CHAPTER ONE

1.1 Background of the Study

The operations of an industry determines the nature and composition of metals in its effluents and the extent of contamination of natural water bodies. Large amounts of different toxic heavy metals are thrown into the environment (Ugwekar and Lakhawat, 2012; Patel and Nisar, 2016). Some industries are known to generate huge amounts of heavy metals in waste water and these are sent into the environment untreated. This has emerged a major challenge to developing countries like Nigeria. Contaminants present in effluent discharge include petroleum products, herbicides and pesticides, fertilizers, heavy metals, detergents, raw sewage, hot water from cooling plants, bacteria and various diseases causing protozoan (Uaboi-Egbenni *et al*, 2010). Contamination of water resource can occur naturally over very long period of time, particularly in response to climatic changes (Nwabanne and Igbokwe, 2012).

Industrialization, like other human activities that impact on the environment, often results in pollution and degradation (Phiri *et al*; 2005; Adekunle and Eniola, 2008; Uaboi–Egbenni *et al*; 2010). Polluted water deteriorates, lowers water quality there by generating negative effects on aquatic life, transfers same by bioaccumulation to humans affecting public health (Ado *et al*; 2015; Ezeonyejiaku *et al*; 2014; Kanu and Achi, 2011). The incidence of heavy metal contamination is attributed to indiscriminate disposal of domestic, industrial, mining and waste waters that are dumped into the water bodies. The heavy metals include lead, nickel, cadmium, copper, manganese, arsenic, mercury, zinc, and iron (Sangodoyin, 1995). The main hazardous contents of water pollutants is heavy metals (Gaherwar and Kulkarni, 2012). Ground and surface waters can be polluted from several sources.

In farming areas the routine application of agricultural fertilizers is a major source of pollution (Egereonu, 2003).

In urban areas, the indiscriminate disposal of industrial effluents and domestic wastes contribute greatly to the poor quality of water (Bai *et al.*, 2011). Most rivers in the urban areas of the developing world today are the end points of effluents discharged from industries. Environmental pollution carries inevitable costs and problems in terms of pollution of the air, water and general degradation of the natural resources (Ogedengbe and Akinbile, 2004). Industrial effluents if not treated or poorly controlled contribute to the pollution of the water or receiving river (Peter and de Britto, 2010). Effluents contain inorganic wastes such as brine, salts, metals and a number of toxic substances which human beings encounter regularly that pose serious health risks. Pesticide residues on vegetable crops, mercury in fish and many industrially produced chemicals may cause cancer, birth defects, genetic mutations or death. Discharge of metals and some nonmetals into water bodies produce serious environmental effects (Adeodu *et al.*, 2015). Rivers play a significant role in the survival of the world, because they serve not only the purpose of water supply for domestic, industrial, agricultural and power generation but are also used for the disposal of sewage and industrial wastes. This therefore puts rivers under tremendous pressure due to human activities. Improper disposal systems of wastes from slaughter houses could lead to transmission of pathogens to humans and cause zoonotic disease such as E. coli, bacillosis, salmonellosis, brucellosis, and helminthes (Akan *et al.*, 2012, Abdullahi *et al.*,2013).

Most of the rivers have been unmindfully used for the disposal of domestic and industrial effluents far beyond their assimilative capacities and have been grossly polluted (Agarwal and Sharma, 1982). The effect of water pollution on human health is of serious nature (Adekola *et al.*, 2016). Gohil and Mankodi (2013) found that the presence of toxic heavy

metals in food chain cause ill health which result in the death of aquatic organisms Bello *et al*., (2014); and Galadima *et al.,* (2011), found that fishes are most affected. Anim-Gyampo *et al;* (2013) ;proved that concentrations of heavy metals in fish tissues were higher than that of their habitats. Bio-accumulation of heavy metals in organisms is known to have over the years resulted in high concentrations of these trace metals in higer levels of the food chain (Kachenko and Surgh, 2004). In 2004 through various studies they showed that heavy metals such as Hg, Ni, Cu, Cd, Pb, Fe, As, Mn and Cr were contaminants in waste water, agricultural soil and green vegetables planted in an industrial area in Australian Newzealand. Drinking water plays an important role in the bodily absorption of trace element by humans. Some trace elements are essential to man, but at elevated concentrations, can cause morphological abnormalities, reduce growth, increase mortality and mutagenic effects (Bhagirathi Behera *et al*., 2012).

The effect of these metals on the aquatic environment and health is of great concern to the students of environment studies. This is more so as the concentration of substances in the body determines the extent of reactions that will take place in such a system. The excess of these microelements and their deficiency plays some effects on the biochemical reactions in the living organisms (Bath and Khan, 2011). Fraga, 2005; highlighted that many heavy metalskj were essential for biochemical and physiological processes when their concentrations are low but become fatal at elevated levels. A lot of anthropogenic discharges and natural releases have caused enrichment of toxic heavy metals in the ecosystem (Ciszewski and Tomas, 2010). Here they can be readily assimilated and accumulated by various intertidal molluscus and may result in potential risk for human health through food chain. Edible marine species (fish, cephalopod mollusks, crustaceans) from the Aldriatic sea were analyzed for heavy metals (Hg, Cr, Cd, and Pb) and poly-chlorinated Biphenyls [PCBs] stricking results were obtained (Storelli, 2008., Cheng and

Yap, 2015). These heavy metals that settle at bottom of the rivers when taken in by the aquatic organisms comprising plant and fishes, get transferred to man at the apex of the food chain. The use of *Eichhornia crassipes* on heavy metal removal had been investigated (Gaherwar and Kulkarni, 2012). River systems are the primary means for disposal of wastes, especially the effluents from nearby industrial set ups. Worldwide water bodies are the primary means for disposal of waste, especially the effluents, from industries that are near them. These effluents from industries have a great deal of influence on the pollution of the water body and alter the physical, chemical and biological nature of the receiving water body (Sangodoyin, 1991). Waste generations by the industries and households have continued to increase. These wastes are indiscriminately disposed-off into the water bodies. This has led to pollution of inland water bodies and coastal waters which subsequently lower water quality (Taiwo *et al.*, 2012).Industrial activities do alter and unbalance the natural cycles of some harmful substances such as heavy metals like Lead, Mercury, Cadmium, Plutonium, and others (Ciszewski and Czajka, 2015). These metals can either be detected in their elemental state which implies that they are not subject to further bio-degradation processes or bound in various salt complexes. In either instance, metal ions cannot be mineralized. Therefore the concentrations of these heavy metals tend to increase up the food chain. Food consumption is the most likely route of human exposure to metals (Nesta Bortey-Sam *et al.*, 2014). Heavy metals cause serious health effects with varied symptoms depending on the nature and quantity of heavy metal ingested. Baird (1999), Liu *et al.*, (2008) and Sethi (2014), acknowledged that most heavy metals are poisonous and pollution by them are the source of systemic diseases. They produce their toxicity by forming complexes with proteins in which carboxylic acid (-COOH), amine (-NH$_2$), and thiol (-SH) groups are involved. These modified biological molecules lose their ability to function

properly and result in death of the cells. When metals bind to these groups,they inactivate important enzyme systems or affect protein structure, which is linked to the catalytic properties of enzymes. These type of toxins may cause the formation of radicals which are dangerous that cause the oxidation of biological molecules (Adepoju-Bello and Alabi, 2005) and (Adepeju, *et al*., 2009). Higher concentrations of lead and Mercury are known to cause irreversible brain damage, auto-immunity (in which the person's immune system functions against the body's own systems). Heavy metalic ions, particularly Mercury(Hg^{2+}), Lead (Pb^{2+}), and Cadmium(Cd^{2+}) are sulphur - seeking and easily bind to $S-CH_3$ and S-H (sul -phydryl groups) in enzyme proteins thus:

$$\text{Enzyme + Hg} \longrightarrow \text{Enzyme +SHg +2H}^+ \qquad (1)$$
$$\text{(Active)} \qquad\qquad \text{(Immobilized)}$$
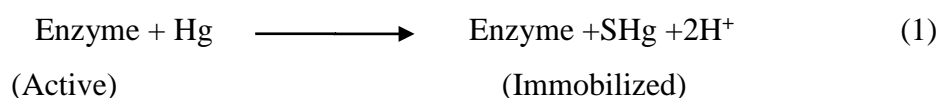
Such "immobilized" enzymes cannot function properly as the other **"active enzyme"** and the host suffers. The exposure of *persons* to higher concentrations of Aluminum has been associated with Alchemies and Parkinson diseases, senility and Prehensile dementa. Arsenic exposure causes among other illness or symptoms cancer, abdominal pain, skin lesions and arsenocosis (Saikia and Gupta, 2012). Cadmium exposure produces Kidney damage and hypertension. Lead is a commutative poison and possible human carcinogen. lead and Cadmium toxicity is well known and recorgnized as major environmental and health risk though they exist naturally (Bakare-Odumola, 2005).

Pb and Ra, do imitate Ca and get absorbed in the bone (Pandy *et al*., 2014). Heavy metals are known to initiate toxic effects by replacing essential nutrients at cation exchange sites in plants. For example Fe deficiency may initiate increased absorption of Cd in pregnant females (Tchounwou *et al.,* 2012; Jadia and Fulekar, 2009). Consistent unregulated indiscriminate dumping of waste into water bodies has worsened aquatic pollution, as bacteria and other microorganisms are multiplied in the ecosystem (Olayemi,1994).

Water whether from underground or surface sources, found in nature is polluted. Pollution may be due to various reasons, namely from sewage, industrial wastes or from natural contaminants. Natural water may contain high amount of turbidity, organic load from decaying leaves, vegetation or fishes. Minerals in solution or suspension forms may contaminate waterbodies such as lakes, rivers, oceans, aquifers and ground waters. Pollutants of air or soil origin end up in water bodies. These pollutants may include heat, organic-oxygen demanding wastes, originating from humans, animals and plant life; heavy metals such as mercury, lead, cadmium, nickel, iron; disease causing pathogens, originating from humans and such other operations, as meat processing, tanning, plant materials, nitrogen and phosphorus; toxic substances such as radio-nuclides, as well as synthetic organic compounds used as insecticides, fungicides, herbicides and even oil spillages. Assessment of water is not only on suitability for human consumption but also in relation to its agricultural, industrial, recreational, commercial uses and its ability to sustain aquatic Life (Taiwo *et al*., 2012). According to an estimate, about 80% of the total population of India are deprived of pure and safe drinking water. A recent study revealed that there were 153,000 villages in India, which had infected water supply. 90% of total drinking water is severely polluted. Ganga River in India is the most polluted river in the world (Baskaran and Britto, 2010).

In Nigeria different regulations put in place to protect marine environment have not been effective in controlling the indiscriminate dumping of refuse, effluent and waste into the open water bodies. The contaminants include chlorides, phosphates, oil, grease, nitrates and heavy metals. The heavy metals most prevalent and occurring above WHO set limits are lead, copper, zinc, nickel, cadmium, chromium, and iron (Ebiare *et al*., 2010). The extraction and processing of heavy metals has given rise to various environmental related sickness,diseases and accidents. Common mining related

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sicknesses observed include vector borne diseases such as malaria, schistomiasis and respiratory track diseases, especially tuberculosis and silicosis, eye diseases especially conjunctivitis (NestaBortey-Sam *et al;* 2015). One of the serious pollutants in the natural environment are heavy metals due to their toxicity, persistence and bioaccumulation prevalences. The impact of anthropogenic perturbation is most strongly felt by the estuarine and coastal environments close to the urban cities. The heavy metals flushed from the hinter lands and coastal areas are deposited on the sediments. Plants and animals (like fishes) the inhabitants of estuarine and coastal environments which cannot escape the detrimental effects of these pollutants in their habitat are used to evaluate the health status of the aquatic ecosystem.These pollutants bio-accumulate being non degradable (Aderinola *et al.*, 2012). Water is a valued natural resource for the existence of all living organisms. River waters are being polluted by indiscriminate disposal and dumping of sewage,industrial waste and a number of human activities which affects their Physio-chemical characteristics. Increasing numbers and amounts of industrial, agricultural and commercial chemicals discharged into the aquatic environments have led to various deleterious effects on aquatic organisms. The aquatic plants and organisms, sediments accumulate these pollutants directly from contaminated water and indirectly transfer same to the food chain. Owing to the large quantities of effluents dumped into these receiving water bodies the natural process of pathogenic reduction (recovery) have proved inadequate for the protection of public health (Kolawole *et al.,* 2011). It is on record that certain plants and algae have been of use in the removal of heavy metals and other pollutants from waste water and contaminated water bodies, these they do by assimilating the pollutants into their tissues and hence making the environment clean (Gaherwar and Kulkarni, 2012). Food consumption had been identified as a major pathway of human exposure to potentially toxic

elements as compared to inhalation, and dermal contacts. Hence the accumulation of PTE's in the environment was of increasing concern due to food safety issues and potential health risks. Soil and sediments serve as the most important sink for heavy metals, contaminants and pollutants in terrestial ecosystems. Soil heavy metal pollution is a world wild problem more so with rapid industrialization and urbanization in the last two decades. Heavy metal pollution in urban and agricultural soils has become significant as high accumulation of heavy metals in surface soil has become a serious threat to human health via inhalation,ingestion, and dermal contact (Jiao *et al*; 2015). The by-product of agricultural activities, urbanization and industrialization resulted in pollution and degradation of available water resources (Waziri *et al;* 2010).

Heavy metal effects on plants. It was observed that plants suffer oxidative strees that damages the cells and interfere with the ionic homeostasis when exposed to heavy metals (Singh, 2011; Manan *et al;* 2015).

 Heavy metal effects on man. Fe is an essential nutrient in the formation of erythrocytes and promotion of normal health in man but when its concentration exceeds certain levels, may cause intestinal corrosion leading to bleeding, vomiting, cardiovascular collapse, shock and possible death (Bello *et al;* 2014; Galadima and Garba, 2012). Mn is an essential nutrient for growthbut at concentration levels above 100ug/L are known to be toxic to man but less than 2ug/L are safe (Gruzewska *et al*; 2014). Excess of Ni inman leads to hypoglycemia, asthma, headache, and nausea, epidemiological symptoms such as cancer of the lungs (Kamran *et al;* 2013). It is observed that some heavy metals are safe and essential at some oxidative states while others are toxic and harmful eg Cr^{3+}facilitate metabolism of glucose and insulin. On the other hand, $Cr^{6+}$is toxic and present carcinogenic effects (Pandey *et al*, 2014; Tchouwou *et al;* 2012).

1.2 Statement of the Problem

The industrialization act of 1976 forced the doors open for the multiplication and establishment of small and medium scale industries in Nigeria alongside residential areas. This development gave birth to industrial clusters near the homes of the industrialists. The attendant problem was the ready contamination of the environment by the processing, harvested and waste products. Multiplication of small and medium scale industries lead to mismanagement of the generated wastes.

The available rivers in the areas had to serve as the only disposal outlet for the wastes which included solid particles, liquid effluents, and other contaminants which are disposed through   the back gates of these industries. The city of Aba, an industrial nerve centre of the South Eastern Nigeria emerged *'postwar-Japan'* of Igboland that had industrial clusters sited near the Aba River, which had to battle with environmental pollution and contamination problems (Adebisi and Fayemiwo, 2010).

Monitoring of the pollution load of the effluents from the agro-based industries becomes necessary from the above reasons. Also the determination of health risks implications using *Telferria occidentalis* and *Talirum triangulare* leaves planted at the Aba River side as an index will x – ray the harzards associated with the effluents carried into Aba River.

1.3 Aim and Objectives of the Study

The aim of this study is to assess the impact of discharged industrial effluents on the physicochemical and trace metal pollutants of Aba River, Abia State, Nigeria. The Specific objectives are to:

(i) Determine the physicochemical parameters of industrial effluents discharged from NBL, PZ and ABT into the Aba River.

(ii) Estimate the pollution status of Aba River using pollution index during two seasons (dry and rain).

(iii) Determine the distributions of heavy metal concentrations in water samples, plant samples of *Eichhnor crassipes* tissues and surface sediments collected from Aba River side, Abia Nigeria.

(iv) Determine the geo-accumulation Index of the heavy metals in the sediments at the Aba River.

(v) Determine the potential human health risks from heavy metals using edible green vegetables (*Telferria occidentalis and Talirum trianglare*) planted near Aba River.side.

1.4 Scope of the Study

This research covered the collection of water samples(effluents) from the designated sites:Up Stream Aba River (USAR), Petterson Zechonis (PZ) ,Nigerian Breweries Limited (NBL), Abattoir (ABT) and Down Stream Aba River (DSAR), whole plants of *Eichhnor crassipes* (leaf, stem and root), soil sediments, leaves of *Telferria occidentalis* and *Talirum trianglare* samples from Aba river side, on bi-monthly basis, ranging from June 2014 to May 2015; a period of twelve months. The agro-based industries were (PZ), (NBL) and the (ABT). The other sites of collection were USAR and DSAR which were reference points of least industrial/anthropological activities upstream and down stream points respectively of the river. The samples were analyzed quantitatively using Atomic Absorption Spectro-photometer (AAS) BUCK 206 and other physicochemical methods which include use of Ultra Violet spectrophotometer for determinations of Phosphates and Nitrates. Electrical conductivity, pH and Turbidity determined with

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respective probe and meters. Gravimetric techniques for Total suspended solids and Total dissolved solids.The parameters obtained were to serve as indicators for the determination of pollution index of the river.

Geo-accumulation index determination of Trace metals on soil sedimentsat respective stations were also carried out.Bio-concentration factor of the heavy metals on plant tissues of *Eichhnor crassipes* (leaves, stem and root) were determined. The determination of possible health risk implications following the consumption of the green vegetables(*Telferria occidentalis and Talinum trianglare* leaves) planted by the river side using target hazard quotient (THQ) were carried out from the results of the analyses.

1.5 Significance of the Study

The study will reveal the pollution status of Aba River through assessment studies of resident pollutants.

Sediment analyses will give information on the geo-accumulation of the trace elements in the environment ofAba River .

Bioconcentration analyses on plant tissues of*Eichhnor crassipes (*water hyacinth*)* will yieldinformation on the trace metal absorption by the respective tissues of the plant.

The potential health risks of these trace elements onthe consumers of *Telferria occidentalis and Talinum triangulare*will be assessed. The generated information on the environmental health of the area will give a betters risk management.

CHAPTER TWO

Literature Review

2.1 Anthropogenic degradation on the environment

The accumulation of heavy metals in aquatic and terrestrial habitats is dramatically on the rise, especially in the industrial countries of the world. The heavy metal contamination ends up infiltrating ecological niches such as soil which consequently reaches underground water and wells (Al-Musharafi *et al*; 2014). The occurrence of heavy metals in the ecosystem is associated with rapid industrial growth, overuse of synthetic agricultural chemicals, or pollution produced by humans (Orisakwe *et al*., 2012).

In Nigeria, most streams passing through cities have been converted into dump sites or latrines, with the consequent public health implications (Haruna and Solomon, 2015). Most industrial effluents contain non-biodegradable, toxic and hazardous wastes which prove high health risk (Ajiwe *et al.*, 1999).

Effluents from cottage industries, municipal sewage, agricultural and urban run-off are discharged into River Landzu bringing about considerable change in the water quality (Yisa and Jimo, 2010). Kasardi River receives heavy discharge of waste effluent from the nearby Taloja industrial belt of Mumbai. Toxic heavy metals like Cr, Cd, Ni, Zn,Cu, Pb and Fe in the river was observed with concentrations higher than the maximum permissible limits. These metals have created threat to the aquatic life and through bio magnifications entered the food chain thereby affecting the human beings (Lakhande *et al*., 2011).

