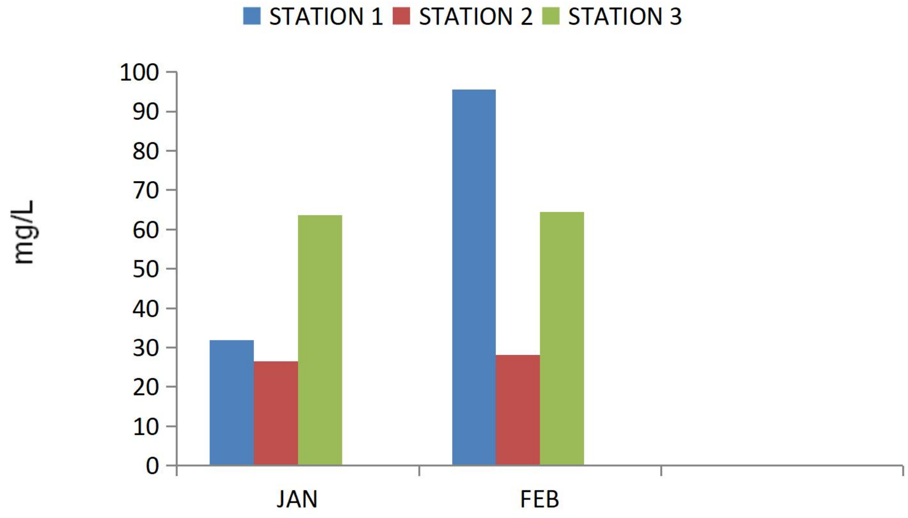

Figure 4.3: Spatial and temporal variation of Total dissolved solids

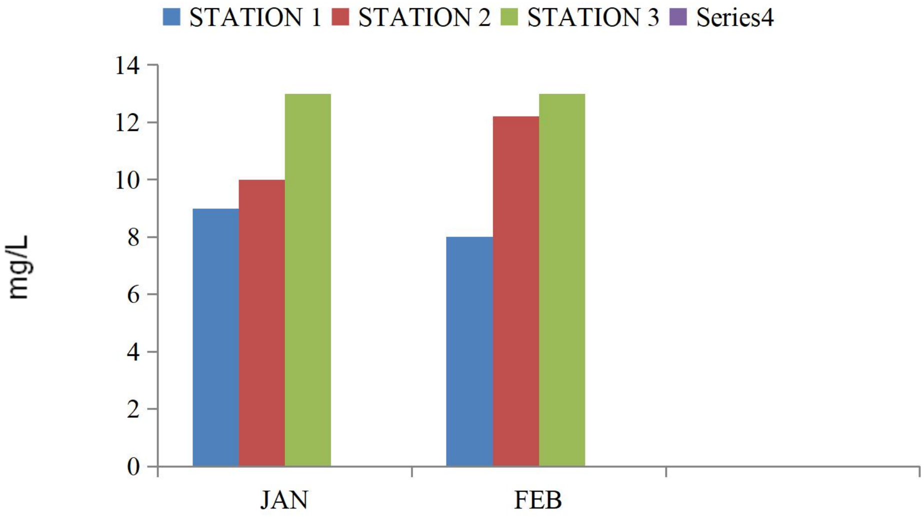

Figure 4.4: Spatial and temporal variation of Suspended Solid

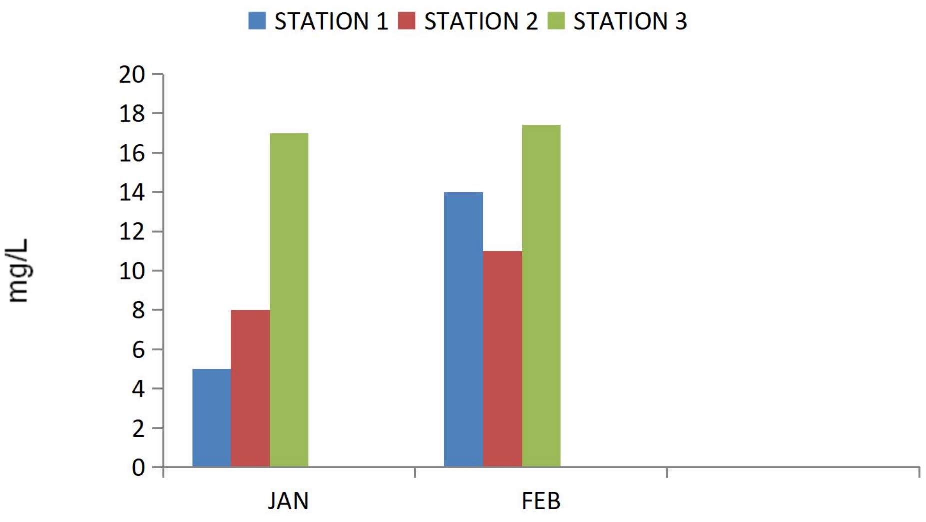

Figure 4.5: Spatial and temporal variation of Turbidity

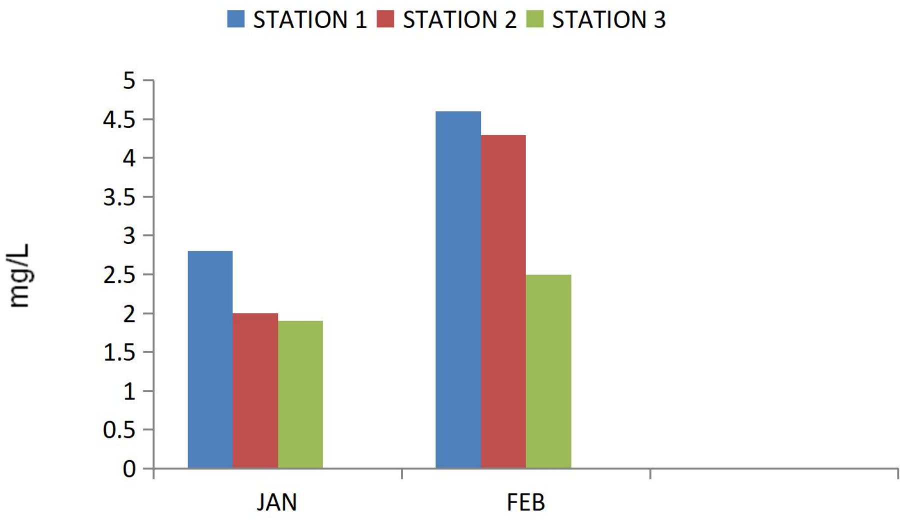

Figure 4.6: Spatial and temporal variation of Dissolved Oxygen

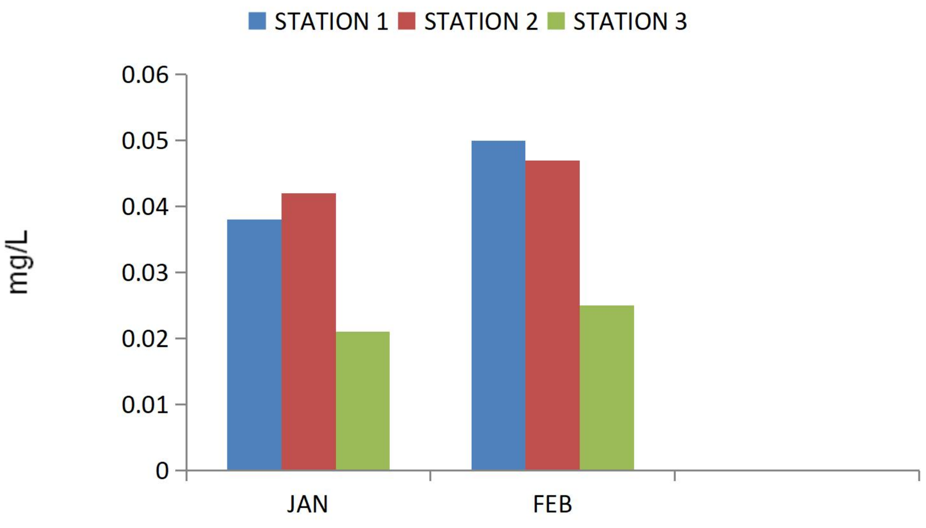

Figure 4.7: Spatial and temporal variation of Alkalinity

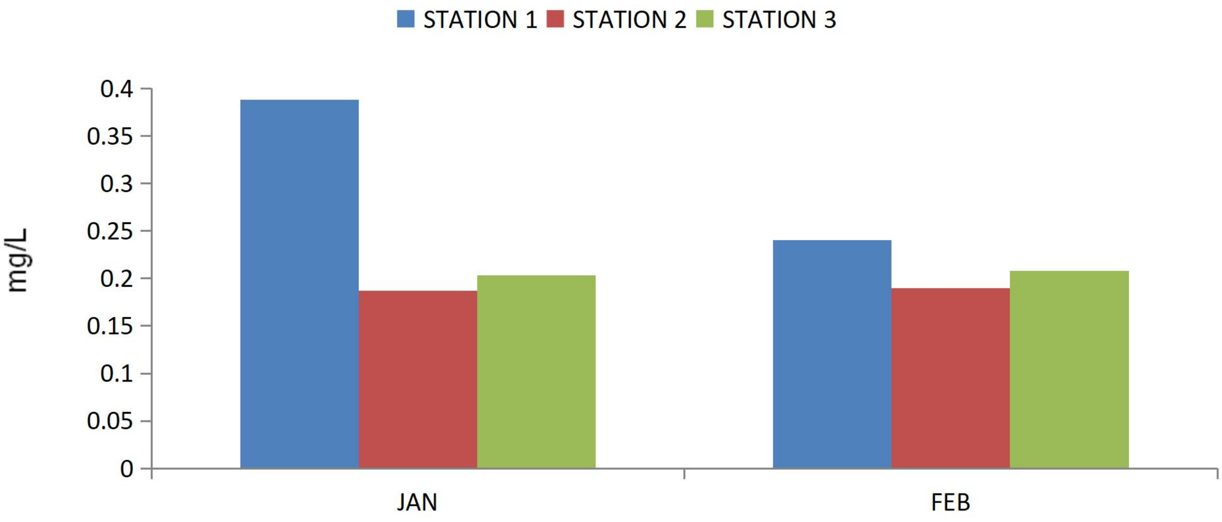

Figure 4.8: Spatial and temporal variation of Sulphate

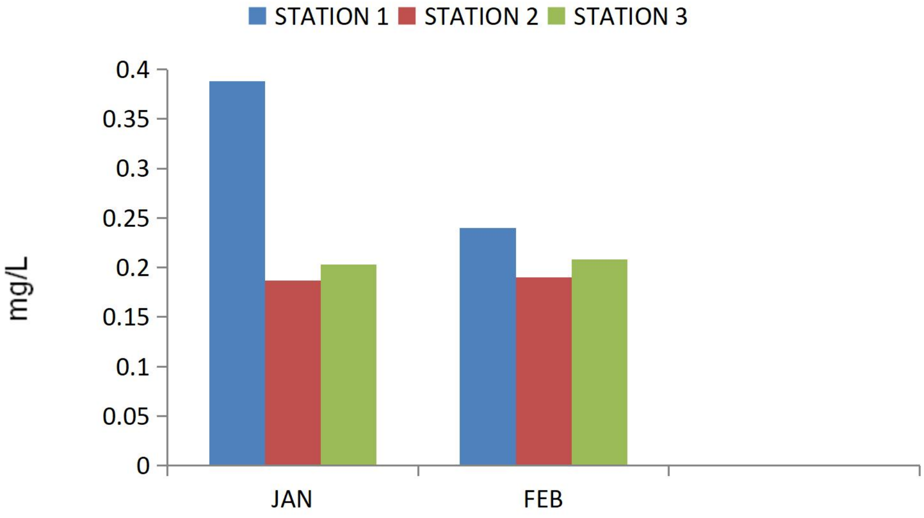

Figure 4.9: Spatial and temporal variation of Ammonium

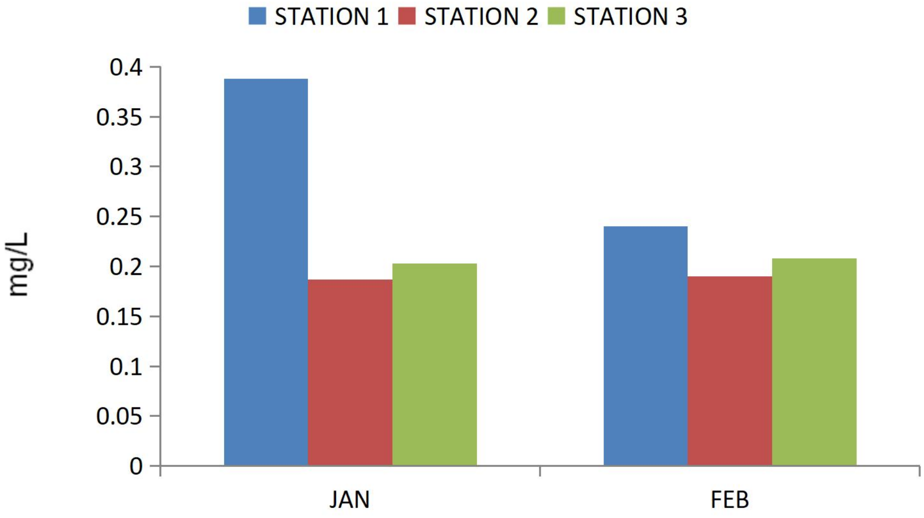

Figure 4.10: Spatial and temporal variation of Chloride

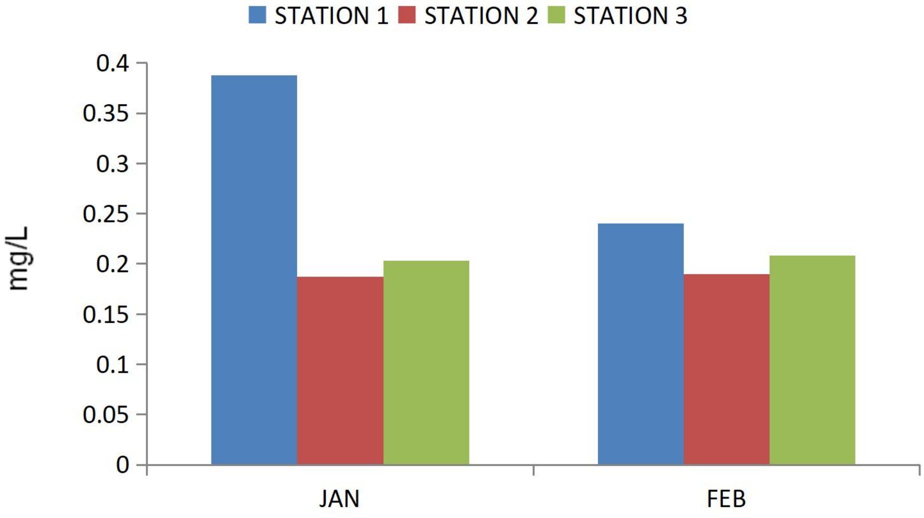

Figure 4.11: Spatial and temporal variation of Magnesium

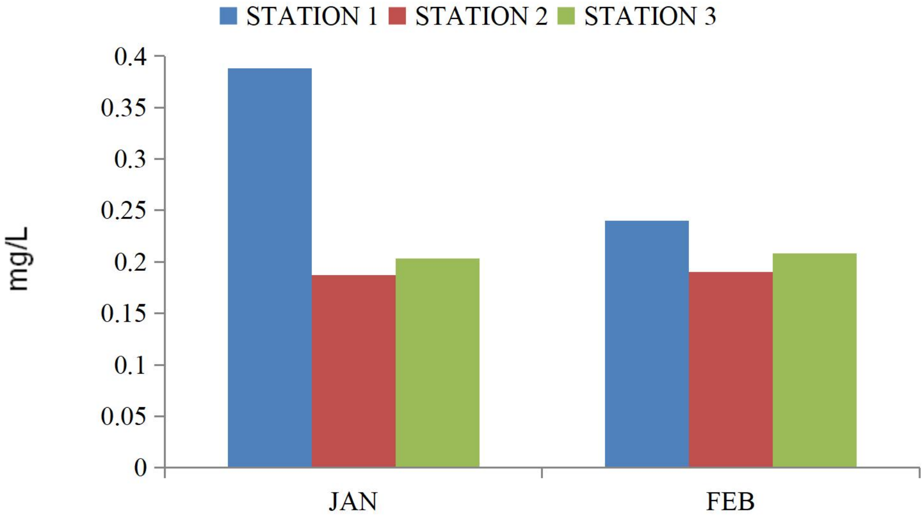

Figure 4.12: Spatial and temporal variation of Iron