Ground water with positive saturation index is encrusting, while ground water with negative saturation index is corrosive (Egereonu and Onuchukwu, 2000). Some pollutants classified as hazardous are strongly toxic even at low concentrations, inflammable, corrosive,

explosive or toxic (Momodu and Anyakora, 2010). Toxic chemicals from industrial waste are discharged into the water bodies, in this way underground and surface waters become contaminated by these toxics. Chemicals like pesticides, herbicides and fertilizers applied by farmers on the farmlands sip, and through the soil into the surface and ground water thereby polluting such water bodies (Fakayode, 2005). Oil spillage destroys farmlands, pollute drinkable water and cause drawbacks in fishing in coastal waters (Udofia, 2005; Atubi, 2015). Estuaries and inland water bodies are the major sources of drinking water in Nigeria that are often contaminated by the activities of the adjoining population and industrial establishments (Sangodoyin, 1995) .The disposal of wastes especially industrial effluents into near river bodies do alter the physical, chemical and biological nature of the receiving water bodies (Sangodayin, 1991). Indiscriminate duping of effluent into open water bodies is done with reckless abandonment, these pollutants are in concentrations above acceptable and permissible levels (Olanyinka *et al;* 2004). These pollutants end up in the rivers and streams (Ekiye *et al;* 2010; Josephine - Edward *et al;* 2016).

Degradation of water quality is most severe in four states; Lagos, Rivers, Kano and Kaduna that contain 80% of the Nations industries (Adekola *et al*., 2002; Adekunle and Eniola, 2008). Human activities and urbanization were recorded as factors that degrade water resources in Owerri Urban and environs (Egereonu and Onuchukwu, 2000). Recycling of sewage effluent are used for farming, and in public parks and industry. The dried sludge product is used as fertilizer in farms (Al-Musharafi *et al;* 2014). Run-off water from fertilized fields carries most of the fertilizer to river which provides nutrients that deplete the oxygen dissolved in the water, this causes the death of fish and other aquatic life, and phosphates in laundering detergents have the same effects (Montgomery, 1995; Egereonu et *al.,* 2003). Use of herbicides and insecticides in agricultural practices which later leaches

into sources of water body (rivers, lakes, streams, pond etc) pose a threat to the quality of water available in nature (Agrawal, 1999).

Trace metals were reported as accumulated in *Clarias gariepinus* exposed to sub-lethal levels of tannery effluent from Oke- Afa canal (Table 2.1) Lagos Nigeria by Gbem*et al*., (2001). Trace metals in varied water and sediment have been reported by some workers (Aderiola *et al*; 2009; Peters, 2007; Awofolu *et al.*, 2005; Tam and Wong, 2000). That demonstrated the degradation of the environment through natural and anthropogenic geo-accumulations.

GEO-ACCUMULATION INDEX (IgeoX)

In the determination of metal accumulation in sediments assessing anthropogenic load to pollution in respect to sediments . The geo-accumulation index (Igeo X) was utilized

This was calculated using the equation

$$\text{Igeo X} = \text{Log}_2 \left[\frac{C_n}{B_n}\right] \qquad (2.1)$$

Where:

C_n = Concentration of metal in sediment

B_n = Concentration of metal in reference environment and 1.5 accounts for possible variation in the background data to lithogenic effects.

Table 2.1: Heavy metals concentrations in surface water, sediments and organs of *clarias gariepinus* **from OKE-AFA canal.**

Site	Pb	Cr	Cd	Mn	Ni	Cu	Zn(mg/kg)
Liver	0.143	0.009	0.061	0.024	0.150	1.8700	6.851
Gut	0.037	0.003	0.014	0.009	0.002	0.7900	2.884
Gill	0.048	0.004	0.010	0.007	0.016	0.0392	0.563
Bone	0.012	0.001	0.002	0.005	0.006	0.1840	0.515
Flesh	0.006	0.001	0.007	0.004	0.008	0.1070	0.387
Sedi	0.095	0.127	0.076	0.092	0.400	1.5730	4.457
Water	0.039	0.120	0.043	0.069	0.033	0.0290	0.068
Total	0.054	0.022	0.033	0.032	0.088	0.6770	2.157

Source: Oluwu *et al*., (2010).

Urban and industrial waste discharged into the Lagos lagoon has had significant impact on the ecosystem (Sangodoyin, 1995). In Surulere, Lagos state, the analysis on heavy metal contamination of ground water showed that 97.96% contained one or more of the three heavy metals (Momodu and Anyakora, 2010). Samples analyzed contained detectable cadmium at levels above the maximum contaminant permissible level of 0.003mg/L (Orisakwe *et al*., 2006).These heavy metals get accumulated on living tissues of plants and animals by the mechanism of bio-accumulation and bio-transfer.

BIO-CONCENTRATION FACTOR

The enrichment factors are calculated to enable the calculation of the actual level of elemental contamination using the Earth-crust as the reference and Fe is normally used as the normalizing metal because it is the major sorbent phase for trace metals and is a quasi -conservative tracer of the natural metal -bearing phase.

$$\text{BCF} = \frac{Concentration\ of\ metal\ in\ sediment\ mg/kg}{Concentration\ of\ metal\ in\ external\ solution\ in\ mg/L} \qquad (2.2)$$

BIO-TRANSFER FACTOR

For heavy metals from sediment to vegetables. The transfer factor is the ratio of concentration of heavy metal in the plant to the concentration of the heavy metal in the soil sediment .The transfer factor for each heavy metal were computed based on the method described by Harrison and Chigawi(1989),according to the following formular

$$\text{BTF} = \frac{P_{S\ (mg/kg)}}{S_t(mg/kg)} \qquad \textbf{(2.3)}$$

Where:

Ps = is the plants metal content originating from the soil sediment.

St = is the total metal contents in the soil sediment.

The heavy metals discharged by industries, traffic, municipal wastes, hazardous waste sites, as well as from fertilizer for agricultural purposes and accidental oil spillages from tankers result in steady increased contamination of ground water(Atubi, 2015; Kent and Johnson, 1994; Berg *et al*; 1992; Osibanjo *et al;* 2011). Asa river in Ilorin, Kwara State,Nigeria were analyzed, in order to evaluate the impact of pollution on the aquatic biota. The

pH was found to range from 6.32-6.45 with mean temperature of 24.3^0C-25.8^0C, the other physicochemical parameters monitored exceeded the recommended levels for surface water (Osibanjo *et a; ,* 2011).

Table2.2: Physio-chemical parameters of effluents from Kaduna Textile industries.

Industry	Total Rounded Figures.
Temp (^0C)	30.00
Color	2,400.00
TDS	1,100.00
Free chlorine	0.50
Nitrate	4.00
Ammonia	1.00
Phosphate	1.00
TSS	400.00
Oil/Grease	7.00
BODs	300.00
COD	1,800.00
Sulphide	0.60

Source: (Butu and Iguisi, 2013). Values in mg/L except temperature.

Table 2.2 showed average values of effluent form five different textile companies that discharge into the Kaduna River. The river serves as the major sink and open sewer for

waste pollutants of most industrial effluents in the city The following heavy metals Ti, V, Mn, Dy, As, La, Sm, Yb, U, Cr, Zn, Fe, Co, Rb, Cs, Ba, Eu, Lu, Hf, Ta and Sb, were identified in the river sediments at various levels of concentrations (Esoka and Umaru,2006). The results of the analyses showed that heavy metals such as Mn, Fe, and Sb had sources that are traceable to human activities such as refuse dump,farmlands, public gutters. Effluents from various settlements in the catchment areas exhibited levels of concentrations more than those that had sources from rock weathered areas, therest sources were of low concentrations. The result further revealed that levels of concentrations of these heavy metals Mn, As, U, Cr, Fe, Co, Zn, Ba, and Sb were high above the WHO standards, for domestic use (Butu and Iguisi, 2013; Marchand *et al.*, 2006; Pekey, 2006; Rognemd and Feld, 1993; Cacci *et al*, 2003; Adekeola and Abolude, 2012).

River Kubani in Zaria Northern Nigeria receives agricultural runoff and municipal waste waters, even with these pollutants the river was utilized for drinking, fishing and irrigation. The concentration of six trace metals (Pb, Zn, Cu, Cr, Ni and Cd) in fish and sediments were investigated. Fracturation of trace metals in the river sediment, in *Clavias gariepinus* and *Oreachornis niloticus* samples were established. There was considerable risk to river water contamination based on the calculated individual trace metal average contamination factor (IACF) obtained for the river sediments from trace metal sequential extractions. The distribution and concentration of trace metals obtained in liver, gills, muscle and bone of fish (*C. gariepinus and O.niloticus*), showed that individuals consuming fish livers might be at risk .Trace metals in muscles of the fish were at low concentrations but from ingestion of toxic metals it rose to unacceptable concentrations.(Uzairu *et al.,* 2009; Meyer, 1997 and 1981; Morgan and Stumm (1991); USEPA,1983; FAO,1983; CCFAC, 2001).

In another study Galma river basin in Zaria was investigated to determine the pollution /relationship to the low fish catches in the river. Physico-chemical parameters of the water and sediments in the upstream area before the Zaria dam, where human and industrial population was low and in the downstream area after the dam where the human population were high and industries concentrated. Results showed that values of pH, total dissolved solids, total suspended solids, hardness, nitrates, and phosphates were higher in the upstream area while values for dissolved oxygen, transparency, and electrical conductivity were higher in the downstream. The physicochemical parameters of the river indicated favorable fish farming production and the river proved suitable for the Zaria municipal water works. Alkalinity and Phosphate were higher than the acceptable limits, this was attributed to the high residence time of the water in the upstream area because of the dam(Nnaji *et al*; 2010; Lee *et al*; 2003; Tukura *et al*; 2000; Davies *et al*; 1991). An attempt was made to quantify levels and distribution pattern of linden in the surface water, sediments and fish (*Chrysichltys furcatus and Tilapia Zilli*). Samples were collected from three stations (Ovwian, Ekakpamere and Ovu) of the Warri river in Nigeria. These were analyzed using High performance liquid chromatography to elucidate the distribution in various environmental compartments. Residual levels in the matrices ranged from below the detection limits(BDL) to 1.37ug/l in water, BDL to 12.66 ug/g dry weight(dw) in sediment, BDL to 16.67 ug/g (dw) in *Chrysichthys furcatus* and BDL to 0.15ug/g dw in *Tilapia Zilli.* These observed values were above the ecological bench marks (0.01ug/l) recommended by the Environmental Protection Agency of Nigerian (EPAN) and EuropeanUnion (EU). They were relatively higher than in previous studies on the Nigerian environment, this calls for regular monitoring of the Niger Delta water bodies (Ezemonye *et al;* 2008; Milby and Samuel.,1968; WHO1989and 1992, Schneider,

1979; Karim *et al;* 1985; Kidwell *et al;* 1995; De Lorenzo *et al;* 2002; Waliszewski *et al;* 2000; Leonard *et al;* 2001; Castilo *et al;* 2000).

Table 2.3 showed dominant pollutants, chemical oxygen demand, cod, total suspended solids, tss (total suspended solids), hardness, and ammonia nitrogen discovered in Kano River basin from three rivers that make up the river basin. The Kano river basin is the main water body in the state. It serves as the major source of water supply to the city and is the major sink for wastes from industrial estates within the state. The river has three main tributaries that make up the Kano river basin which are the Salanta, Chellewa and the Bompai Rivers. The river was found to be contaminated with the following pollutants in sufficient concentrations, high chemical oxygen demand, total solid, hardness, calcium carbonate and ammonia nitrogen, as the pollution index of the rivers were greater than 1.0 and of low water quality. These rivers were used extensively for domestic water supply, irrigation, fishing, and recreation but the quality of the water has been found to be unsuitable for these purposes (Middelkoop, 2000).

The pollution index is calculated

$$Pij = \frac{\sqrt{Max(Ci/li)^2 + Mean(Ci/lij)2}}{2} . \qquad (2.4)$$

The relative values   of Ci/lij is the expression of pollution index.i is the number of ith item of water quality and j is the number of jth item water used . Each value of (Cij) shows the relative pollution contributed by the single item. A value of 1. 0 is the critical value for each (Ci/lij). Values greater than 1.0 indicates that the water requires some special treatment before use for specific purpose.Horton,1965; Egereonu *et al*; (2012)

Table 2.3: Dominant pollutants in Kano River .

Rivers	Salanta	Bompai	Challawa	Total
COD	8557.4	1166.9	598.7	2600.00
TSS	16934.6	1458.0	1609.0	20,000.00
Hardness	12349.6	2506.8	1332.0	5,100.00
$CaCO_3$	5150.0	530.0	400.0	6,00.00
NH_3-N	5150.0	530.0	400.00	6,000.0

Source: Dan'Azumu and Bichi 2010. All values in (mg/L).

Heavy metal concentrations of River Gongolain Adamawa State, Nigeria was assessed using Atomic Absorption spectrophometer. The study revealed high concentrations of heavy metals in the sediment samples as compared to the water samples, this is because sediments are the major depository of metals, in some cases holding up to 99% of the total amount of metal present in the system. The concentration of Mg in both water and sediment samples was higher than those of the other elements. While the concentration of Mg, Zn, Pb and Cr are high during the dry season compared to those of Cu, Mn, and Cd. Most of the values fell within the allowable limits of the WHO/NAFDAC except for those of Pb, Cd, and Cr. This may be as a result of runoff from refuse dump around the area (Waziri and Ogugbuaja ,2010).

2.2: Metals in Surface Water

Table 2.4 showed total effluents from industries and households (in tones/yr) in Port Harcourt. Pollutants of concern listed in the table include oil and grease, nitrogen, phosphorus and biological oxygen demand. The major source of pollution in the state is the

petroleum industry. Other major contribution to this pollution includes Iron and steel, fertilizer and petrochemical plants. Another source of concern is the mixed disposal of municipal and industrial wastes, solid wastes in water bodies and poor sewerage system. Effluents from households are discharged into the open drain, gutters and water bodies (Ajao and Anurigwo, 2010).

Table: 2.4 Contaminants in Household and Industrial effluents in PortHarcourt (values in mg/L)

Parameters/Industry	Industries	Septic/Oil	Total Rounded
BODs	4374.00	8808.00	13,000.00
TSS	3533.00	6178.00	19,500.00
Oil	2313.00	2313.00	4,700.00
N	362.00	2966.00	3,300.00
P	836.00	360.00	1,200.00

Source: Anurigwo, (2010).

In a study in the Ogbia Local Government Area of Bayelsa State, Tilapia fish and sediment samples were collected and analyzed for heavy metals from the Kolo creeks of the state. following standard methods.Four metals Cu, Pb, Cd and Niwere recorded inincreasing order of mean concentrations as follows; Cu>Pb>Cd>Ni. Copper was significantly more abundant in the sediments, gills and muscle tissues than other elements with rangingconcentrationsfrom 10.73 to 16.61 mg/kg, 3.32 to 5.20 mg/kg and 2.48 to 4.89 mg/kg respectively. Except for Ni ,other elements were more abundant in the gills than other muscle tissues. The concentrations of these metals exceeded

the maximum concentration internationally allowable tolerance limits in drinking water, suggesting that Kolo creek water were polluted and hence calling for prompt interventions. (Biney and Becko, 1991; Bariweni *et al;* 2000; FEPA, 2003; Olowu *et al;* 2010 ; Addo *et al;* 2011).

Analytical studies on heavy metal pollution of river Oramiriukwa in Owerri, Imo State, revealed that manganese and lead had concentrations exceeding the WHO respective set limits for drinking water quality. Results of geo-chemical analysis show that surface and ground water in Owerri (Otamiri and Nworie rivers) have high concentrations of Nitrate and total dissolved solids (Egereonu and Ibe, 2003).Physiochemical analysis of the river Niger at Onitsha bank, Nigeria, revealed that the result when evaluated in the light of the WHO standard the water was found unsafe for human consumption. The characteristics of the river Niger and its tributaries which were determined by some of the industrial effluents discharged into the river have been reported to contain heavy metals (Egereonu, 2003).

Spatial and seasonal concentrations of heavy metals, Zn,Fe,Cu and Pb in water columns and the African Catfish *Clarians gariepirus* of River Niger were determined using Atomic Absorption Spectrophotometer. Mean concentrations of analyzed metals were significantly higher in catfish than water columns.(P>0.05). Bioaccumulation of heavy metals in catfish indicated that river Niger was experiencing impairment. Mean concentration of Zinc (3.988) and Cu (0.876) in catfish were within WHO and UNED/FEPA permissible limits in aquatic foods, but Fe (5.232) in cat fish far exceeded   their limits. Prolonged eating of catfish contaminated with these heavy metals may pose serious human health risks (Ajiwe *et al*., 1999 and 2002).

In 1981 Ajayi and Osibanjo wrote on the increased industrial activities   which led to pollution stress on surface waters both from industrial, agricultural and domestic sources in

Ibadan, Nigeria (Ajayi and Osibanjo, 1981).In 2011 Osibanjo and fellow researchers worked on the impact of industries on surface water quality using river Ona and Alaro in Ibadan to highlight the resultant health of the environment. In 2010 an analysis on water samples from two rivers (River Ora and River Alaero) in Oluyole industrial estate, Ibadan Nigeria (investigating the impact of industrial discharges on the surface water quality) the results obtained indicated that most of the parameters analyzed (pH, Total Hardness, chloride, Sulphate, Nitrate and dissolved solids) were more than the WHO set standards. However the levels of Nitrate, chloride, total Phosphorus, Total solids, Oil and Grease were higher in the industrial zone than those found in the upstream of both rivers (Osibanjo *et al*., 2011).

Some trace metals (Zn, Fe, Pb and Cu) in gills and tissues of *Clarias gariepinus* and *Oreochromis nilotcus* being most abundant fish species in water body from Ogbese River in Ondo state, Nigeria were investigated by Olawusi-Peters *et al*.,(2014).

Most industries in Oluyole industrial estate use large quantities of water but without efficient waste water treatment plants, but routinely discharge their wastes directly into the streams and rivers.The open and indiscriminate dumping of solid wastes in drainages and river-banks is one of the most critical problems facing the city of Ibadan (Ogedengbe and Akinbile, 2004).In the South Western, Nigeria city of Ibadan an assessment of surface water(SW), Sediment (SD) and Aquatic Fish (AF) from selected major rivers and Lagos Lagoon indicated high COD(72.8-8.292 mg/L), BOD(30.8-143 mg/L) and DO(1.04-6.68 mg/L) levels. Lead levels in the surface water for all the locations were found to have exceeded the WHO/NIS set standards for drinking water. Cadmium levels in sediments from Oni, Ona, Ogun and Ogunpa rivers also exceeded the Canadian Interim Sediment Quality guidelines (ISQG) of 0.60 mg/kg.

Fish from Lagos lagoon were most polluted with Pb, Cr, Ni, and Cu. The metal pollution index order was Pb>Cu>Co>Ni>Cr>Cd (Etim and Adie 2012). In 2013, a study carried out analyzed sediment samples from several locations within the Owena Multipurpose Dam and for trace metals such as Pb, Cd, Cu, Cr, Ni, Fe, Mn, and Zn, making use of Atomic Absorption Spectrophotometer methods. Samples of three types of fish were used (*Clarias gariepinus, Clarias anguillaries* and *Oreochromis niloticus*) collected from the dam, analyzed for those trace elements concentrations. Results of the heavy metals revealed significant seasonal variations,in most measured parameters. All metals monitored were detected in all the fish samples except Cadmium, that was not detected in the trunk of *Oreochromis niloticus*. These values were within the acceptable limit standards for human consumption, for now it does not constitute a health hazards but bioaccumulation of these trace metals could be lethal(Ipimorti and oshodi, 1993; Asaolu *et al.*, 1997; Adefemi *et al;* 2004; Obodo, 2004; Aiyesanmi, 2008; Oyahkilome *et al;* 2013). Warri Refining and petrochemical company limited, Ekpan Warri, generated effluent and discharged same into a natural receptor, River Ijana. Bioaccumulation of heavy metals over time in aquatic ecosystem has been reported by some scientists. The elevated level of heavy metal concentration in the Niger Delta aquatic environment as a result of industrial discharges from refining operations were elaborated on by Baird,(1999).

The study on Yobe River Nigeria in 2010 indicated the interrelationships between physiochemical water pollution indicators (Warizi and Ogugbuaja, 2010). A subsequent study was made using some water quality indices obtained from the Yobe River Nigeria in making prediction through annual projections in 2012. The objective of the research on River Ngada was to determine the degree of heavy metal contamination and the

extent to which the sediment quality of the river had deteriorated correlating data obtained from site analyses.

CORRELATION CO-EFFICIENT, R (SPEARMANNS)

$$R = 1-6\sum \frac{d^2}{n(n^2-1)} \qquad (2.5)$$

D = difference in each pair of ranks.

N = number of objects being ranked.

R = defined in such a way that when the ranks are in perfect agreement R equals +1 and when they are in perfect disagreement R equals -1.

Metals such as Cu, Zn, Co, Mn, Fe, Cr, Cd, As, Ni, and Pb in sediments were determined using Perkin-Elmer 300 Atomic Absorption Spectrophotometer. The metals increased with increasing sediment depth, indicating age long geo-accumulation of heavy metals from anthropogenic activities/sources. The study revealed further that the levels of all metals studied were higher than the WHO set standards on sediment guide line limits. This trend if continued unabated most likely the food web in this study environment might be at the risk of induced heavy metal contamination (Waziri *et al.*, 2012).

Kabwe in Zambia located about 150 kilometers north of the Nation's capital, Lusaka is in close proximity to the copper belt zone, Zambia's thriving industrial base with rich deposits of zinc and lead discovered there. Mining and smelting operations left the city poisoned by debilitating metals in the water with potential dangers of lead contamination. In one study the dispersal in soils of Lead, Cadmium, Copper, Chromium and Zinc extended over a 20km radius at levels much higher than those recommended by WHO was reported (Marie *et al;* 2004). A small water way runs from the mine to the center of the town used to carry waste

from the once active smelter. About 255,000 people were potentially affected with the Lead and Cadmium metals from the mines and processing plant (Leteinturier *et al*., 2001; Leteinturier *et al*., 2001; Dale, 2003; Pekey, 2006; Tembo *et al.*, 2006).

Sum gayit, Azerbaijan is a major soviet industrial center housing more than 40 factories that manufacture industrial and agricultural chemicals which include synthetic rubber, chlorine, Aluminum, detergents and pesticides,120.000 metric tons of harmful emissions were released into the air annually, the industry left the city heavily contaminated which left the city exposed to a combination of high-level occupational and environmental pollution problems. The untreated sewage and mercury-contaminated sludge from Chloro-alkali industries dumped haphazardly in an around water bodies. About 275,000 people are potentially effected with organic chemicals, oil, and heavy metal pollutants including mercury from petrochemical industries that are discharged into water bodies. Sumgayit had one of the highest morbidity rates during the Soviet Era and the legacy of illness and death persisted *(*Bickham *et al*; 2003; Andruchow *et al; 2006,*)

Shanxi province at the heart of China's enormous 3000,000 people affected by Organic Chemicals, Lead and Arsenics from industrial complexes and expanding coal provide about Two thirds of the Nation's energy. Linden has been identified as most polluted cities with residents claiming that they literally choke on the coal dust in the evenings. Hundreds of unregulated coal mines, steel factories and refineries have polluted indiscriminately the environment and surface water bodies. Population health risk due to dietary intake of heavy metals in the industrial area of Hulubao city China (Zhen *et al.,* 2007).

Tiarying in Anhu province is the largest Lead production bases in China with an average lead concentration in soil and water ten times Natural Health standard. About 140,000 people are affected by lead and heavy metals from the mining and processing industries

in the province. In the Zhejiang province in China is located Haux town, in southwestern Dongyang city. The Haux, industrial park, houses thirteen chemical estates Dongyang municipal government ordered the closure of these thirteen industries over the chemical pollution stemming from them. There were drums of chemicals abandoned inside the factory premises and untreated waste water covered with concrete slabs. Severe agricultural loses were reported in the area. About 53,000 people potentially affected with heavy metals and chemicals like tr-ifluralin released from the Huaxi industrial park (Blacksmith Institute, 2014).

Lan Zhou, the capital of Chinas Genus city is highly industrialized and includes the petrochemical manufacturing industries and oil refineries. Heavy industrial emission and the ore of coal, the primary fuel source are the main sources of pollution. Illegal industrial discharges are common and very frequent. The city of Lanshou is situated on a tributary of the Yellow River and is a major contributor to increasing pollution problem. About three million (3,000,000) people are potentially affected by Air pollution, chemical and heavy metal pollution ofthe Yellow river.

About 100,000 people in Nwanshan China are potentially affected by mercury emissions from 13 large scale mercury mines which accounts for 12% global anthropogenic emissions into the atmosphere. Mercury contamination extends throughout the city's air, surface water systems and soils. Concentrations in soil and water range from 24.3 to 348mg/kg about 16 to 232 times the maximum national standards for mercury contamination. More than 20,000 tons of mercury was produced in Wanshan between 1950's and 1990. In the Dominican republic city of Hains about 85,000 people are potentially affected by lead pollution with blood and soil levels several orders of magnitude above accepted limits. This contamination is caused by the past industrial operation of the nearby Metaloxa battery plant. A study in August 1997 with 146 children revealed levels of 32 µg/dl. The study

revealed that 28% of children required immediate treatment and that 5% had lead levels above 79 µg/dl (Zheng, *et al*., 2016).

In India, Mahad industrial estate 1,800 tons of hazardous sludge was accumulated in the estate. The industrial estate of Shri Mahesha chemicals Ltd. houses an abandoned Hydrochloric acid plant. The Raksha chemical estate housed toxic waste but also hazardous materials from a nearby industrial operation in Karnataka. Hazardous wastes were dumped illegally on the premises of defunct industries Raksha chemicals Limited and Shri Mahesh chemicals. About 300,000 people were potentially affected by these heavy metals and organic pollutants with severe contamination of the local soil and water ways (Maharashan Pollution Control Board, 2005).

A factory in Ranipet manufactured Sodium Chromate, Chromium salts and basic Chromium Sulphate, Tanning powder that was used locally in the Leather tanning process. The Ramil Nadu Pollution Control Board (TNPCB) estimates that about 1,500,000 tons of solid wastes accumulated over two decades of plant operation lie without check in an open yard (three to five meters high. It is estimated that about 3,500,000.00 people are potentially affected by pollutants of 38 Hexavalent Chromium, Azodyes used in the tanneries (TNPCB, 1996).

Sukinda valley in the state of Orissa contain 97% of India'schromite ore deposits and one of the largest open cast Chromite ore mines in the world. Twelve mine industries operate without any environmental management plans and over 30 million tons of waste rocks are spread over the surrounding areas and of the Brahmani river banks. Untreated water is discharged by the mines into river. The area is also flood-prone, resulting in further contamination of the water ways. Approximately 70% of the surface water and 60% of the drinking water contain tetravalent chromium at more than double natural and international

standards and levels of over 20 times the standards have been recorded (Singh *et al*; 2005). All the solid and liquid wastes are dumped into the Brahmani River, which is the only water source forthe residents. The air and soils are also heavily impacted. The town of Vapi marks the southern end of India's "Golden Corridor", a 400km belt of industrial cluster towns in Nandesari, Ankleshwar, and vapi regions. There are over 50 industrial estates in this region including more than 1,000 individual industries that extend over more than a thousand acres. Many of these are chemical manufacturing estates, producing petrochemicals, pesticides, pharmaceuticals, textiles, dyes, fertilizers, leather products, paint and chloro-alkali. The waste product discharges contain heavy metals, cyanides, pesticides, complex aromatic compounds (such as polychlorinated biphenyls, PCBs), and other toxics (Osibanjo *et a*l., 1994. Bhata, 2011). Vapi and the Ankleshwar areas were declared 'critically polluted" by the central pollution control Board of India (CPCB) in 1994. This followed a survey that revealed that there was no system in place to dispose of industrial waste at these estates. An analysis on the ground and surface waters which found exceedingly high levels of heavy metals including ones such as mercury, lead and zinc (Bhata, 2011).

Mercury in Vapi's ground and surface water was reported to be 96 times higher than WHO health standards. Effluents drain directly into the Damanga and Kolak Rivers. The downstream of the Kolak River is now unable to support much biological life, active dumping is also reported in progress at least in one industrial site. About 71,000 people are potentially affected with these pollutants of chemicals and heavy metals from these industrial estates (Agrawal, 1999b; Sharma *et al;* 2006). An assessment of the water quality of Mahanadi and its tributary rivers and streams, the Atharabanki river and Taldanda canal adjoining Paradip was analyzed using four parameters pH, dissolved oxygen, biological oxygen demand, and biological oxygen demand and fecal coli

form. The findings highlighted that the deterioration of the water quality in the river was due to industrial and human activities. Multivariate statistical technique approach were applied to prepare heavy metal pollution index (HPI) of the Subarnarrekha River flowing through the Indian state of Jharkhand which included studies like principal component analysis (PCA) Factor analysis and cluster analysis (CA) to identify the sources of heavy metals along the river basin(Kumar *et al.*, 2012).

Striking relationships were uncovered in the Mala Panew river sediment pollution by heavy metals highlighting that heavy metal concentrations at levels of similar heights are similar throughout the valley. The results indicated that sediment associated heavy metals accumulated within particular river reaches, and change downstream. The wide, natural reaches of the river valley have been serving as sinks for metal -associated sediments in the 20th century. The points are the secondary pollution source, whereas the narrow valley reaches in which flow regulation caused incision of the river channel serving mainly transition zones for the pollution sediments conveyed in the valley (Ciszewski *et al*., 2004).

Since 1922, adults and children in La Oroya, Peru-a mining town in Peruvian Andes and the site of a poly-metallic smeller were exposed to the toxic emission and industrial wastes from the plant. Currently 35,000 inhabitants of the area are potentially affected by the dangerously high lead levels found in children and adult blood. A survey conducted by the Peruvian ministry of health in 1999 revealed blood lead levels among the local children to be dangerously high, averaging about 33.6 µg/dl for children between the ages of 6 months 10years. Neurologists at local hospital stated that even new born babies have high blood lead levels inherited while still in the womb 5ug/dL.

Huancavelica is the largest mercury processing district in the western hemisphere and majority of the mines have been operating since the Spanish colonial era of 150 years ago. The Huancavelica mercury plant provided the mercury for silver extraction in the Potosi silver mines in the upper PERU (now Bolivia). About forty thousand (40,000) people are potentially affected. Sulphur dioxide concentration in the soil, water and vegetation exceeded the World Health Organization (WHO) standard by 10 times. Limited testing revealed Lead, Arsenic and Cadmium in soil and water contamination throughout the town (Bocio and Domingo, 2005; Petroczi and Naughton, 2009).

A 64 kilometer Matranza Riachuelo River flows from Buenos Aires into the Riadela Plata Estuary. The river basin is Argentina's worst environmental hotspot with more than 3,500 polluting tanneries, oil, chemical and metal plants, illicit sewage pipes and 42 open garbage dumpsites along the river. Up to 4.5 million people are potentially affected by Organic contamination, heavy metals such as lead, mercury, chromium and other industrial residues. Ninety percent of Bangladesh 270 registered tanneries are located in hazaribagh of just 62 acres of land. Many of these tanneries use none or semi mechanized systems and employ antiquated processing methods. These tanneries generate 7.7 million liters of liquid waste and 88 million tons of solid waste every day, 15,000 cubic meters of this untreated chemical wastes flows directly into the Buringanga River. About 500,000 people are potentially affected by metals including hexa-valent chromium and organic chemicals from the tanneries (Blacksmith Institute, 2014).

The Usolye and Sayansk chemical plants used mercury in the production of caustic soda and other cleaning agents from the early 1970's. The Usolye chemical plant admitted discharging 2.5 metric ton of metallic mercury into the Angara River each month. The mercury from the stream traveled several miles downstream and concentrated in the sediments of the Bratsk Reservoir, which was used for drinking water. The Angara River

then flowed into the Yenisei River which emptied into the Arctic Ocean. According to Yuri Udodor, head of Federal Committee on Ecology (FCE) in the state of Irkutsk, this region has the highest rate of discharge of metallic mercury into the environment in all of Siberia.The Bratsk Aluminum Plant has been polluting its surrounding to such a great degree that the town of Chikanorsky was evacuated in 2001 due to repeated health emergencies. The zone has been declared an ecological disaster zone. About 2.8 million people potentially affected with pollutants of mercury and other heavy metals and chemical from the Chemical and Aluminum plants.

Eichhornia crassipes (Water hyacinth) one of the aquatic plant species used for waste water treatment,has proved very efficient in removing pollutants like suspended solids,biological oxygen demand, organic matter, thus converting sewage effluents to relatively clean water. The plant holds promise as a natural water purifying agent. *Eichhornia crassipes* was tested for the removal of two important toxic heavy metals Cr and Zn from water under experimental conditions. The plants were found to perform extremely well in the removal of Cr and Zn from water solutions at low concentrations. It was capable of removing up to 100% of Zn and Cr during the 10 to 15 days incubation period (Gaherwar and Kulkarni, 2012).

The ability of water hyacinth to absorb and trans locate Cd, Pb, Zn, Cu and Ni, was studied in the Eth-Chung wetlands. These trace metals were found translocated in plant tissues. The ratio results were in order of Cu>Pb>Cd>Ni>Zn. Water hyacinth plants h ad a high bioaccumulation of these trace metals when grown in water environments with low concentrations of the five elements. or the roots 3 to 15 times higher than those of the shoots. The concentrations in the roots tissues were found to be in the order of Cu>Zn>Ni>Pb>Cd. Wetland plants (water Hyacinth) were used for the phyto-remediation of trace elements in natural and constructed wetlands. The absorption

capacity of the water hyacinth was tested in an experiment and was found to have performed exceedingly very well in the removal of Zn and Cr. The phyto accumulation of heavy metals Cr, and Zn by water Hyacinth was studied with revealing results indicating accumulation of Cr and Zn in shoots and roots increase with passage of time (Gaherwar and Kulkarni, 2012).

2.2.1 Metals in Vegetables

Anthropogenic and natural means have contributed to increasing concentrations of heavy metals in the environment.Mining and smelting activities contribute to the increasing levels of heavy metals in the environment and in the top layer of soil which consequently get to crops via their uptake.These are absorbed and accumulated by plants or get adsorbed on aerial surfaces of plants.Vegetable-growing areas, mostly situated near or by the river beds of industrial clusters have elevated concentrations of heavy metals in their tissues.These heavy metals affect human health (Kachenko and Singh, 2006; Agrawal *et al*; 2007).

Potential Human Health Risk Assessment

Target Hazard Quotient (THQ) is calculated using

$$THQ = \frac{EFr \ x \ EDtot \ x \ RFIMCs \ x \ 10^{-5}}{R_f \ D_O \ x \ BW_a \ x \ ATn} \quad (2.6)$$

Efr = exposure frequency (350days/yr)

Edtot = exposure duration total (30 years)

MCs = metal concentration (ug/g) in edible river food.

RfDo = Reference dose, oral (mg/kg/day)

Bwa = body weight adult (65kg)

ATn = Average time for non carcinogens(day)

NON CACINOGENIC RISK ASSESSMENT

The non-carcinogenic risk of some trace elements were predicted from their target hazard quotient (THQ) .

$$THQ = \frac{CDI}{R_f D} \qquad (2.7)$$

CD = Chronic Daily intake via ingestion .

RfD = Oral Reference Dose of the contaminant (mg/kg/day)

When the THQ values for the total exposure is above 1.0 it indicates that the estimated exposure is potentially a concern and of possible adverse health effects on human health.

Concentrations of the heavy metals Cd, Pb, Cu, ni, Mn, zn and Fe in soils of uranium-bearing dumps (Sudety Mts. Sw Poland, the dumps containing a high proportion of poly-metallic minerals), as well as in two tree species (*Salix caprea L., Betula pendula Roth.*) and a shrub (*Rubus idaeus L.*), which frequently occur in this area, in spite of being disturbed by mining activities in the past. The accumulation ratio values of heavy metals were calculated. It was revealed that all the species examined, especially the tree species, accumulated high concentrations of heavy metals, above the average values given for plants in literature (Wisłocka *et al*., 2006). The results of research on the content of iron in a sub-total form in the soils of metal industry areas and the content of iron in the grass growing in the test area. Research on the content of iron in soils and grasses was carried out in 2009-2010. The results indicated that the content of iron in soils taken from the premises of the metals industry plant was greater than in soils from areas not covered by direct anthropogenic pressure. The content of iron found in soils was from 1, 06% dw to 8, 13% dw with the content of 0, 6% dw in the control areas. The plants studied showed the

presence of iron at the level of 0,027-0,104% dwwith a content of 0,009% dw in the control areas. The accumulation of iron in the soils of the area under research is the result of a long term industrial activity (which started in 1876), based on the manufacture of rolling stock and steel elements (Fruzinska, 2011).

2.3 Sediment Contamination

Another issue of major environmental concern is the pollution of estuarine sediments with chemical contaminants. A wide variety of organic compounds and metals were discharged into the estuaries and rivers from industrial,agricultural, and urban sources. The contaminants were adsorbed onto suspended particles and eventually settled to the sediments. There they exert toxic effects on the benthic community that lives in the sediments and indirectlyaffect human health as well. Metals are generally not harmful toorganisms at concentrations normally found in estuarine and river sediments. Some, like Zinc, are essential for normal metabolism but are toxic above a critical threshold (Ikem *et al*., 2003; Swennen and Vander - Sluys 2002).

The impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent, to the urban areas. Surface sediment often exchanges with suspended materials, thereby affecting the release of metals to the overlying water (Pekey, 2006). Heavy metals from incoming tidal water and fresh water sources are rapidly removed from the water body and deposited onto the sediments. The top few centimeters of the sediments reflect the continuously changing present-day degree of contamination, whereas the bottom sediments record its history. Plants and animal species such as fishes are the inhabitants that cannot escape from the detrimental effects of these pollutants(Tam and Wong, 2000). The accumulation of three heavy metals; Cr, Cd and Pb in periwinkle (*Tympanotonus fuscatusvar radula*) shell

and soft tissues, water and sediment collected from four stations along Elechi Creek course were studied. Elechi Creek receives effluents discharges from heavily industrialized and highly populated settlements. Plants and organisms have been known to develop a protective defense against the deleterious effects of essential and inessential heavy metals and other xeno-biotic that produced generative changes like oxidative stress in the body. The plant, Water Hyacinth was selected because it could grow in sewage, polluted and waste water, there it absorbs and digest the pollutants thus converting sewage and waste waters, industrial effluents into relatively clean water. The bio-accumulation potentials of the toxic and heavy metals were removed from these environments by this plant, when used in phyto-purification process. Plants adaptability in polluted aquatic environment without production of toxic byproducts from the heavy metals Pb, Hg, Cu, Zn and Cr should be harnessed in heavy metal purification of the environment (Davies *et al*, 2006).