Table 4.2: Correlation Table of Water Physicochemical Parameters with paracetamol in Water and Sediment of Ogba River

	pH	*EC*	*TDS*	*SS*	*TURBIDITY*	*DO*	*ALKALINITY*
pH	1						
EC	-0.33375	1					
TDS	-0.64517	0.935556	1				
SS	-0.58822	0.958652	0.99738	1			
TURBIDITY	0.327327	-0.99998	-0.93313	-0.95669	1		
DO	0.465969	-0.98959	-0.97665	-0.98963	0.9885826	1	
ALKALINITY	-0.42124	0.995536	0.964715	0.981233	-0.9948697	-0.99875	1
HARDNESS	0.495041	-0.98427	-0.98324	-0.99385	0.9830447	0.99945	-0.99655153
SULPHATE	-0.17514	-0.86964	-0.63923	-0.69319	0.8729797	0.789517	-0.81915756
AMMONIUM	-0.08161	-0.91228	-0.70884	-0.758	0.9150479	0.843824	-0.86954932
CHLORIDE	-0.76346	0.863631	0.986021	0.971385	-0.8601777	-0.9272	0.90735797
MAGNESIUM	0.741849	-0.87971	-0.99096	-0.97866	0.8764536	0.938997	-0.92066636
IRON	0.8308	-0.80194	-0.96125	-0.93879	0.7978531	0.879582	-0.85474698
WATER	-0.92894	-0.03897	0.316453	0.247005	0.0457734	-0.10527	0.05551965
SEDIMENTS	-0.54897	0.971135	0.992795	0.998862	-0.9694879	-0.99536	0.98931352

Table 4.2: Correlation Table of Water Physicochemical Parameters with paracetamol in Water and Sediment of Ogba River

HARDNESS	*SULPHATE*	*AMMONIUM*	*CHLORIDE*	*MAGNESIUM*	*IRON*	*WATER*	*SEDIMENTS*
1							
0.768740189	1						
0.825573244	0.9955525	1					
-0.93910874	-0.5021645	-0.58139995	1				
0.949881257	0.53027807	0.607791771	-0.9994612	1			
0.894867771	0.40246461	0.486916351	-0.9937466	0.989546184	1		
-0.13817639	0.52720455	0.444807321	0.47008663	-0.440863421	-0.5657	1	
-0.99800015	-0.7267751	-0.788252232	0.95895144	-0.967742271	-0.92129	0.200505	1