2.4 Sources of Water Pollution

The sources of water pollution may be divided into **point** and **non-point** sources. The point sources have well defined origin, such as the outlet from plant or from a municipal sewer line. Nonpoint sources refer to wide spread, seemingly insignificant amounts of contaminants which, cumulatively, threaten water quality. Point sources are easily identified. Examples: sewage treatment plants, large injection wells, certain industrial plants, livestock facilities, landfills, and others. They are regulated by the state water quality agency and the Environmental Protection Agency (EPA), and are issued a National Pollutant Discharge Elimination System (NPDES) permit when they meet regulations. Point sources established generations ago are often 'grandfathered' into compliance with some areas of the law. Hence, we find some point sources located in what would now be considered an inappropriate location. Examples: septic systems, road drainage, agricultural

runoff, lawn fertilizers, underground fuel storage tanks, and small businesses. Most are not required to have a permit. Individually, each may not be a serious threat, but together they may be a significant threat (Simons et *al;* 1993).

The **non- point** sources are difficult to control. Some non-point sources include run off from agricultural farmlands, construction sites, urban runoffs, land disposals, and resource extraction .The quality of ground water is subject to a number of chemical threats. There are many possible sources of chemical contamination and these include wastes from agricultural lands. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons, heavy metals, such as Cd, Pb, Hg, Zn, Fe, Cu, Cr, Mn and Ni etc, bacteria, particularly coli forms; and general municipal and industrial wastes (Simons *et al*., 1993). Millions of tons of fertilizers and pesticides (e.g., herbicides, insecticides, rodenticides, fungicides, and avicides) are used annually in Nigeria, Africa and in the United States for crop production. In addition to farmers, homeowners, business utilities (e.g., golf courses) and municipalities use these chemicals. A number of these pesticides and fertilizers (some highly toxic) have entered and contaminated ground water following normal, registered use. Some pesticides remain in soil and water for many months to many years (Zakrzewski, 1991). Another potential source of ground water contamination is animal wastes that percolate into the ground from farm feedlots. Feedlots should be properly sited and wastes should be removed at regular intervals (Ground water, 2002).

2.4.1 Urban Pollutants

The sources of urban pollutants to water are municipal sewage, run-off from streets and landfills and industrial effluents. Soil and sediments of estuaries and wetlands in Northwest of Persian Gulf are recently polluted with different heavy metals because of municipal and industrial wastewaters (Soleimani et *al;* 2009).

2.4.2 Elemental Pollutants

Trace elements are those elements that occur at very low concentrations to a few parts per million or less in a given system. Some of these are recognized as nutrients required for animal and plant life. Of these many are essential to life sustenance at low levels of concentrations but toxic at higher levels of concentrations. Some of these elements such as lead, or mercury, have toxicological and environmental significance and are among the most harmful of the elemental pollutants (Sabine and Wendy,2009; Walling *et al*., 2003).

2.4.3 Heavy Metals

Over the past two decades, the term "heavy metals" has been used increasingly in various publications and in legislation related to chemical hazards and the safe use of chemicals. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or eco-toxicity. There is also a tendency to assume that all so-called "heavy metals" have highly toxic or eco-toxic properties (John, 2002). Heavy metals, such as cadmium, copper, lead, chromium and mercury are major environmental pollutants, particularly in areas with high anthropogenic pressure. Heavy metal accumulation in soils is of concern in agricultural production due to the adverse effects on food safety and marketability, crop growth due to phyto-toxicity, and environmental health of soil organisms (Nagajyoti and Sreekanth, 2010). Heavy metals are

individual metals and metal compounds that can impact human health. These are all naturally occurring substances which are often present in the environment at low levels. In larger amounts, they can be dangerous (Sabine and Wendy, 2009). Due to the increasing pollution, concentrations of various chemical compounds have increased in the aquatic environments. Water contaminants have a high potential risk for the health of populations. Non-essential metals, such as mercury, lead and cadmium, are not known to play any metabolic functions and can be toxic for humans, even at very low concentrations (Annabi e*t al.,* 2013). Many sources contribute heavy metals to the soil from where they are trans-locatedinto different plant partsvia the root uptake.

Accumulation of heavy metals and their uptake by different plant parts depend on the concentrations of available heavy metals in the soil and form of metals. Positive metal ions are attracted to negative charges like hydroxyl groups[OH^-] and electron pairs of oxygen in the structure of clay minerals and to the carboxyl[CH_3COO^-] and phenolic groups of organic substances, while negative ions are attracted to positively charged hydrous oxides of Fe and Al. Some of the heavy metals that can occur in a variety of wastes include Zinc, copper, lead, chromium,mercury, silver and nickel, these can cause either acute or chronic effects on organisms in receiving waters. Heavy metals constitute a core group of aquatic pollutants via its bio-accumulative and non-biodegradable properties in food (Baharom andIshak,2015).The effects of the heavy metals depends on the dissolved ionic forms of the metal(Cu^{2+}or Zn^{2+}) than hydroxides $Cu(OH)_2$ or carbonate complexes (Welch,1992). The heavy metals include essential elements such as iron and Zinc, as well as toxic metals like cadmium and mercury. Copper is one of the most abundant trace metals and for almost all organisms. It is an essential micronutrient, excess of Cu in human body (more than 470 mg) is toxic, may cause hypertension, sporadic fever, uremia, coma. Copper also produces pathological changes in brain tissue. However,

Cu is an important cell component in several metallo enzymes. Lack of Cu causes anaemia,growth inhibition and blood circulation problem (Avenant-Oldewage and Marx, 2006). Iron, the main source of increased Fe concentrations in the aquatic environment is acid mine mineral, steel processing and industrial runoff .Iron is a key element of the globe. According to various sources, it constitutes 30-40% of the composition of the Earth. In its base state it constitutes about 90% of the Earth's core (Avenant-Oldewage and Marx, 2006). Iron (as Fe^{2+}) concentrations of 40 µg/L can be detected by taste in distilled water. It is chemically active, it is present in the form of oxides, hydroxides, sulfides, carbonates, silicates, sulfates, chlorides and cyanides. Metals in the form of pure elements do not have a negative impact on the environment because they are not soluble in water and weakly concentrated solutions of salts, acids and alkalis. Metal compounds are potentially toxic, because they can be dissolved, dissociated and can penetrate cell membranes of organisms (Fruzinska, 2011). Iron is present in food in two forms: as heme Fe (derived from fresh foods such as meat, chicken or fish (Zakrzewski, 1991) and as a non-heme Fe (present in inorganic forms of plant foods such as cereals, legumes, grains, nuts, and vegetables). The heme form of Fe is easily absorbed by the body, and absorption rates of 25% are obtainable from the content of animal flesh under normal conditions, while 40% absorption is achievable when the body is deficient in this element (Hernández-Castro *et al.*, 2015).

It is one of the essential mineral for humans and animals. Degree of absorption depends upon solubility and stability of compound. It is a component of blood cells and liveral metallo enzymes. However, more than 10 mg per kg of body weight causes rapid respiration and pulse rates, congestion of blood vessels, hypertension and drowsiness. It increases hazard of pathogenic organisms, as many of them require Fe for their growth. In well-water, iron concentrations below 0.3 mg/L were characterized as unnoticeable, whereas levels of 0.3–3 mg/L were found acceptable. Iron (Fe^{2+}) in drinking-water supplies, iron (II) salts are

unstable and are precipitated as insoluble iron (III) hydroxide, which settles out as a rust-coloured silt. Anaerobic ground waters may contain iron (II) at concentrations of up to several milligrams per liter without discoloration or turbidity in the water when directly pumped from a well, although turbidity and color may develop in piped systems at iron levels above 0.05–0.1 mg/L. Staining of laundry and plumbing may occur at concentrations above 0.3 mg/L. Iron also promotes undesirable bacterial growth ("iron bacteria") within a waterworks and distribution system, resulting in the deposition of a slimy coating on the piping. Some metalloids are significant water pollutants. Arsenic, Selenium, and Antimony are of particular interests (Ottawa, 1990., WHO, 1996).

Cadmium: The increasing amounts of heavy metals entering aquatic environments can result in high accumulation levels of these contaminants in fish and their consumers, which pose a serious risk to ecosystems and human health. The levels of muscle bioaccumulation of Hg, Cd, Zn, Cr, and Pb, generally may not exceed the safe levels for human consumption, the constant presence of heavy metals in concentrations near those limits considered safe for human consumption, is a reason for concern, and populations who constantly consume fish from polluted rivers should be warned (ArAntes *et al;* 2016).

Potentially toxic elements (PTE) such as Cd, Pb, Hg and As are widely dispersed in the environment naturally or anthropo-genically by agriculture and industrialization (Yongzhong *et al*; 2010). Pollutant cadmium in water may arise from industrial discharges and mining wastes. Cd is very toxic, 50 mg may cause vomiting, diarrhoea, abdominal pains, loss of consciousness. It takes 5–10 years for chronic Cd intoxication. During first phase, discoloration of teeth, loss of sense of smell, mouth dryness occurs. Afterwards it may cause decrease of red blood cells, impairment of bone marrow, lumber pains, disturbance in calcium metabolism, softening of bones, fractures, skeletal deformations, damage of kidney, hypertension, tumor formation, heart disease, impaired

reproductive function, genetic mutation, etc. Chemically , Cd and Zn are very similar and these two are found in water in the +2 oxidation state, Cd replaces Zn in enzymes that contain the latter metal. These two are common water and sediment pollutants in harbors surrounded with industrial installations. More than 100 ppm concentrations have been found in harbor sediments (Santos, 2013; Petroczi et *al*; 2009).

$$2\{CH_2O\} + SO_4^{2-} + H^+ \longrightarrow 2CO_2 + HS^- + 2H_2O \qquad (2.8)$$
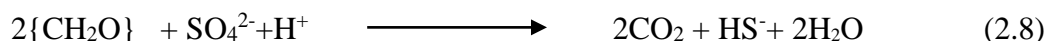
When water stagnates the anaerobic microbial reduction of sulphate produces sulphide,

$$CdCl + HS^{-1} \xrightarrow[\text{\textit{Chloro complex in sea water}}]{} CdS_s + H^+ + Cl^{-1} \qquad (2.9)$$

Zinc (Zn^{2+}) is essential element for humans, animal and plants. It is also an important cell component in several metallo enzymes. Infants need 3–5 mg/day, adult males 15 mg/day, pregnant and lactating females 20–25 mg /day. However, heavy doses of Zn salts (165 mg) for 26 days causes vomiting, renal damage, cramps, etc(Phiri *et al.*, 2005; Cha Khabi *et al.*,2008; Xudong *et al.*, 2015).

Lead: (Pb). More than 400 mg of lead in human body can cause brain damage, vomiting, loss of appetite, convulsions, uncoordinated body movements, helplessly amazed state, and coma. It is retained in liver, kidney, brain, muscle, soft tissues, and bones. Leads to high rate of miscarriages, affects skin, and respiratory system, damages kidney, liver and brain cells. Disturbs endocrine system, causes anaemia, and long term exposure may cause even death. Inorganic lead from many mining and industrial sources in water are in the +2 oxidation state such as Leaded gasoline which is a major source of atmospheric and terrestrial lead and most of which enters natural water systems. Lime stone bearing lead and galena (Pbs), contribute lead to natural water. Disused car batteries when

discarded contribute lead to the natural waters.   Old   water   pipe lines do contribute lead to the water body (Petroczi et *al*; 2009; Nesta et *al*; 2015).

Mercury: (Hg). This   heavy   metal   is found   as   trace component of many minerals. Mercury   is   ubiquitous around the globe   and occurs   in the environment in   various speciated   forms including   Hg0, inorganic   Hg(I)   and Hg(II)   species, and a series of organic forms   with   RHgX (especially MeHgX)   and Me_2Hg being the most common (Morrison *et al*; 2015).   Mercury is very toxic. Excess mercury in human body (more than 100 mg) may cause headache, abdominal pain, diarrhoea, destruction of haemoglobin, tremors, very bad effects on cerebral functions and central nervous system, paralysis, inactivates functional proteins, damage of renal tissues, hyper coagulability of blood, mimamata disease, and even death. It may cause impairment of vision and muscles and even coma. It disturbs reproductive and endocrine system. Also causes insomnia, memory loss, gum inflammation, loosening of teeth, loss of appetite, etc. Mercury can enter the air as a vapour, then drop both as dry and wet deposition, it settles to the bottom as sediment, get absorbed by phytoplankton, or be ingested by zooplankton and microorganisms, or small fishes and bigger fishes as a high stage of food chain as transformation process life. It is noted that as a result of anthropogenic sources, mercury deposition to aquatic systems has increased over the past century (Petroczi et *al.*, 2009). Mercury used as electrode in electrolytic chlorine gas generation, organic mercury are in fungicides, compounds used include   ethyl mercuric chloride, C_2H_5HgCl. The   alkyl   mercury resists degradation thereby   forming environmental problem. Mercury   enters the environment   from   a number of sources such as old batteries, broken thermometers, lawn fungicides, and pharmaceutical products. The unexpected high   concentration of mercury found in water   and   fish   tissues   are   from   formation   of   soluble   mono methyl mercury ion,CH_3Hg^+,   and   volatile   di-methyl mercury,$(CH_3)_2Hg$,   by   the   anaerobic   bacteria

methyl cobalamin in sediments found mostly in alkaline waters and in sediments with decaying matters.

$$HgCl_2 \xrightarrow{\text{methyl cobalamin}} CH_3HgCl + Cl^- \qquad (2.10)$$
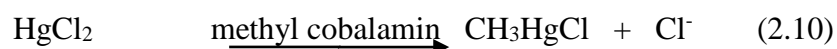
Arsenic (As) occurs in the Earths' crust at an average of 2-5ppm,it combines with phosphate minerals and enters into the environment along with some phosphorus compounds, such as lead arsenate,$Pb_3(AsO_4)_2$; sodium arsenate, Na_3AsO_3; and paris green,$Cu_3(AsO_3)_2$.

Arsenic contamination of ground water has occurred in various parts of the world, becoming a menace in the Ganga-Meghna-Brahmaputra basin (West Bengal and Assam in India and Bangladesh). Recently arsenic has been detected in Cachar and Karimganj districts of barak valley, Assam, bordering Bangladesh (Saikia and Gupta, 2012). Arsenic contamination in ground water is a major problem in more than 20 countries all over the world which includes Asian countries (Thailand, Taiwan, Mainland China, Vietnam and the Ganges Delta of Bangladesh and West Bengal, India). In North East India, arsenic has been detected in 21 districts of Assam, three districts of Tripura, six of Arunachal Pradesh, four of Manipur and two of Nagaland. This element enters the environment further through mine tailings from by-products of copper, gold, and lead refining which accumulates as waste materials. Humans are exposed to inorganic and organic arsenic through environmental, medicinal, and occupational exposures. Both inorganic and organic arsenic are present in food in different amounts. The high mobility and bioavailability of dissolved arsenic may be easily taken up by humans (Han *et al*; 1998). The compound is converted to more mobile and toxic, methyl derivatives by bacteria.

Asenic oxides, sulphides, and chlorides are used in a variety of industries, such as manufacture of colored glass, ceramics, and semi conductors.Particles of asenic are large

and attack the upper respiratory tract resulting in chronic coughs, bronchitic like symptoms. Asenic trioxide (As_2O_3) is a suspected humancarcinogen (Zakrzewski, 1992)

Tin: Organo-Tin compounds are potentially significant water pollutants because of their use in or near water bodies. Other applications include preservation of wood, leather paper, and textiles. Tributyl tin (TBT) compounds such as tributyl chloride and related compounds have been used as bactericidal, fungicidal and insecticidal in the environment The tributyl tin (TBT), used as biocides include the hydroxide, Naphthenate, bis-(tributhyltin) oxide, and tris-(tributhylstannyl) phosphate.

Manganese is essential for mammals but in concentration greater than100 ppm becomes toxic, and causes growth retardation, fever, sexual impotence, muscles fatigue, eye blindness (Protano *et al.*, 2014).

Chromium: There are four states in which the Cr ion is found: Cr^{2+}, Cr^{3+}, Cr^{5+} and Cr^{6+}. It is in the hexavalent form where Cr is allowed to cross biological membranes of aquatic organisms. Any chromium compound is toxic but haxavalent Cr greater than 70 mg is very toxic. It causes cancer, anuria, nephritis, gastrointestinal ulceration, perforation in partition of nose. It penetrates cell membrane and badly affects central nervous system. Causes respiratory trouble, lung tumors when inhaled. May cause complications during pregnancy, has adverse effects on aquatic life. Trace amount of Cr^{3+} is essential for normal glucose, protein and fat metabolism and hence it is an essential trace element in diet (Avenant-Oldewage and Marx, 2006).

Aquatic plants are well known in accumulating and in concentrating heavy metals. In a study with several physiological responses of aquatic vascular plant, *Nasturtium officinale* (water cress), which at elevated concentrations of copper, zinc and nickel were investigated it was found that *Nasturtium officinale* were able to accumulate both copper and zinc at

upper levels, but was able to accumulate to nickel at low levels. Results showed the presence of Hg, Cd, Zn, Cr, and Pb in all *P. corruscans* collected from the Paraopeba River. Moreover, the results indicated a variation between the heavy metals levels in the analyzed muscle, liver and spleen tissues, as also registered by Taweel *et al.,* (2013).

Nickel: More than 30 mg may cause changes in muscle, brain, lungs, liver, kidney and can also cause cancer, tremor, paralysis and even death (Kara, 2005).

Foam on lakes, rivers, and streams: Surface waters naturally contain dissolved organic compounds. Some of these are surface-active agents or surfactants as they are commonly called. Like soap, surfactants lessen the surface tension of water.Plants and algae inhabiting watersheds and surface waters produce many organic compounds, some of which have surfactant properties. Natural surfactants include carboxylic fatty acids derived from plant lipids and lignins from wood, to name a few. These are released into water and contribute to a large variety of soluble organic material collectively referred to as dissolved organic carbon (DOC). Surfactants are amphipathic molecules, that is, they contain both hydrophilic (water-attracting) and hydrophobic (water-repelling) components. The hydrophilic component can form bonds with water and competes with other water molecules as they attract one another. In this manner, surfactants reduce the overall attraction between water molecules, thus diminishing surface tension. The waste also includes detergents that create a mass of white foam in the river waters. All these chemicals are quite harmful or even fatally toxic to fishand other aquatic populations (Lakhande *et al*., 2011).

2.4.4 Solid Wastes in Water

Sources of solid wastes in water include households, industries, markets, schools, hospitals, hotels, natural sources, such as erosion andbush fires. The variety changes from location to location and is enormous and examples include paper, textiles,

plastics, rubber, leather, wood, charcoal, dirt, sand and stones, agricultural residues, animal refuse, metal scraps etc. In some cases these solid wastes are dumped directly into or close by the water body, which are leached into the stream by rain water. Finer and soluble wastes percolate through the soil to the ground water (Phiri *et al.,* 2005).