4.2. Distribution of Paracetamol in Ogba River

This indicates the occurrence of paracetamol in water for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.18125 – 0.16985 µg/ml in station 1 with a mean value of 0.17555 µg/ml, 0.6324 – 0.9788 µg/ml in station 2 with a mean value of 0.8056 µg/ml, 0.47257 – 0.46296 µg/ml in station 3 with a mean value of 0.467765 µg/ml. The stations 2 recorded the highest paracetamol value of 0.9788 µg/ml. Station 1 recorded the lowest value of 0.16985 µg/ml.

For sediments, the occurrence of paracetamol for the 3 sample stations recorded during the period of investigation as seen in Table 4.1 ranged between 0.38986 – 0.326129 µg/kg in station 1 with a mean value of 0.357995 mg/kg, 1.35074 – 0.15986 µg/kg in station 2 with a mean value of 0.7553 µg/kg, 2.71139 – 1.13426 mg/kg in station 3 with a mean value of 1.9228 µg/kg. The stations 3 recorded the highest paracetamol value of 2.71139 µg/kg. Station 2 recorded the lowest value of 0.15986 µg/kg.

Table 4.3: Summary of the spatial distribution of paracetamol in Ogba River

PARAMETERS	STATION 1 Mean ± SE (Min – Max)	STATION 2 Mean ± SE (Min – Max)	STATION 3 (Min – SE) (Min – Max)	P-VALUES
Water(µg/ml)	0.17±0.008 (0.16-0.18)	0.80±0.24 (0.63-0.97)	0.46±0.006 (0.46-0.47)	$P > 0.05$
Sediment(mg/kg)	0.35±0.04 (0.32-0.38)	0.75±0.84 (0.15-1.35)	1.92±1.11 (1.13-2.7)	$P > 0.05$

NOTE: $P > 0.05$= Not significant different, $P < 0.05$= Significantly different

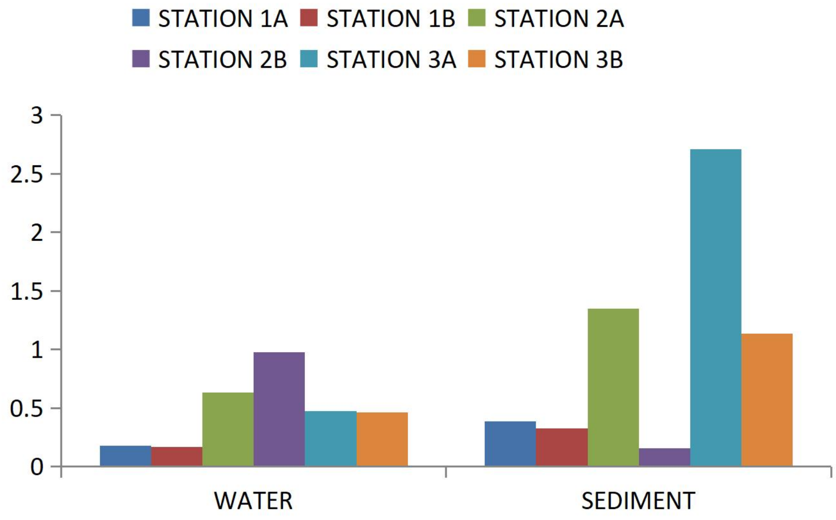

Figure 4.13: Bar chart representation of the mean concentration of Paracetamol in water and sediments

CHAPTER FIVE

DISCUSSION AND CONCLUSION

5.1 DISCUSSION

Good observation of paracetamol in water and sediments is important because it provides needed information for water resources management and most pharmaceuticals are required within the recommended limits in the human body for the smooth functioning of metabolic activities.