2.4.5 Chemicals and Industrial Wastes in Water

Industrialization, urbanization and population explosion have caused a high rate of waste generation in Nigeria. Chemical wastes in water include dissolve metals and their salts, acids, bases, and inorganic compounds, solvents and solutions, etc. The effluents from the industries may include fluorine, waste water, heavy metals, dyes, colorants, esters and alcohols. The pollution potential of these effluents depends on the nature of industries around the water body (Phiri *et al.,* 2005). These chemicals include nutrients comprising nitrates and phosphates derived from municipal waste waters which are inorganic nutrients that promote plant and algae growth, which have detrimental effects on rivers and lakes; algae can be toxic to cattle and spoil the taste of water (Esoka and Umaru, 2006). Waste liquids from textile industries due to dye stuff, sulphates, sulphides, copper, zinc lead, phenolics and wastes from the manufacture of pulp and paper contain sulphides, chlorides, lingocellulozic wastes, metercapenes and mercury etc. Canals are highly polluted by sewage disposals from hotels, hospitals, houses and municipal wastes. Of much concern are those wastes that resist bio-degradation but enter the aquatic and human systems. Heavy metals can affect the aquatic organisms as toxic substances in water and sediment or as a toxicant in the food chain (Zyadah and Abdel-Baky, 2000). It was discovered in a study that fish can bioaccumulate heavy metals from a polluted environment and could be a risk factor for accumulation of heavy metal in humans after a long time that would lead to dangerous diseases.

2.4.6 Chemicals and Petroleum Products

Underground and aboveground storage tanks are commonly used to store petroleum products and other chemical substances. Crude or refined oil products spill or accidental discharge or the disposal of used or exhausted lubricants and waste oils, have detrimental effects on the environment mostly on the aquatic life. These results mostly from equipment failure or during transfer operations as between ships and shore. Wherever spillage takes place, the more volatile components of the spill is evaporated into the atmosphere while the more dense parts sink to bottom of the sea and settle with the sea sediments. If an underground storage tank develops a leak, which commonly occurs as the tank ages and corrodes, its contents can migrate through the soil and reach the ground water (Ground water, 2002).

A correlation exists between exposures to oil spillage and development of health problems. A study examined the effects of environmental degradation on human health in nine selected oil communities in Delta State, Nigeria. Water samples collected from sea, rivers, streams, boreholes, and lagoons from Niger Delta contain benzo – pyrene at concentrations above WHO permissible limits. The consumption of fish, vegetables and other aquatic food from such locations are prone to bioaccumulation of the respective heavy metals with incidence of cancer risk being high (Atubi, 2015). Local communities within oil producing countries in Africa often face formidable environmental challenges that generate conflicts and concerns around exploitation, environmental impact, and health risks (Adekola *et al.*, 2016). In Nigeria, palm oilmill effluents are discharged directly and untreated into the nearby agricultural lands and surface waters in its raw form especially by small scale processors. This may also contribute significantly to the pollution load of the river and affect the quality of the river for other uses (Josephine Edwards *et al.,* 2016).

2.4.7: Agricultural Debris in Water

These arise from three sources, thus animal rearing practices, fishing and farming. In farming, herbicides, fungicides, insecticides and fertilizers are made use of and are subsequently transported to the surface and ground water. These constitute a treat to aquatic life and all forms of life that depend on water. Contamination by pesticides, phosphates and insecticides that drain off to streams and rivers by runoff or leached into the ground water are toxic to man. The Kepone group of insecticides are potential hazards encompassing a variety of chemicals such as morex, aldrin, dieldrin and heptachlor, when drained off to streams and rivers by runoff or leached into the ground water, poses potential poisons to aquatic life. Abnormalities in cell growth, many liver lesions and cancer have been attributed to contamination of water by kepone. These insecticides on reaching the coastal water result in death of fishes. The following chemicals above 0.1ppm in water can be lethal to some fish, such chemicals as DDT, endrin, heptachlor, parathion, malathion. Plants growing in metal-polluted sites exhibit altered metabolism, growth reduction, lower biomass production and metal accumulation. Various physiological and biochemical processes in plants are affected by metals (Nagajyoti and Sreekanth, 2010).

Other debris in water includes phenols, tannins, nitrates, dioxins, sulphates, phosphates and cyanides. Dioxin is lethal to man. Polar compounds are believed to penetrate cell membranes through protein filaments; while non-polar compounds enter through lipid matrix. Electrolytes (HCl, H_2SO_4, NH_4Cl, $NaSO_4$) enter mainly in the non-ionized form and thus the pH of the solution applied to the skin affects the permeability.

Some chemicals found in the environment such as carbon Tetrachloride (CCl_4), and organophosphate insecticides found in water and the environ penetrate the skin

(stratum corneum). Organo- phosphate insecticides are organic compounds that contain phosphorus ,most of which are organic derivatives of ortho-phosphoric acid. Some of the organo-phosphate insecticides are esters of ortho-phosphoric acid. Toxicity of ortho-phosphate insecticides vary, as little as 120.0 mg has been known to kill a man, while 20.0 mg has killed a child. Most accidental poisoning had been through the skin. It is a systematic poison; that is one that is transported through the body to sites remote from its entry site. The organo-phosphate compounds produced as industrial poisons are deadly in minute quantities (known as nerve gases). Tri methyl phosphate is moderate in toxicity when taken in, but Tri-ethyl phosphate $(C_2H_5O)_3PO$, damages nerves and inhibits acetylcholinesterase. tri-o-cresylphosphate in the water body is noxiously toxic and exposure causes degradation of the neurons in the body's central and peripheral nervous system with early symptoms of vomiting, diarrhea and nausea which leads to partial or complete paralysis. The carbonates are pesticides widely used as insecticides on lawns or gardens. Carbo-furan has a high water solubility and acts as plant systemic insecticide which when taken up by plant roots and leaves, the insects are poisoned by the plant material on which they feed. It has a strong tendency to bind to soil and sediments. They are toxic to animals as they inhibit the formation of actyl cholinesterase without undergoing bio−transformation first and are taken as direct inhibitors. Polychlorinated Bi-phenyls (PCB) have been found world over in water, sediments, bird and fish tissues. The dumping of PCBs' on the rivers and riversides, being virtually insoluble, dense, hydrophobic materials accumulate in the rivers' sediments, causing serious concern as a result of their bio-accumulation in fish. Heavy metals are normal constituents of marine environment that occur as a result of pollution principally due to the discharge of untreated wastes into rivers by many industries (Wang *et al*., 2010.). Bioaccumulation of heavy metals

in tissues of marine organisms has been identified as an indirect measure of the abundance and availability of metals in the marine environment (Babatunde *et al;* 2012).

The concern for the environment in and around the Aba River is neither new nor is it isolated in the study of science and environment. In some of the studies the actions of the host community to the environment and workers in it sparked off such, while in some others as this, observations of the local scenario prompted the research. In this research physical and physicochemical parameters, heavy metals, sediment and plant tissues (leaf, stem and root) in the water body, were investigated. The environment have never been cared for though it sheltered all that is alive on the planet Earth and have suffered from anthropogenic activities of man which tends to destroy or sacrifice the environment on our table of uncontrolled industrialization, urbanization and plan-less economy of today. The determination of traces of heavy metals in the natural waters, plant parts and sediments plays important role in the aquatic environment hence giving vital information on the pollution status of the river.

2.4.8 Natural Sources.

Some substances found naturally in rocks or soils, such as iron, manganese, arsenic, chlorides, fluorides, sulfates, or radio-nuclides, can become dissolved in ground water. Other naturally occurring substances, such as decaying organic matter, can move in ground water as particles (Ground water, 2002). The global environmental outlook report indicates that about 30% of the world's population lack access to safe drinking water (Haruna and Solomon, 2015).

The Aba river has for some time now had increased anthropogenic activities, ranging from industrial to agricultural based outfits. Pollutants are known to accumulate in

the sediments and marine organisms living in such domain transferred to man at the apex of the food chain. Public health concern in respect of the pollutants high potential risk draws attention to the environmental pollution status.

2.5 Gap in Literature.

ln literature heavy metal determinations in *Eichhnor crassipes* (water hyacinth) and some green vegetables are abound in research but little has been put up in this regard relating to *Telferria occidentals* (fluted pumpkin) and *Talinum trianglare(*water leaf*)* as bio indicators or waste water cleansers. In the public health risk determinations these two green leaves have not been brought to light on the possible bio-accumulative effects of the heavy metals from the consumption of these leaves. Again the heavy metal geo-accumulation status of Aba River sediment have not been sufficiently cited.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The reagents used include: Standard ferrous ammonium sulphate (Anala reagent), Fe $(NH_3)_4SO_4$; potassium hepta-oxochromate (iv), K_2CrO_7(AR); Ferroin indicator solution, Mercury (ll) sulphate (AR), Ag-H_2SO_4 solution, iron powder, zinc metal, nickel metal, cadmium metal, lead metal. copper metal, potassium permanganate salt (gpr), silver nitrate (gpr) solution, hydroxyl ammonium sulphate, potassium chromate solution, Conc Hydrochloric acid (British Drug House), Conc Sulphoric acid (BDH), Conc nitric acid (BDH), Conc hypochlorus acid (BDH), Sodium thiosulphate (General Purpose Reagent), Starch solution, Phenol di-sulphonic acid, Sodium hydroxide (BDH), Conc ammonia (BDH), solochrome black T indicator, ethylene diamine tetra acetic acid (EDTA) solution, bromocresol green.

Apparatus: (i) Incubator bottles (Broun). 125, 250 or 300ml capacity with ground glass.

(ii) Air cooled incubator. This is thermostatically controlled at 20ºC and from where all lights was excluded to prevent formation of dissolved oxygen (DO) by algae in the sample.

Reflux apparatus consisting 250, 300 and 500ml erlenmeyer flasks with quick fit ground glass joints/necks fitted with liebig condensers. Hot plate for heating.

3.1.1 Location of Study Area

Aba River is a tributary of Imo River and is the major river that passes through Aba town and flows through the Azumini River to the Atlantic Ocean. It is located on Longitude 7º 19'E to 23'E and latitude 5º10'N in Aba, Abia State, Nigeria. The river runs

through the industrial layout of the commercial city of Aba with industrial and domestic effluents, hotels, eating houses, wastes and abattoir washings, dotted along the river side being discharged directly into the river. The area has a land mass of 198km^2. The commercial and industrial city of Aba is located in close proximity to the river. The areas of interest in this research were stations chosen along the course of the river that channels their wastes into the river(fig.1.1).

The rainfallin this area is about 2285 mm and rain falls from March to November with a relative humidityof 80% and a meantemperature of 27°C (Ogu and Ogwo, 2014). Most parts of the area are flooded during the rainy season due to poor drainage system and construction. The dry season in the area runs from November to March and is characterized by dry, cold and windy weather, with little or no rainfall. The temperature is highest in December and lowest in February due to the Harmattan. The study area falls within the humid tropical rainforest climate maps.

Fig 3.1 Map of Nigeria

Fig 3.2   Loction Map of Studty Area.

Table 3.2: The GPS Coordinates of the Different Sampling Stations

Sampling station	Latitude	Longitude
Up Stream (USAR)	$05^0 07^i 693^{ii}$N	$007^0 22^i 668^i$E
Petterson Zechonis (PZ)	$05^0 16^i 472^{ii}$N	$007^0 22^i 749^i$E
Nigerian Breweries (NBL)	$05^0 16^i 55^{ii}$N	$007^0 22^i 43^{ii}$E
Abattoir (ABT)	$05^0 72^i 62^{ii}$N	$007^0 22^i 43^{ii}$E
Downstream (DSAR)	$05^0 72^i 75^i$N	$007^0 22^i 44^{ii}$E

Source: Aba Municipal Local Government Area

Sample   Stations

Guided by a geographical positioning system(GPS),sampling sites were systematically located (Table1.1) and were selected due to their easy accessibility and representativeness of the affected part of the Aba River (Table1.1). The site at the Upstream (USAR) was chosen as   the reference   point with minimal recorded anthropogenic activity taking place at that site. A stretch of about 2.4 Kilometers of the river   channel   was examined for this study from the discharge points. The stations chosen for the study along the river course were USAR, PZ, NBL, ABT and DSAR, a distance of about ½ Kilometers from each station were analyzed.

3. 2 Sampling

At each site of sampling to evaluate the environmental impact of the effluents on the river, sediments samples, whole plant   and water samples collected were taken to the laboratory for analyses. On the days of sampling, samples were taken from sations starting from   the hours of 10am to 3.00pm. Triplicate samples were at each site pulled together to form an aggregate sample for the case of sediments   and   plant samples. Bi-monthly collection of samples were carried out for the period of this study June 2014 to may 2015 incusive.

3. 3 Water Samples

Water samples were collected in pre-cleaned plastic containers   labeled in respect of the sites and stored in an ice chest and transported to the laboratory. The samples for physicochemical analyses were fixed by the   addition of 10cm^3 concentrated hydrochloric acid that prevents atmospheric oxidation. Triplicate samples were collected from far side, mid stream and near sides of the river at each of the designated sites. The collection at each site were pulled   together to form   an   aggregate   sample. A

collection depth of 24 inches was observed at each sampling site. The samples were kept in an ice chest while in transit to the laboratory.

3.4 Whole Plant Samples

The plant samples were harvested as whole plants (leaf, stem and root) from the five sites along the course of Aba River. They were washed to remove sand, debris and some organic matters that may cling to the plant bodies. The plant samples were taken to the crop science laboratory of the Federal University of Technology Owerri , for identification and preservation. Three different plant species were collected at each site, which are Eichhnor*crassipes* (water hyacinth), *Telferia occidentalis* (Fluted pumpkin) and *Tallinum triangulare* (Water leaf)**.** The plant tissues were cut and separated into plant parts (leaf , stem and root) and packaged accordingly in black polythene bags for respective plant part analyses.

3.5. Sediment Sampling for Chemical Analysis

Five sampling stations were established along the Aba River course in order to give a comprehensive idea of overall quality of the river sediments. The samples were taken on a bi- monthly interval visit to the stations for a period of twelve months (June 2014 - May 2015). The stations include; Upstream Aba River (USAR) the reference station with least visible industrial and anthropogenic activities, Petterson Zechonis (PZ), Nigerian Breweries (NBL), Abattoir (ABT) and Downstream Aba River (DSAR) with a distance of ½ kilometers from each station were analyzed.

At each sampling station, samples were collected from the bottom sediments using ekman grab techniques. Eight sample replications were collected from each station homogenized in large plastic containers to form compositerepresentative sample for the site. The samples were taken to the laboratory in an ice chest, air dried for seven days

in the open laboratory at $30^{\circ}C$, further dried in the rotary oven (digested with a mixture of concentrated hydrogen peroxide H_2O_2 and nitric acid HNO_3.) and moisture extractor at $105^{0}C$. The samples were ground, sieved with 2ụm mesh size. 1.0g of the fine dried grains were preserved in the refrigerator for subsequent analysis of the heavy metals,Fe,Ni, Cr, Cu, Cd, Zn,Mn and Pb in the samples. The concentrations of these heavy metals were determined in mg/kg using the Atomic Absorption Spectrophotometer (Umar and Opaluwa, 2010).

3.6 Trace Metal Analyses

3.6.1 Digestion of Water Sample (Trace Metal Analysis)

Whatman No1 filter paper was used to filter $100cm^{3}$ of the water sample into a 250ml conical flask. $10cm^{3}$concentrated nitric acid was added followed by $10cm^{3}$ of 50% HCl. The sample was digested on a hot plate at $115^{0}C$ with anti pumps for two hours in a fume cup board, on cooling the water samples were quantitatively transferred to a $100cm^{3}$volumetric flask, labeled and dated.

Distilled de-ionized water was used to make up to the mark before determinations of concentrations of trace metals were made, by the use of Buck 206,Atomic Absorption Spectrophotometer (Ademorati,1996,AOAC, 1980).

3.6.2 Digestion of Sediment Sample (Trace Metal Analysis)

Dried,ground, and sieved sample 1.0g was weighed into a $100.0cm^{3}$ beaker and digested with a 20 cm^{3} acid combination method of HNO_3 and $HClO_4$ in a ratio of 1:4,was added to the sample, covered with a watch glass. In the fume cupboard on a hotplate, the digestion was carried out by heating to near dryness. The digest was allowed to cool,leached into a 250 cm^{3} beaker with 5 cm^{3} of 20% (v/v) HNO_3. The

resulting solution was filtered using an acid-washed filter paper (whatman No.42), the filtrate was made up to 100 cm³ with distilled de-ionized water in a 100 cm³ volumetric flask.

3.6.3 Blank Preparation (Sediment).

A blank was prepared similarly as described for the sample with the exclusion of the sediment sample.

3.7 Digestion of plant parts (trace metal analysis).

The plant parts were first air dried in the laboratory bench tops for seven days. To get rid of moisture,they were dried in the oven (moisture extractor) at 105^0C. These were cut into small sizes and ground to near powder using pestle and mortar, sieved to collect >2ųm sieve (mesh) size, and to remove matters not properly ground and coarse particles. 5.0g sample were kept for subsequent analyses. The samples were weighed into pre-weighed dry crucible. The crucibles and samples were covered, placed in a muffle furnace, the temperature gradually increased to 500^0C for about two hours. Samples were removed, allowed to cool to room temperature in a desicator and stored at 4 to 5^0C. The ashed samples 1.0g each placed in acid washed glass beaker, digested by the addition of 10 cm³ of 0.25M HNO_3 was heated to near dryness, followed by the addition of a second 10 cm³ of 0.25M HNO_3 and $3cm^3$ of concentrated $HClO_4$. This mixture was heated in the fume cupboard. Sample solutions were obtained by leaching the residues with 4.0 cm³ of 2M HCl, diluted to 100 cm³ with distilled de-ionized water, labeled and dated.

3.7.1 Sample Blanks (Trace metals)

Sample blanks were prepared as per respective sample preparations with non-inclusion of the sample (salt or metal). The prepared blank was stored in plastic containers and labeled accordingly for the determinations of metal concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn respectively .

3.8. Preparation of stock solution (trace metal analysis)

Stock solutions of metals were prepared by dissolving one gram of the metal compound or its salt in different amount of aliquots of acid mixture and diluted to 1litre with de-ionized water. Standard solutions prepared from stock solution were usually of 1000 ppm. The stock solutions were stored in plastic bottles, dated and labeled accordingly (AOAC,1980) .

3.9 Determination of trace elements using Atomic Absorption Spectrophotometer (AAS, BUCK Scientific 206)

Calibration of Instrument

The instrument was first calibrated before determinations of heavy metal concentrations were made with it. Calibration curves were made using the working standard solutions for the respective elements. The concentrations of the trace metals were determined using the Atomic Absorption Spectrophotometer (AAS). The instrument was switched on and allowed to run for 10 minutes to equilibrate before the tests were commenced. The working conditions of the instrument were ascertained at this point , analysis made optimal, confirmed in respect of each element being analyzed.

Among the conditions include lamp current, correct band pass, flame type, resonance wavelength and fuel flow rate. With the working standard solutions aspirated into the

flame with respective cathode lamps for each metal correctly in position, the corresponding absorbance for each concentration recorded. The calibration curve for each metal was thereby obtained. A blank test was ran immediately after each metal determination by carrying out the same processes with the omission of the sample. When the sample was aspirated into the flame, the sample was reduced to free atoms that was able to absorb resonance radiation from its hallow cathode lamp.

The amount of light absorbed was related to the concentration of the analyte as given by Beer-Lamberts' Law.

$$A \quad = \quad Ebc \qquad\qquad\qquad (3.1)$$

Where,

A = absorbance;   E =molar absorptivity; C = Concentration of the analyte

The corresponding concentrations of the metals in mg/L obtained versus the results of the absorbance for the working standard solution for metal were plotted. Sample concentrations were obtained from the standard graph for respective element.