5.2 Paracetamol occurrence at the three stations

According to (Stackelberg *et al.,* 2007), Paracetamol is one of the most frequent pharmaceutical products in approximately 75% of natural water such as rivers. Intentionally high intake can cause nausea, vomiting, right upper quadrant abdominal pain, jaundice and even death. In water paracetamol concentration values were 0.16-0.97µg/ml in Ogba River. Similarly, in the USA, the paracetamol was detected at range 0.026µg/ml in Las Vagas wash waters (Boyd RA and Furlong ET, 2002); 0.031 µg/ml in New Jersey stream water (Alvarez *et al*., 2005) and 0.117µg/ml in Colorado River (Snyder SA., *et al*. 2006). In sediments, the concentration of paracetamol in Ogba River were 0.15-2.71µg/ml.

In this study, concentrations for paracetamol were found in the water of Ogba River. Paracetamol in River for the 3 stations recorded during the period of investigations as seen in table 4.2 ranged from 0.16 – 0.18 µg/ml in station 1 with a mean value of 0.17 µg/ml, 0.63 – 0.97 µg/ml in station 2 with a mean value of 0.80 µg/ml and 0.46 – 0.47 µg/ml in station 3 with a mean value of 0.46 µg/ml .station 2 recorded the highest paracetamol value of 0.97 µg/ml ,while station 1 recorded the lowest value of 0.18 µg/ml. Recent studies conducted in the greatest concentrations of paracetamol were observed in Almeria (Gomez, *et al*., 2007), 37.458g/L in STP influent in Madrid

(Rosal, *et al*., 2010), and 19.850g/L in STP influent in Catalonia (Pedrouzo, *et al*., 2007). It was also discovered to be at a level of 56.9g/L in STP influent in Seoul, North Korea (Choi *et al*., 2008), 84g/L in STP influent samples in Stockholm, Sweden (Ganiyat, 2013), and 0.07g/L in STP effluent in Selangor, Malaysia (Al-odaini, *et al.*, 2005).

5.3 Heavy metals concentration at the three stations

Copper is essential for good health. However, consumption of water that contains higher than normal levels of copper, may result to nausea, vomiting, stomach cramps or diarrhea. Intentionally high intakes of copper can cause liver and kidney damage and even death. (Obasi and Akudinobi, 2020). Copper concentration values (0.105 – 0.182 mg/l) were below the WHO permissible limit of 2.0 mg/l. Similarly, Anake *et al.*, (2014) reported concentration values of copper (0.04 - 0.75 mg/l) in 0ta; Oboh and Egun (2017) reported concentration values of 0.02 – 0.07 mg/l in Agbor *et al*., 0.019 mg/l in Oke – Afa by Oluseyi *et al.,* (2014).

Iron was detected at abnormal levels in majority of the groundwater samples collected at different locations within Benin metropolis. Iron concentration values were (0.203 – 0.842mg/l). The concentration where well above the WHO (World Health Organization) permissible limit of 0.01 mg/l. Other authors, (Ayedun *et al*., 2011; Ogbeibu *et al*., 2012) have reported similar findings. (Ayedun *et al*., 2011) 0.06-0.59 mg/l by a much higher value of iron 0.44–2.08 mg/l in Ekurede-Urhobo Warri. Although iron is the second most abundant metallic element in the earth's crust, it's concentration in groundwater is due to large deposits in the earth's surface (Edet *et al*., 2011). Results of extensive consumption of drinking water containing high Fe concentration level are haemosiderosis (liver-damage disease), diabetes mellitus, arteriosclerosis, and many other neurodegenerative diseases (Nagendrappa *et al.,* 2010; Brewer 2009).

Zinc has been found to have low toxicity to man, but prolonged consumption of large doses can result in some health complications such as fatigue. The concentration values (0.180 – 0.388 mg/l) of zinc recorded in this study were within WHO (2011) permissible value of 1.5 mg/l. This could be that the zinc in its natural mineral form (sphalerite) did not dissolve into groundwater bodies via leaching in all examined locations (Broadly *et al.,* 2007). In similar studies on groundwater, Akpoveta *et al.,* (2011) recorded zinc values of (0.09 – 0.11 mg/l) in Benin city and Ugah *et al.*, (2018) recorded zinc concentration values of (0.05 - 0.30 mg/l) in Uromi.