Determination of manganesse, iron, lead, cadmium, zinc, chromium and copper by atomic absorption spectrophotometer.

Standard metal solution : A series of standard metal solutions were prepared by dilution of the following stock metal solution with water containing $1.5cm^3$ conc HNO_3.

i.   Manganese: 3.076g manganese sulphate ($MnSO_4.H_2O$) was dissolved in 200 cm^3 distilled water,1.00 cm^3 =1.00mg Mn

ii.   Lead : 1.598g lead nitrate was dissolved in about 200 cm^3 of distilled water and 1.5 cm^{3}ml of Conc HNO$_3$ added, mixed and made up to 1000 cm^3 with distilled water.1.0 cm^3= 1.0mg Pb

iii.   Cadmium: 1.00g cadmium metal was dissolved in a minimum volume of 1M HNO$_3$.1.00 cm^3=1.00mgCd

iv.   Nickel : 1.273 nickel oxide(NiO)was dissolved in a minimum volume of 10%(v/v)HCl and then diluted with 1000 cm^3 of distilled water,1.00 cm^3= 1.00 mg Ni

v.   Zinc: 1.00g zinc metal was dissolved in 20 cm^{3}ml 1M HCl and diluted with 1000 cm^3 of distilled water,1.00 cm^3 =1.0mgZn

vi.   Iron: 5.0503g of iron (ii)Ammonium Sulphate, Fe(NH$_4$)$_2$(SO$_4$), was dissolved in distilled water and then made up to 1litre with distilled water[1ml = 1mgFe.

vii.   Chromium: 2.8285g of anhydrous K$_2$Cr$_2$O$_7$ was dissolved in distilled water and made up to 1litre.1 cm^3= 1mgCr.

viii.   Copper metal: 1.0gwas dissolved in 50 cm^3 of 5M HNO$_3$ acid. The solution was diluted to 1liter with de-ionized water in a 1dm^3 volumetric flask.1 cm^3=1mg Cu

Standardization: At least five concentrations of each stock standard metal solution were prepared by diluting aliquots of the stock solution to 100 cm^3.Each standard was aspirated in turn into the flame and the absorbance recorded. A calibration curve for each element to be determined was plotted on a linear graph paper, the absorbance of standards versus their concentrations in mg/L.

Analysis of samples : The nebulizer was rinsed by aspirating water containing 1.5 cm^3 Conc HNO$_3$.The instrument was zeroed by aspirating the blank. The samples werethen atomizedand the absorbance recorded.

Calculation : The concentration of each metal ion in mg/L was calculated by referring to the appropriate calibration curve(this was obtained automatically from an attached software computer system).

3.10: Determination of Temperature

This was carried in-situ at all the sites. The apparatus used for measuring temperature was the mercury in glass centigrade thermometer. The thermometer was placed vertically and the bulb containing the mercury was immersed in the water/effluent. This was allowed to stand still for about 2minutesfor the reading to be steady. This was taken and noted in^{0}C. The readings were taken to the nearest half degree (Ademorati, 1996; APHA, 1998).

3.11: Determination of Chloride in Water

This anion was determined by titration of the water sample with silver nitrate solution procedure. To 100 cm^3 of the water sample was added 5% solution of potassium chromate (1.0 cm^3) and was titrated with 0.1M silver nitrate solution to the first appearance of a buffer color(AOAC,2002);(APHA ,1998).

Calculation:

$$\text{Chloride content (mg/l)} = \frac{V x M x E x 1000}{V1} \qquad (3.2)$$

Where:

V=volume, M= Molarity, E=Equivalent weight of chloride, V_1 = volume ofsample used.

3.12: Determination of pH

Thiswas taken in-situ at all the sites using Hannamicroprocessor pHmeter(HANNA 211). The electrode was rinsed with distilled water and wiped dry. The pH electrode was rinsed in a beaker containing a little of sample. Sufficient volume of sample was poured into the beaker to allow the tips of the electrode to be immersed to a depth of about 2ml. The electrode was kept about 1ml from the sides of the beaker and the bottom of the beaker. The temperature adjustment dial was adjusted accordingly.

3.13: Determination of electrical conductivity

This was taken in-situ at all the sites using Hanna microprocessor Electrical Conductivity meter(HANNA EC 215). The conductivity cell was rinsed with at least three portions of the sample. The temperature of the sample was then adjusted to 26.01ºC and allowed to stabilize to temperature of the river . The conductivity cell containing the electrodes was immersed in sufficient volume of the sample. The conductivity meter was turned on and the conductivity of the sample recorded (APHA, 1998).

Calculation,

First, the cell constant, K (cm^{-1}) was calculated.

$$K = R \text{ (kCl) x } C_t \text{ cm} \qquad\qquad (3.3)$$

where:

R (kCl) isthe measured resistance of the standard potassium chloride solution.

C_t = conductivity ($uScm^{-1}$) of thestandard potassium chloride solution

when t $= 25^0C$.

C$_s$ =   conductivity of the sample which is given

$$C_s = \frac{K}{Rs} = \frac{R(KCl)xCt}{Rs}. \qquad \text{Siemen per meter(S/M)} \qquad (3.4)$$

Where

R$_s$ =   measured   resistance of the water sample.

3.14 Biological Oxygen Demand

Preparation of Dilution Water

The distilled water is stored in a large aspirator with cotton wool plugged to at the mouth as to permit saturation of sufficient dissolved oxygen, (DO). The water samples were pre-treated with 0.5M acid or 1.0M   alkali   to about pH 7. Several dilutions of the prepared sample was done so as to obtain adequate drop in oxygen content, for the river water.

$10cm^3$ of sample were measured into the BOD bottles in duplicates with the aid of large tip volumetric pipette. The   stoppers were filled without leaving air bubbles.

Determinations of the initial DO on the undiluted sample were obtained by taking readings with probe inserted   into the water samples (YSI Model 58). The blank were incubated with the other five diluted samples.

The general equation for the determination of a BOD value is.

$$BOD \text{ (mg/l)} = \frac{D_o - D_d}{P}$$ (3.5)

where

D_o =   The initial DO of the sample at collection site,

D_d =   The final DO of the sample after   5days incubation,

P   =   The Percent dilution

3.15 Chemical Oxygen Demand

Principle = Oxidation of wastes by potassium hepta–oxo chromate (VI) $K_2Cr_2O_7$ produces green chromic compound. The greater the wastes were oxidized,   the deeper the green color and the greater the COD. The absorbance of the green color will vary with the intensity   of the color hence the COD.

Sample Preparation

250 cm^3 of the water sample was introduced into a 100.0cm^3 round bottom flask, 10cm^3 of $KMnO_4$ (0.0125M) was added followed by 10cm^3 of 20%v/v H_2SO_4.. This was mixed gently warmed at 27 ^{0}C forfour hours. The mixture was examined at intervals when the pink color of permanganate tends to disappear;10cm^3 of $KMnO_4$ was added. After four hours,1cm^3 of potassium Iodide solution was added and titrated with 0.0125 M of $Na_2SO_3.5H_2O$, using starch indicator, blue color appears titrate to colorless end point (AOAC,1980).

Blank preparations:

As above for sample with distilled water. Condenser washed with distilled water and made up to 150cm³. Preparations are kept room temperature.

Calculation

$$COD(mg/L) \ = \ \frac{ml \ of \ blank - ml \ required \ of \ sample \ x1000}{A \ x \ volume \ of \ sample \ used} \qquad (3.6)$$

where A   =   Total volume of 0.0125M KMnO₄ added to samples.

Calibration Curve

Organic compoundswith theoretical COD known values used for calibrations. Glucose has a theoretical value of 1.067g/g and potassium acid phthalate 1.176g/g.

Glucose (4.688g) was dissolved in 250ml of distilled water. 1ml of this solution = 20mg COD.

3.16 Dissolved Oxygen in Water

The stopper was carefully removed from the bottle and in turn 1cm³ manganese sulphate solution added, followed by 1cm³ alkaline/iodide azide solution. The stopper was carefully replaced after each addition so as to avoid inclusion of air bubbles. Thoroughly mix the contents by inversion and rotation until a clear supernatant water is obtained. 1cm³ concentrated sulphuric acid was added with the tip of the pipette below the level of water and the stopper replaced . This was mixed well by rotationuntil the precipitationhas completely dissolved. 100.0cm³ of the solution   was pipetted into a 250.0cm³ conical flask and it was immediately titrated against standard solution of sodium thiosulphate 0.0125M (using freshly prepared starch solution as

indicator). This was added when the solution was pale yellow. Titration was carried out in duplicate.

Calculation

$$DO = \frac{Molar\ mass\ of\ oxygen\ xMxV_1}{\frac{V_2}{VV_1}(V_1 - V_2)} \tag{3.7}$$

where

M : the molarity of the thiosulphate.

V : the volume of the thiosulphate.

V_1 : the volume of the bottle, with stopper in place, $(V_1 - V_2)$.

V_2 : the volume of the aliquot taken for the titration (Ademorati,1996).

3.17 Nitrate Determination in Water

$50cm^3$ of the sample was pipette into the porcelain dish and evaporated to dryness on a hot water bath. phenol di-sulphonic acid was added to the residue by constant stirring with a glass rod. Concentrated solution of sodium hydroxide and distilled water was added with stirring to make alkaline.

This was filtered into nesslers tube and made up to 50ml with distilled water. Absorbance was read at 410 nm using a spectrophotometer after the development of the color.

The standard graph was plotted by taking concentration along the X axis and the spectrophotometric readings along the Y axis. The value of Nitrate was found by comparing absorbance of sample with the standard curve and expressed in mg/L.

$$\text{Conc of sample} \ = \ \frac{\textbf{Absorbance of sample x conc of standard}}{\textbf{Absorbance of standard}} \qquad (3.8)$$

3.18 Total Nitrogen in Water

25 cm^3 of the sample was mixed with 45cm^3 of concentrated ammonium chloride solution, 25 cm^3 were collected and 1.0 cm^{3}f coloring agent was added to it. The total nitrogen concentration was calculated as read directly using DR4000 spectrophotometer at 543nm.

3.19 Total Dissolved Solids (TDS)

Total dissolved solids was determined using APHA 2510A TDS139 tester (APHA,1998). The fiber filter disc was prepared by placing it, wrinkled side up, in the filtration apparatus. Vacuum was applied and the disc washed with three successive 20 cm^3 washings of distilled water. Continuous suction was then applied to remove all traces of water. A clean evaporating dish was heated to 180°C in an oven for 1hr, cooled and stored in a desiccators until needed. It was usually weighed immediately before use. A sample volume was chosen to yield 200mg dried residue. 50 cm^3 of well mixed sample was filtered through the glass fibre filter, it was washed with three successive 10ml volumes of distilled water, allowing complete draining between washings. Suction was continuously applied for about 3mins after

filtration was completed. Filtrate was transferred to a weighed evaporating dish and evaporated to dryness on a steam bath. The evaporating dish was finally dried for at least 1hr in an oven at 180ºC, cooled in a desiccator to balance temperature and weighed.

Calculation,

$$TDS \ = \ \frac{A-B \ mg/L}{Sample \ volume \frac{mg}{L}} \qquad (3.9)$$

A = weight of dish + solids (mg)

B = weight of dish before use (mg).

3.20 Total Suspended Solids

$100cm^3$ of the water sample ($50 \ cm^3$) was measured into pre weighed dish and evaporated to dryness at 105^0C on a steam bath. The evaporated sample was dried in an oven for about an hour at 105ºC, cooled in a desiccator and recorded for constant weight (Ademorati, 1996, APHA, 1998).

3.21 Determination of Total Suspended Solids.

Total suspended solids was determined by subtracting the result of total dissolved from total solids (Ademorati, 1996, APHA, 1998).

Total Suspended Solids = Total Solids - Total Dissolved Solids

(TSS)   =   (TS) - (TDS)   (3.10)

3.22 Determination of Water Hardness

Hardnesswas measured using standard analytical method of APHA(1998.).$50cm^3$ of the water sample was introduced into a beaker and 1ml buffer solution of ammonia solution was added. Three drops of solochrome Black indicator was added and the

solution swirled properly. The mixture was titrated with 0.01M solution of EDTA until the color changed from wine red to pure blue with no tinge remaining. The total hardness of the water sample was calculated,

$$\text{Total hardness (mg/L)} = \frac{\text{Volume of Titrex} \quad 10}{\text{Volume of Sample (cm}^3)} \qquad (3.11)$$

3.23 Measurement of Acidity

This was done by using the water samples as required.

The pH of each water sample was measured with acalibrated pH meter. A clean burette was rinsed with distilled water followed by severalrinsing with 0.025M NaoH.

The burette was filled with the alkaline solution, $100.0cm^3$ of the water sample to be analyzed was measured into a conical flask using a pipette filler. This was titrated to a phenolphthalein or meta-cresol purple end point. For samples withhighly acidic effluents smaller volumes of samples ($10.0cm^3$) were used for the test.

Triplicate titrations on each sample being investigate was performed.

Where the alkaline color of the indicator was observed before addition of the titrant zero acidity was reported and the test proceeded to alkalinity test.

Calculations

Acidity was calculated and expressed in terms of milligrams of calcium carbonate per liter .

$$\text{Acidity} = \frac{\text{ml}NaOH \ titrant \ x \ Normality \ of \ NaOH \ x \ 50ml}{ml \ of \ water \ sample} \qquad (3.12)$$

3.24 Determination of Alkalinity

A 50be cm^3 beaker was rinsedwith several quantities of 0.02M HCl. The burette was filled with the HCl acid solution (0.02M) making sure thatthere are no air bubbles. 100 cm^3 of the water sample to be analyzed was measured into a 250 cm^{3}onical flask.

The water sample was titrated in the presence of bromocresol green. Triplicate titrations on each sample being investigated.

Calculations

Alkalinity is expressed in terms of milligrams of calcium carbonate per liter.

$$Alkalinity = \frac{(\textbf{M HCl titrant}) \textbf{ x } (\textbf{50,000})}{(\textbf{mL of water sample})}. \qquad\qquad -(3.13)$$

3.25 Turbidity

Select EPA 180 was the measurement mode.

The sample was placedin a clean dish, a dry turbidity vial. This was caped securely and wiped off excess liquid or finger prints with a soft cloth. The sample was placed into the AQ4500 sample chamber and covered with the vial cap.The measure key on the instrument was pressed on. The result displayed on the instrumentand printed out for further use. When the result was less than 40ntu procedure for thesample was repeated.

The result when greater than 40ntu the sample was diluted with one or more volumes of turbidity free water until the turbidity falls below 40 ntu units. The Turbidity of the original sample was then computed from the turbidity of the diluted sample and the dilution factor.

Calculation Nephelometric

Turbidity units (NTU)   = A x (BxC)/C   (3.14)

A is ntu found in diluted sample

B is volume of dilution water mL

C is sample volume taken for dilution, mL.

This is a measure of the amount of suspended particles in the water. Algae,suspended sediment and organic matter can cloud the water making it more turbid. Suspended particles diffuse sunlight and absorb heat. This can increase temperature and reduce light available for algal photosynthesis. Where the turbidity is caused by suspended sediment, it is an indicator of erosion, either natural or man made. The sediments can also carry pathogens, pollutants and nutrients (Clean water Team, 2010).

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Physicochemical Parameters

The results of physicochemical properties for the various sampling sites are shown in Tables 4.1 to 4.5 for the rainy season.

TABLE 4.1: Physicochemical Properties of Water Samples (USAR) From Aba River 2014 Rainy Season

Parameters	Mar	Apr	May	Jun	July	Aug	Sept	Oct	Mean
Temp (^{o}C)	28.6	27.82	27.8	27.5	27.7	27.7	27.4	28.5	27.88
Cl (mg/L)	131.0	98.8	98.6	30	32	118	119	105	91.55
NO_3^- (mg/L)	0.45	1.79	1.78	1.43	1.45	1.88	1.9	3.46	1.77
PO_4^{-3}(mg/L)	1.469	1.723	1.721	3.28	3.26	1.28	1.278	1.425	1.93
Acidity(mg/L)	27.8	54.17	27.8	131.3	131.3	122.5	282.5	282.6	132.49
Alkal(mg/L)	40.1	20.96	20.98	5	5.1	9.8	9.8	4.2	14.49
TOC(mg/L)	12.7	41.36	41.34	34.5	34.3	44.8	44.6	42.6	37.03
COD(mg/L)	117.3	212	211	115	113	130	128	338	170.54
BOD(mg/L)	69	33.65	33.68	43	45	59	60	58	50.17
Turb(NTU)	14	5.07	5.09	18	20	2	3	0.35	8.44
TSS(mg/L)	12.5	31	30.31	44.1	43.4	50.6	50.8	2.4	33.14
TDS(mg/L)	19.6	63.08	63.1	84	86	96.8	96.6	2.4	63.95
EC(us/cm)	1.94	10.82	10.71	30.8	30.6	31.48	31.45	0.02	18.48
Ph	4.8	5.65	5.66	5.85	5.86	5.56	5.58	6.57	5.69
Hardn(mg/L)	40	56.2	58.1	68	66	67.5	67.8	140	70.45

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400$_U$SC m^1, T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010), FMEnv, 1991)

In Table4.1 the temperature of the effluents ranged from 27.4 ^{0}C in September to 28.6^{0}C in march ,above that reported for winter (15 – 25 ^{0}C) but below that for summer (30-48^{0}C) by Al-Musharafi *et al*; (2014), but are similar to that by Adekunle, (2009), the temperatures were below the WHO set guide lines of (30-32 ^{0}C) for surface water. Temperature being an important water quality with regard to survival of aquatic organisms hence the temperature of the river cannot be said to be comfortable to the aquatic life and the stress induced may lower the fish resistance, Ghazali (1995). This temperature will affect the water chemistry and also influence the amount of oxygen that can be dissolved in water,the rate of algae photosynthesis and other aquatic plants,metabolic rates of organisms and sensitivity to toxic wastes, parasites and diseases,even timing of reproduction and migration (Clean water Team, 2010). The chloride ion concentration ranged between 30 mg/L in June and 131 mg/L in March. The result 131 mg/L was the highest concentration attained at this site in the season, which was not above the Federal Ministry of Environment FMEnv (1991) and WHO stipulated guide lines of 250 mg/L. The rainy season may have caused much dilution of ions in the river. The chloride ion is known for maintance of acid –base balance (Ekpete, 2002). This report is similar to that by Adekunle, (2009).

The NO_3^- ionconcentrations ranged from 0.45 mg/L in March to 3.46 mg/L in October. This report is similar to the findings of Phiri, (2005) and within set standards by FMEnv (1991). The phosphate ion concentration ranged from 1.278 mg/L in September to 3.28 mg/L in June, with a mean of 1.93 mg/L for the season. Alkalinity was observed to be lower than 100 mg/L set standard. It ranged from 4.2 mg/L in October to 40.1 mg/L in March. The results fell within WHO stipulated limits of 100 mg/L and are similar to the reports of Onwughara *et al*; (2013).

Acidity values ranged from 27.8 mg/L in March to 282.6 mg/L in October. The total organic carbon in the rainy season at this site ranged from 12.7 mg/L in March to 44.8 mg/L in August, the seasons mean was 37.03 mg/L. The values for the chemical oxygen demand was very high as compared to the accepted levels of 10 mg/L .The COD results ranged between 113.0 mg/L in July to 338 mg/L in October. The mean for the rainy season was 170.54 mg/L. All the results were above WHO acceptable limit of 10 mg/l. The biological oxygen demand had the highest value of 69.0 mg/L in March and the least value of 33.65 mg/L in April. All the values were above the WHO stipulated standard of 6.0 mg/L the minimum survival concentration. Turbidity ranged from 2.0 NTU in August to 20.0 NTU in July. The mean turbidity in the season was 8.44 NTU. The upper values were above the WHO set limit of 5 NTU. This result is similar to reports by Adekunle, (2009). The result for the Total suspended solids was highest in September at 50.8 mg/L and least in October 2.4 mg/L with mean TSS of 33.14 mg/L. The results were found to be above WHO limit of 10 mg/L, though close to the report of Akubugwo *et al*; (2012) . The total dissolved solids had the highest value of 96.8 mg/L in August and the least value of 2.4 mg/L in October. The rainy season average was 63.95 mg/L. The results were within WHO stipulated limit of 1000 mg/L

The electrical conductivity had the highest value of 31.48 µS/cm in August while the least conductivity value was in October 0.02 µS/cm. These values were within WHO (2002) set limitsof 500 µ S/cm. These results differed from the results of Phiri *et al*; (2005), Adekunle, (2009); Bhagirathi *et al* (2012).

The pH was least in the month of March on a value of 4.8 , which was strong acidic that may cause a stress to the aquatic life in the river. The highest pH was 6.57 in the month of October. WHO accepted pH level being 6.5-8.5 for safe aquatic

sustenance of life.   These reports were similar to those obtained by Phiri*et al;* (2005). The highest total hardness for the river at the USAR was in the month of October (140 mg/L) and the least value was 40.0 mg/L in March. This was below WHO/FMEnv limit of 500 mg/L.

Table 4.2: Physicochemical Properties of Water Samples (NBL) from Aba River 2014 Rainy Season

Parameters	Mar	Apr	May	Jun	July	Aug	Sept	Oct	Mean
Temp(^{o}C)	23.8	26.8	26.9	26.4	26.6	27.1	27	23.6	26.03
Cl(mg/L)	134	94.1	93.6	56	57	41	40	81	74.59
NO_3^-(mg/L)	0.76	3.18	3.15	1.51	1.63	1.75	1.78	7.24	2.63
PO_4^{-3}(mg/L)	5.91	1.35	1.39	1.89	1.92	1.3	1.5	1.71	2.12
Acidity(mg/L)	40.3	59.1	58.91	65	70	91	90.5	188	82.85
Alkal(mg/L)	22	14.85	14.82	10.2	10.4	16.2	15.9	14	14.8
TOC(mg/L)	56	36.61	36.78	45	43.2	39.1	37.8	38.61	41.64
COD(mg/L)	295	260.8	261.4	112	110	132	136	512	227.4
BOD(mg/L)	77	33.8	35.49	44	48	58	56	60	51.54
Do(mg/L)	92	48.61	48.72	67	69	69	71	112	72.17
Turb(NTU)	18	4.86	4.88	3.1	3.5	2	2.5	1.7	5.07
TSS(mg/L)	10.8	31.5	33.41	46	48	40.8	42.7	3.7	32.11
TDS(mg/L)	15.9	58.34	53.38	80.3	81	78.2	76.4	4.8	55.42
EC(us/cm)	1.87	7.85	7.58	14.1	13.8	`12.7	11.73	0.05	8.71
pH	3.88	5.57	5.59	5.74	5.47	5.61	5.41	5.86	5.52
Hardn(mg/L)	24	37	35	53	52	67	69	78	51.88

(WHO)Temp=25^{0}C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO$_3$=45 mg/L,PO$_4$=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400υSC m^1, T/Hardn=500mg/L, Alkan=30mg/L,(WHO,2008,EPA(2010),FMEnv, 1991)

Temperature can affect the toxicity of metals and other toxicants as well.The rate of the animal or fish metabolic rate can be increased by the rise in temperature enhancing the rate of toxicant uptake and or the stress induced may lower the fish resistance (Ghazali, 1995). Low temperature range at of 23.6 to 27.1 ^{0}C implies that this station will have

low dissolved oxygen for the biota. The water chemistry of the aquatic organisms will be affected by the low temperature leading to fish migration and possible deaths.

The temperature at this site was least in the month of October being 23.6^0C and highest in the month of August 27.1^0C and a seasonal mean temperature of 26.03^0C which was below the allowable temperature for surface water set by Federal Ministry of Environment (FMEnv 1991)/WHO(2002) at 30-31^{0}C, Al-Musharafiet al; (2014). These temperature are similar to that obtained by Adekunke, (2009), Bhagirathi et al; (2012). The chloride ion concentration was highest in the month of March 134 mg/L and least in September 40 mg/L while the mean for the season at this site was 74.59 mg/L.These values were within the minimum permissible limits of WHO/FMEnv of 250 mg/L and are close to reports of Bhagirathi et al; (2012) and similar to that by Adekunke, (2009). The nitrate ion concentration had the highest concentration in the month of April 3.18 mg/L and the least in march 0.76 mg/L this being close to that obtained by Phiriet $al;$ (2005), with a mean of 2.63 mg/L. The results obtained were all below the FMEnv/WHO set standards. The results were similar to that outlined by Adekunle et al; (2007). The phosphate ion concentration was highest in March 5.91mg/L and least in August 1.30 mg/L, a seasonal mean of 2.12 mg/L. The acidity was recorded highest in the month of October 188 mg/L and lowest in March 40.3 mg/L with a seasonal mean of 82.85 mg/L. The alkalinity was lowest in June 10.2 mg/L and highest in March 22.0 mg/L, mean alkalinity of 14.8 mg/Lwhich is below FMEnv/WHO limit for surface water at 100 mg/L.High alkalinity in march /april /may may be attributed to clean water at the station which made people use much water for washings and bathing increasing HCO_3^- ions in the river. The low level alkalinity in June /July could be that the water turbid and dirty following land runoffs and prevented people from using the water at this station

for bathing and washing. These results are similar to the reports by Bhagirathi *et al*; (2012).

The Total organic carbon was highest in March 56.0 mg/L and least in April 36.61 mg/L,with a seasonal mean of 41.64 mg/L. Chemical oxygen demandwas highest in October 512 mg/L and least in July 110 mg/L. The mean concentration was 227.4 mg/L. This result was above FMEnv/WHO limit of 10 mg/L.The biological oxygen demand was least in April 33.8 mg/L and highest in March 77.0 mg/L, these results were above FMEnv/WHO value of 6.0 mg/L. These reports were similar to those of Phiri *et al;* (2005). Dissolved oxygen ion concentration was least in April 48.61 mg/L and highest in October 112 mg/l, and a seasonal mean of 72.17 mg/L and were above FMEnv/WHO value of 7.5 mg/L. Low dissolved oxygen values recorded in april and may indicates that the NBL industry may have released high oxygen demanding wastes while the points of high dissolve oxygen may be attributed to much water volume diluting the oxygen consuming wastes following heavy rain.

Turbidity ranged from 1.70 NTU (least value) in Oct to 18.0 NTU in March a seasonal mean of 5.07 NTU. This result was within the FMEnv/WHO set acceptable allowable limits for surface water of 50 NTU.The lower limits are close to the reports by Bhagirathi *et al*; (2012) and that of Adekunle (2009). The total suspended solids was highest in July 48.0 mg/L and least in Oct 3.70 mg/L with mean of 32.11 mg/L which was within the limits given by FMEnv/WHO of 30 mg/L.The season experienced a general increase in TSS as contaminants tend to accumulate down stream with runoffs entering the river.

The total dissolved solids were highest 81.0 mg/L in July and least in October 4.8 mg/L,with a mean of 55.42 mg/L. These results were below the limits given by FMEnv /WHO of 500 mg/L.

The electrical conductivity was least in October 0.02 µS/cm and highest in June 25.9 µS/cm, with a seasonal mean of 14.6 µS/cm and these results are below FMEnv and WHO limit of 500 µS/cm . The significant increase in EC indicates entry of dissolved electrolytes or electrolytic ions which is proportional to the ionic concentrations.The pH was least in March 4.87 and highest in October 5.98, with a mean of 5.49 and these results were below FMEnv and WHO limit of 6.5-8.5. The low pH values in Marchindicates highly acidic system as against WHO set pH of 6.5 to 8.0. This pH will induce a stress condition on the aquatic organisms. The mean pH of 5.2 emphasizes a strong acidic river. This tells that more H^+ or H_3O^+ions were in solution than OH^- ions.

These reports were similar to those of Phiri *et al;*(2005). The total hardness(TH) of the site was least in March 24 mg/L and highest in October 78 mg/L with a mean of 51.88 mg/L. The highest result obtained was similar to the lowest result obtained by Bhagirathi *et al*; (2012). These results were within the acceptable limit set by FMEnv and WHO(500 mg/l).

Table 4.3: Outline the result for physicochemical parameters in Aba River in the rainy season at PZ site.

Table 4.3: Physicochemical Properties of Water sample for Aba River (PZ) 2014/15 Rainy Season

Parameters	Mar	Apr	May	Jun	July	Aug	Sept	Oct	Mean
TempoC	26.6	23.86	23.68	26.8	26.6	26.57	26.75	26.5	25.92
Clmg/L	132.2	92.5	94.1	39.5	40	106	108	91	87.91
NO_3^{-1}mg/L	0.69	2.35	2.53	1.58	1.85	1.56	1.65	4.75	2.12
PO_4^{-3}mg/L	4.57	1.68	1.63	2.34	2.43	1.89	1.986	1.196	2.22
Aciditymg/L	38	41.23	41.32	56.23	56.35	87.9	88.1	26	54.39
Alkalmg/L	37.8	18.45	18.74	10.38	10.4	11.8	12.6	20	17.48
TOCmg/L	14.8	38.27	38.29	37.5	37.6	45.8	46.4	33.8	35.53
CODmg/L	248	184.9	184.4	106	108	121	119	328	174.91
BODmg/L	88	41.32	41.36	54	56	66	68	69	60.46
Domg/l	122	56.5	57.85	79.1	78.6	80	82	14	71.26
Turb(ntu)	22	9.8	9.6	5.1	5.4	11	13	0.7	9.58
TSSmg/L	12.63	35.2	35.16	40.1	42.5	43.5	45.8	44	32.41
TDS	26	60.1	61.04	87.1	85.3	93	95	3.8	63.92
EC(us/cm)	1.58	9.93	9.95	25.9	25.7	21.96	21.78	0.02	14.6
pH	4.87	5.32	5.45	5.6	5.88	5.12	5.73	5.98	5.49
Hardnmg/L	37	38	41	56	54	60	178	174	79.88

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400υSC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO,2008, EPA(2010),FMEnv, 1991)

The temperature at this site was least in the month of May being 23.68^{0}C and highest in the month of June at a temperature of 26.8^{0}C and a seasonal mean temperature of 25.92^{0}C. This result was similar to that by Bhagirathi *et al;* (2012). This is within the temperature for surface water set by Federal Ministry of Environment (FMEnv,1991) at 30-31^{0}C. The chloride ion concentration was highest in the month of March 134 mg/L and least in September 40 mg/L,while the mean for the season at the site was 74.59 mg/L. These values were within the minimum permissible limits by WHO/FMEnv of 250 mg/L and are close to reports set by Bhagirathi, *et al*; (2012) and Adekunke, (2009). The nitrate ion concentration had the highest concentration in the month of April 3.18 mg/L and the least in march 0.76 mg/L, with a mean of 2.63 mg/L. The readings obtained were all below the FMEnv and WHO allowable standards of 50.0 mg/L. The phosphate ion concentration was highest in March 5.91mg/L and least in August 1.3 mg/L, a seasonal mean of 2.12 mg/L. The acidity was recorded highest in the month of October 188 mg/L and lowest in March 40.3 mg/L with a seasonal mean of 82.85 mg/L. The alkalinity was lowest in June 10.38 mg/L and highest in March 18.74 mg/L with a mean alkalinity of 17.48 mg/L (rainy season); these results arewithin FMEnv and WHO set limit for surface water of 100 mg/L. These results are similar to Bhagirathi *et al;* (2012). The Total organic carbon was highest in March 56.0 mg/L and least in April 36.61 mg/L with seasonal mean of 41.64 mg/L. Chemical oxygen demand was highest in October 512 mg/L and least in July 110 mg/L. The mean concentration was 227.4 mg/L.This result was above FMEnv and WHO limit of 10 mg/L. The biological oxygen demand was least in April 41.32 mg/L and highest March 88.0 mg/L. The observed decrease in BOD level in April/May may be that effluent from the industry might have been washed away by the storm water and affected the water quality in the river. This results are similar to that by Bhagirathi *et al*; (2012) but are above FMEnv

and WHO set value of 6.0 mg/L. Dissolved oxygen ion concentration was least in April 48.61 mg/L and highest in October 112 mg/L, and a seasonal mean of 72.17 mg/L which results are above FMEnv and WHO set value of 7.5 mg/L. Turbidity ranged from Oct 0.70 NTU least value to 22.0 NTU in March aseasonal mean of 9.58 NTU. This result was within the FMEnv and WHO set acceptable limits for surface water of 50.0 NTU. This result is similar to some sites in that by Adekunle, (2009). The Total Suspended Solids (TSS) was highest in July 48.0 mg/L and least in March 10.8 mg/L, a mean of 32.11 mg/L which result was within the set limit by FMEnv and WHO of 30 mg/L. The Total Dissolved Solids (TDS) were highest in July 81.0 mg/L and least in October 4.8 mg/L,with a mean of 55.43 mg/L. These results were below the limits set by FMEnv and WHO of 500 mg/L. This result gave the highest TDS to be the least for that reported by Bhagirathi *et al*; (2012). The electrical conductivity was least in October 0.05 µS/cm and highest in June 14.1 µS/cm,with a seasonal mean of 8.71 µS/cm. The low conductivity in the months of March/April with a corresponding low Turbidity may be attributed to salting out of dissolved salts from the water column and subsequent settling at the river side. From the months of April to September a sharp increase in EC from 9.93 us/cm[1] to 21.25 us/cm[1] with a corresponding observed increase in TDS is as a result of dissolved solids.

The results are below FMEnv and WHO set limit of 500 µS/cm.This result is not similar to the result obtained by Phiri *et al*; (2005), Adekunle (2009);Bhagirathi *et al*;2012). The pH was least in March 4.88 and highest in October 5.86, with a mean of 5.52. These results were below FMEnv and WHO set limit of 6.5-8.5. These results will have adverse health effects on the life of the aquatic animal and plants as they are acidic. The total hardness of the site was least in March 24 mg/L and highest in October 78 mg/L with a mean of 51.88 mg/L.The high values of T/Hardness in the

months of June/July of 54.0 mg/L to Oct/Nov 17.0 mg/L could be from anthropogenic activities of farming, bathing and washing of clothes by villagers leading to high hardness of water.These results were with the acceptable limits of FMEnv and WHO, (2002).

Table 4.4: Physicochemical Properties of Water Sample for Aba River (ABT) 2014/15 Rainy Season

Parameters	Mar	Apr	May	Jun	July	Aug	Sept	Oct	Mean
Temp(^{o}C)	27.4	27.2	27.5	27.5	26.5	26.9	26.4	28.5	27.24
Cl(mg/L)	166	162	144.3	130	132	150	170	117	146.41
NO_3^- (mg/L)	0.39	3.36	3.42	2.3	2.1	1.08	1.05	6.38	2.51
PO_4^{-3}(mg/L)	1.63	1.71	1.51	2.26	2.24	1.82	1.79	1.62	1.82
Acidity(mg/L)	63.1	116.14	118.2	167.5	165.7	122.8	124.7	245	140.89
Alkal(mg/L)	52.5	25.3	27.28	36.3	34.2	24.1	22.8	12	29.31
TOC(mg/L)	42	43	45.14	40.8	41.6	42.7	42.5	52.7	43.81
COD(mg/L)	192	194	193.2	145	143	120	121	325	179.15
BOD(mg/L)	69	41.43	43.3	63	65	51	53	7.3	49.13
Turb(ntu)	11	16.15	17.1	45	44	12	14	2.5	20.22
TSS(mg/L)	12.1	40.64	41.1	58.3	58.5	55.7	55.9	3.2	40.88
TDS(mg/L)	25.6	61.4	60.36	88.7	89.1	94	95	37	68.9
EC(us/cm)	3.09	18.75	18.87	487.6	49.3	42	41.94	0.04	27.82
pH	5.65	5.52	5.55	4.98	4.96	5.83	5.85	6.18	5.57
Hardn(mg/L)	28	45	43	81.9	81.6	67	65	85	62.06

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400$_U$SC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010), FMEnv, 1991)

The temperature of the effluents at the ABT site ranged from 26.4 in September to 28.5 ^{0}C in October, and a mean of 27.24 ^{0}**C** which was below the WHO guide lines of (30-32 ^{0}C) for surface water. The temperature of the water will not support aquatic

life. This result was close to that obtained by Haruna and Solomon (2015); Bhagirathi *et al;* (2012) and Adekunle, (2009).The chloride ion concentration was ranged between 130 mg/L in June and 170 mg/L in September at this site with a mean concentration of 146.41 mg/L for the season. The mean concentration was within the Federal Ministry of Environment (FMEnv 1991)and WHO stipulated guide lines of 250 mg/L. The rains may have caused much dilution of ions in the river.The reports are close to that by Bhagirathi, *et al*; (2012) and Adekunke, (2009). The NO_3^- ion concentrations ranged from 0.39 mg/L in March to 6.38 mg/L in October, as against 50 mg/L set by (FMEnv 1991). The phosphate ion (PO_4^-) concentration ranged from 1.62 mg/L in October to 2.26 mg/L in June, with a mean of 1.82 mg/L for the season. Alkalinity wasobserved to be lower than 100 mg/L; set standard ranging from 12.0 mg/L in October to 36.3 mg/L in June and a range 29.3 mg/L. Acidity values ranged from 63.1 mg/L in March to 245.0 mg/L in October with a mean of 140.39 mg/L. The total organic carbon in the season at this site ranged from 42 mg/L in March to 52.7 mg/L in October (the seasons mean was 43.81 mg/L). This result was close to that by Harunaand Solomon, (2015). The values for the chemical oxygen demand (COD) was very high as compared to the accepted levels of 10 mg//L.The COD results ranged between 325.0 mg/L in October to 120 mg/L in August. The mean for the season was 179.15 mg/L. The Biological Oxygen Demand had the highest value of 69 mg/L in March and the least value of 7.3 mg/L in October. The mean concentration was 49.13 mg/L, while the WHO setstandard was 6.0 mg/L.BOD levels were high in the months of March ,June and July did not vary much between April and May, also between August and September. The higher values meant that there were greater quantities of degradable wastes from the industrial effluents. The BOD varied significantly during the rainy season between months.

The turbidity values was ranged from 2.5 NTU in October to 45 NTU in June. The mean turbidity in the season was 40.68 NTU. This result is similar to results obtained by Adekunle, (2009). This result was within the FMEnv and WHO set limits for surface water of 50.0 NTU.