Cadmium and its compound have been found to have several health effects in humans. The health effects of cadmium exposure are exacerbated by the inability of humans to digest and excrete it when consumed because the cadmium is re-absorbed by the kidney, thus limiting its excretion. Indigestion of cadmium can cause stomach irritation resulting to vomiting and diarrhea, long-term exposure to cadmium leads to its deposition in bones. Also, cadmium can cause testicular degeneration, a potential risk factor for prostate cancer. Engwa *et al.*, (2019). Although the WHO (2011) guideline concentration values for cadmium in drinking water is 0.003 mg/l; a below detectible limit (BDL) of cadmium concentration was observed in this study. Similarly, Oboh and Egun (2017) reported a BDL concentration in Agbor and Oyem *et al.,* (2015) also reported a BDL concentration in Agbor. In contrast, higher cadmium values of 0.005 to 0.007 mg/l in Benin city and very high values of 10.62 mg/L - 15.67 mg/L in Abakaliki were reported by Akpoveta *et al.* (2011) and Obasi and Akudinobi (2020) respectively.

Lead was observed to be at normal level at all three locations with a concentration value (0.021 – 0.034 mg/l) which is above the WHO permissible limit value of 0.01 mg/l. High concentration of lead in the human body causes cancer, blood disorders, hypertension, and low birth weights. Long-term exposure may also give rise to kidney damage. Engwa *et al.*, (2018). Similar lead concentration values (0.00 - 0.02 mg/l) was reported by Oboh and Egun (2017) in Agbor and Olobaniyi *et al.,* (2007) recorded lead values (0.00 – 0.04 mg/l) in Agbor.

Manganese (Mn) plays a vital role in the metabolism of cholesterol, fat, and glucose. Its deficiency causes hyperglycemia, elevated body fat, and decreased sperm count, while at high concentration it is toxic and carcinogenic (Chishti *et al.,* 2011). Manganese concentration values (0.028 – 0.050 mg/l) recorded in this study were within WHO (2011) permissible limit of 0.05 mg/l. similar findings reported manganese concentration value of 0.02 mg/l by Yusuf *et al*., (2018) in Benue and 0.000 - 0.0022 mg/l by Popoola *et al*., (2019) in Lagos.

CONCLUSION

The samples of water and sediments collected from the three different stations in Ogba River were found to be contaminated with paracetamol and heavy metals.

The concentration of heavy metals in Ogba River varied spatially across the different stations sampled. The result of the water sample from the three stations sampled were observed to be high in the concentration of iron, with a mean value exceeding the WHO limit set for drinking water quality.

RECOMMENDATIONS

The substantial margin of safety for consumption of very low concentrations of pharmaceuticals in drinking-water suggests that appreciable adverse impacts on human health are very unlikely. As such, concerns over pharmaceuticals should not divert attention and valuable resources of water suppliers and regulators from other priorities such as pathogenic microbial water quality issues. The low risk to human health from current levels to exposure in water suggests that development of formal guideline values for pharmaceuticals and the installation of specialized treatment processes to reduce trace concentrations of pharmaceuticals are not warranted.

Routine monitoring programme for pharmaceuticals in water sources and drinking-water and additional or specialized drinking-water treatment to reduce very low concentrations of pharmaceuticals in drinking-water are not deemed necessary due to the limited public health benefits.

Reduction of human exposure to pharmaceuticals through drinking-water can be achieved through a combination of preventive measures, such as regulations, public guidance and consumer education to encourage the proper disposal of unwanted pharmaceuticals and minimize the introduction of pharmaceuticals into the environment.

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