The results for the Total Suspended Solids (TSS) was highest in July at 58.5mg/L and least in October at 3.2 mg/L, the seasons mean TSS was 40.68 mg/L. The total dissolved solids had highest value of 95.0 mg/L in September and the least value of 25.6 mg/L in March. The seasonal average for TDS was 68.90 mg/L. This result was within the set values by WHO/FMEnv of 500mg/L. The electrical conductivity had the highest value of 49.3 µS/cm in July while the least conductivity value was in October (0.04 µS/cm). This result was within the set values by WHO/FMEnv of 500 µS/cm. The pH was least in the month of July 4.96, which is strongly acidic and could cause stress to aquatic life at the site. The highest pH was 6.18 in the month of October. This value was similar to that of Harona and Solomon, (2015) and WHO/FMEnv accepted pH level of 6.5-8.5 which is safe aquatic sustenance of life. The highest total hardness for the river at the site was in the month of October 85mg/L and a least value of 28.0 mg/L in March. The seasonal mean hardness was 62.06 mg/L.

Table 4.5: Physicochemical Properties of Water Sample for Aba River (DSAR) 2014/15 Rainy Season

Parameters	Mar	Apr	May	Jun	July	Aug	Sept	Oct	Mean
Temp (^{o}C)	27.5	27.5	27.65	27.63	27.4	27.2	27.33	27.9	27.46
Cl (mg/L)	158	123.2	125.1	100	101	156	158	102	127.91
NO_3^- (mg/L)	1.86	3.54	3.45	27.5	27.4	27.4	27.33	21.5	17.5
PO_4^3(mg/L)	3.47	1.74	1.75	2.56	2.57	1.24	1.24	1.42	2.00
Acidity(mg/L)	67.5	88.67	88.76	96	95	105.1	105.3	160.5	100.85
Alkal(mg/L)	10.81	34.5	34.25	10	11	12.9	13	30	19.56
TOC(mg/L)	23.7	44	43.9	44.3	44.5	48.8	48.5	35.8	41.69
COD(mg/L)	130	160	159.4	120	118	121	122	230	145.05
BOD(mg/L)	93	46.85	46.88	74	76	64	65	8.34	58.26
DO(mg/L)	102	61.8	61.84	87	88	72	73	26	71.46
Turb(NTU)	32	14.9	14.8	20	18	9	10	13	15
TSS(mg/L)	22.7	45.23	45.25	62.3	62.5	56.9	56.8	39	44.45
TDS(mg/L)	25.6	61.1	60.4	85.3	87.2	95	93	36	63.9
EC(us/cm)	1.94	12.23	12.25	31.1	30.4	31.5	31.45	0.03	18.86
pH	6.05	5.83	5.85	5.52	5.58	5.88	5.6	5.8	5.76
Hardn(mg/L)	59.2	65	63	71	70	45.9	45.8	50.1	58.75

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400$_U$SC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010),FMEnv, 1991)

The temperature of the water body has a direct relationship with the chemical reactions in the water and biochemical reactions in the living organisms habiting the water. The temperature at thissite wasleast in the month of August 27.2^{0}C. highest in the month of May (27.65^{0}C),with a seasonal mean temperature of 27.46^{0}C. These results were below the acceptable temperaturefor surface water set by Federal Ministry of Environment (FMEnv 1991) (30-31^{0}C). These results were similar to that of Adekunle, (2009). It could be stated that this temperature range was not optimal for the sustenance of aquatic life. The chloride ion concentration was highest in the months of March and September at 158 mg/L. concurrently and least in June 100 mg/L, with the mean for the season at the site as 127.91 mg/L.The rainy season may have caused much dilution of ions in the river.The values are close to that by Bhagirathi *et al*; (2012)and Adekunke (2009). The nitrate ion concentration had the highest concentration in the month of June 27.5 mg/L and the least in March 1.86 mg/L, with a mean of 17.5 mg/L.The values obtained were all below the FMEnv and WHO standards of 50.0 mg/L. The phosphate ion concentration was highest in March 3.47 mg/L and least in the months August and September 1.24 mg/L respectively, and a seasonal mean of 2.0 mg/L. The acidity was recorded highest in the month of October 160.5 mg/ and lowest in March 67.5 mg/L,with a seasonal mean of 100.85 mg/L. The alkalinity was lowest in June 10.0 mg/L and highest in October 30.0 mg/L, with a seasonal mean alkalinity of 19.6 mg/L (below FMEnv and WHO limit for surface water at 100 mg/L).The result were similar to Haruna and Solomom, (2015). The Total organic carbon was highest in August 48.8 mg/L and least in March 23.7 mg/L with seasonal mean of 41.69 mg/L. Chemical oxygen demand was highest in October 230 mg/L and least in July 118 mg/L. The mean concentration was 145.05 mg/L. The result at this site was above FMEnv and WHO set limit of 10 mg/L for the season. The biological oxygen demand was least in April

46.85 mg/L and highest July 76.0 mg/L,with a seasonal mean of 58.26 mg/L, these results are above FMEnv and WHO set value of 6.0 mg/L. Dissolved oxygen ion concentration was least in October 26.0 mg/L and highest in March 102 mg/L, with a seasonal mean of 71.46 mg/L, which results are above FMEnv and WHO set value of 7.5 mg/L. The sharp decrease in DO level between September at 73 mg/L and October 26 mg/L indicated introduction of organic loads into the river which required high level of oxygen for chemical oxidation . Sharp decrease in DO in between March 102 mg/L and April 61.8 mg/L with corresponding increase in EC in the same periods from 1.94 us/cm⁻ March to 12.23 us/cm⁻ proved deterioration in water quality.

Turbidity ranged from 1.30 NTU least value in October to 32 NTU in March, a seasonal mean of 1 5.0 NTU. This.This result was within the FMEnv and WHO set limits for surface water 50 NTU. The total suspended solids was highest in July 62.5 mg/L and least in October 3.9 mg/L, a mean of 44.45 mg/L, (within the set limit by FMEnv and WHO of 30 mg/L). The total dissolved solids were highest in August 95.0 mg/L and least in October 3.6 mg/L, with a mean of 63.9 mg/L. These results were below the limits set by FMEnv and WHO of 500 mg/L. The electrical conductivity was least in October 0.03 µS/cm and highest in August 31.5 µS/cm, with a seasonal mean of 1 8.86 µS/cm .These results are below FMEnv and WHO set limit of 500 µS/cm. The pH was least in June 5.52 and highest in March 6.0, with a mean of 5.76. These results are below FMEnv and WHO set limit of 6.5-8.5 and are good for aquatic life. The total hardness of the site was least in September 45.8 mg/L and highest in June 71.0 mg/L with a mean of 58.75 mg/L. These results were within the acceptable limits set by FMEn/ WHO.

Physicochemical Parameters (Dry Season)

The results of physicochemical properties of Aba river are shown in Tables 4.6 to 4.10 for the dry season.

Table 4.6: Physicochemical Properties of Water Sample for Aba River (USAR) 2014/15 Dry Season

Parameters	NOV	DEC	JAN	FEB	MAR	MEAN
Temp(^{o}C)	28.4	28.6	28.4	28.8	28.6	28.56
Cl(mg/L)	104	100	102	129	131	113.2
NO_3^-(mg/L)	3.48	0.76	0.78	0.43	0.45	1.18
PO_4^{-3}(mg/L)	1.43	1.115	1.113	1.47	1.467	1.32
Acidity(mg/L)	28.6	72.5	72.6	27.5	27.8	96.6
Alkal(mg/L)	4.4	7.9	7.8	40	40.1	20.04
TOC(mg/L)	42.5	40.4	40.2	12.8	12.7	29.72
COD(mg/L)	387	113	111	118.1	117.3	169.3
BOD(mg/L)	58	51	52	67	69	59.4
DO(mg/L)	188	68	66	110	109	108.2
Turb(NTU)	0.38	3	3.5	12	14	6.58
TSS(mg/L)	2.2	42.8	42.7	12.8	12.5	22.6
TDS(mg/L)	2.6	87.3	85.5	19.4	19.6	42.88
EC(us/cm)	0.08	1.35	1.33	1.96	1.94	1.32
Ph	6.59	5.34	5.36	4.96	4.98	5.45
Hardn(mg/L)	142	82	78	42	40	76.8

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400USC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010), FMEnv, 1991)

From Table4.6 the temperature of the effluents ranged from 28.4^0C in months of November and January respectively to highest in $28.8\ ^0C$ in February with a seasonal mean temperature 28.56^0C which was below the WHO set guide lines of $(30\text{-}32^0C)$ for surface water. This temperature is not good for the aquatic life. This result is similar to that by Adekunle (2009). The chloride ion concentration ranged between 100 mg/L in December to highest march where the site concentration was 131mg/L.This result is similar to that by Bhagirathi *et al*; (2012) and Adekunle (2009). The mean concentration was 28.56 mg/L, which was not above the Federal Ministry of Environment (FMEnv 1991)and WHO stipulated guide lines of 250 mg/L. The season under study may have lacked much rain resulting in high ion concentration observed.The NO_3^- ion concentrations ranged from 0.43 mg/L in February to 3.48 mg/L in November with a mean of 1.18 mg/L, as against 50 mg/L (FMEnv 1991). The phosphate ion (PO_4^{-3}) concentration ranged from 1.113 mg/L in January least to 1.47 mg/L highest in February with a mean of 1.32 mg/L for the season. Alkalinity was observed to be lower than 100 mg/L set standard ranging from 4.4 mg/L in November to 40.1 mg/L in March, mean of 20.04 mg/L.

Acidity values ranged from 28.6 mg/L in November to 72.6 mg/L in January. The total organic carbon (TOC) in the season at this site was ranged from least value of 12.7 mg/L in March to 42.5 mg/L in November, the seasons mean as 29.72 mg/L. The values for the chemical oxygen demand (COD) was very high as compared to the accepted levels of 10 mg/L.The COD results ranged between 387.0 mg/L in November to 111.0 mg/L in December. The mean for the season was 169.28 mg/L. The biological oxygen demand (BOD) had the highest value of 69.0 mg/L in March and the least value of 51.0mg/L in December, with a mean of 59.4mg/L. The WHO set standard was 6.0mg/L. The turbidity ranged from 0.38 NTU in November to 14.0 NTU in March.

The mean turbidity in the season was 6.58 NTU . This result is similar to that obtained by Adekunle, (2009) and was within the FMEnv and WHO limits for surface water (50NTU). Low turbidity from November 2014 to January 2015 indicates higher dissolved oxygen available to aquatic biota, at February high turbidity dissolved oxygen exceeds WHO maximum of 110 mg/L and oxygen begins to form bubbles in blood stream of fish leading to fish death. NO_3^- Nitrate concentration over the period on this station was within WHO permissible limit of >10mg/L

The results for the Total Suspended Solids (TSS) was highest in December (42.80 mg/L) and least in November (2.2 mg/L) the seasons mean TSS is 22.6 mg/L. The Total Dissolved Solids (TDS) had the highest value of 87.3 mg/L in December and the least value of 2.6 mg/L in November. The dry season average was 42.88 mg/L. The Electrical Conductivity (EC) had the highest value of 1.96 µS/cm in February while the least conductivity value was in November (0.03 µS/cm). Values of EC in February and March of 1.96 µs/cm to 1.94 µs/cm compared to 0.08 µs/cm and 1.35 µs/cm for November and December respectively indicates entry of a mild to heavy pollutants in February, may be ions from a construction site washings and cleaning factory equipment and premises.

The pH of 4.96 was least in the month of February at this site, which is strongly acidic. This value that could cause stress to the aquatic life at the site. The highest pH was 6.59 in the month of November and a mean pH of 5.45, WHO accepted pH level being 6.5-8.5 for safe aquatic sustenance of life. The highest total hardness for the river at the site was in the month of November (142mg/L) and a least value of 40.0mg/L in March. This result was within WHO /FMEnv limit of 140mg/L.

Table 4.7: Physicochemical Properties of Water Sample for Aba River (NBL) 2014/15 Dry Season

Parameter	NOV	DEC	JAN	FEB	MAR	MEAN
Temp(^{o}C)	23.7	25.8	25.6	23.6	23.8	24.5
Cl(mg/L)	83	321	318	135	134	198.2
NO_3^-(mg/L)	7.26	0.29	0.22	0.74	0.76	184
PO_4^{-3}(mg/L)	1.74	1.07	1.09	5.88	5.91	3.14
Acidity(mg/L)	190	67.5	68.3	41	40.3	81.42
Alkal(mg/L)	16	13.8	13.6	20	22	17.08
TOC(mg/L)	38.67	33.1	32.8	58	56	43.71
COD(mg/L)	516	124	122	298	295	271
BOD(mg/L)	58	49	51	75	77	62
Domg/L	116	54	58	89	92	81.8
Turb(NTU)	1.9	3	3.2	14	18	8.08
TSS(mg/L)	3.5	41	40.3	10.04	10.8	21.2
TDS(mg/L)	4.5	82.3	83.1	16.2	15.9	40.4
EC(us/cm)	0.03	1.56	1.44	1.78	1.87	1.34
pH	5.68	5.83	5.76	4.83	4.88	5.4
Hardn(mg/L)	76	56	58	26	24	48

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400$_U$SC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010),FMEnv, 1991)

The water chemistry of the water will be affected by the general low temperature of the river, there will be slow metabolism, algae photosynthesis will be affected, fish

reproduction in respect of hatching of eggs will be hampered. Dissolved oxygen will be low as the river be slowed down and dissolved oxygen is affected by the velocity of the river. Fish might migrate to better ecosystem.

The temperature at this site was least in the month of February (23.6^{0}C) and highest in the month of December at a temperature (25.8^{0}C) witha seasonal mean temperature of 24.5^{0}C. This report is close to that obtained by Al-Musharafi et al; (2014) and Bhagirathi et al; (2012). This result was below the acceptable temperature for surface water (FMEnv, 1991) at 30-31^{0}C. The chloride ion concentration was highest in the month of December 321 mg/L. This result was above set value of 250 mg/L by Federal Ministry of Environment (FMEnv, 1991)/WHO for surface waters. The chloride value was least in November 83 mg/L. The mean for the season at the site was 198.2 mg/L and similar to Bhagirathi et al; (2012). The nitrate ion NO_3^- concentration had the highest concentration in the month of November (7.26 mg/L) and the least in January (0.22 mg/L) with a mean of 1.84 mg/L . The results obtained were all below the FMEnv and WHO set allowable standards of 50.0mg/L. The phosphate ion PO_4^{-3} concentration was highest in March 5.91 mg/L and least in December 1.07 mg/L, a seasonal mean of 3.14 mg/L. These results are close to that by Phiri, et al; (2005).

The acidity was highest in the month of November 190 mg/L and lowest in March 40.3 mg/L , a seasonal mean of 81.42 mg/l. The alkalinity value was lowest in January (13.6 mg/L) and highest in March (22.0 mg/L), mean value of 17.08 mg/L which is below 100 mg/L FMEnv and WHO limit for surface water. The Total organic carbon (TOC) was highest in February 58.0 mg/L and least in January 32.8 mg/L, seasonal mean of s 43.71 mg/L. Chemical oxygen demand(COD) was highest in November (516 mg/L) and least in January (122 mg/L). The mean concentration was 271.0 mg/L. These results are similar to that of Lakhande et al; (2011) but were above

FMEnv and WHO limit of 10 mg/L. The Biological Oxygen Demand (BOD) value

was least in December (49.0 mg/L) and highest in March 77.0 mg/L, with a mean

of 62.0 mg/L, these results are above FMEnv and WHO set value of 6.0 mg/L but are

close to results by Phiri *et al*; (2005). BOD values found above 80 mg/l for the months

of Feb and Mar effected adverse   effects on aquatic life due to depleted oxygen   in

water. Similar conclusions were made by Shah (2014).

Dissolved oxygen   concentration was least in December (54.0 mg/L) and highest in

November (116.0 mg/L) with a seasonal mean of 81.80 mg/L which results are above

FMEnv and WHO value of 7.5mg/L. Turbidity ranged from 1.90 (NTU) in November

to 18 NTU in March with a seasonal mean of 8.08 NTU. The Total Suspended Solids

(TSS) was highest in December, 41.0.0 mg/L and least in November, (3.5 mg/L), with

a mean of 21.2 mg/L, (within set limit by   FMEnv and WHO of 30 mg/L. The Total

Dissolved Solids (TDS) were highest in January,83.1 mg/L and least in November 4.5

mg/L,with a mean of 40.40 mg/L. The increase in TDS from 3.6mg/L in Nov through to

87 mg/L in Jan with a corresponding increment in conductivity   over the same period

from 0.04 us/cm^{-1} to 1.3 us/cm^{-1} may be attributed to non salting out of dissolved

salts which are not settling at the river beds. The high TDS values of 87 to 88 mg/L

may cause   salinity problems if used in irrigation waters. These results were below

the limits set by   FMEnv and WHO of 500 mg/L .

The Electrical Conductivity(EC) value was least in November 0.03 μS/cm   and highest

in March, (1.87 μS/cm), with a seasonal mean of 1.34 μS/cm, (results are below FMEnv

and WHO   set limit of 500 μS/cm). The pH value was least in February, 4.83 and

highest in December 5.83, with a mean of 5.4,(these results were below FMEnv and

WHO   set limit of 6.5-8.5). These results   are close to that obtained in Malawi by Phiri,

et al; (2005). The pH value   will be abnormal for   the aquatic animals and plants

because it is highly acidic. The total hardness of the site was least in March 24 mg/L and highest in November, 76 mg/L, with a mean of 48 mg/L. These results were within the 500 mg/L acceptable limits by FMEnv and WHO .

Table 4.8: Physicochemical Properties of Water Sample for Aba River (PZ) 2014/15 Dry Season

Parameters	NOV	DEC	JAN	FEB	MAR	MEAN
Temp(^{o}C)	26.4	26.8	26.9	26.5	25.6	26.64
Cl(mg/L)	93	96	98	136	132	111
NO_3^-(mg/L)	4.75	0.43	0.48	0.65	0.69	1.4
PO_4^{-3}(mg/L)	1.169	0.98	0.894	4.75	4.57	2.47
Acidity(mg/L)	27.1	67.6	67.8	35	38	47.1
Alkal(mg/L)	22	11.6	11.2	38.1	37.5	24.08
TOC(mg/L)	35.4	38.3	38.5	14.6	14.8	28.32
COD(mg/L)	325	96	98	246	248	202.6
BOD(mg/L)	71	62	63	86	88	74
DO(mg/L)	15	74	76	124	122	82.2
Turb(NTU)	0.9	8	7	24	22	12.38
TSS(mg/L)	4.7	38.6	38.7	12.2	12.6	21.36
TDS(mg/L)	3.6	88	87	25,6	25	45.8
EC(us/cm)	0.04	1.28	1.3	1.54	1.58	1.15
pH	5.98	5.4	5.22	4.85	4.87	5.26
Hardn(mg/L)	174	65	68	32	39	76.6

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 g/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400ʊSCm^1, T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010), FMEnv, 1991).

The temperature at this site was least in the month of November being 26.4 ^{0}C and highest in the month of January at a temperature of 26.9 ^{0}C, with a seasonal mean temperature of 26.64 ^{0}C . This report is close to that by Al-Musharafi *et al*; (2014).This result fell below the acceptable allowable temperature for surface water set by Federal

Ministry of Environment (FMEnv 1991) at 30-31 ^{0}C. The chloride ion concentration was highest in the month of February, 136 mg/l which was similar to Adekunle, (2009) and least in November, 93.0 mg/L,which was similar to Bhagirathi *et al*; (2012). The mean chloride concentration for the season was 111.0 mg/L. This result fell below the acceptable allowable chloride ion concentration for surface water set by Federal Ministry of Environment (FMEnv 1991) at 250 mg/L. The nitrate concentration had the highest concentration in the month of November (4.75 mg/L) and the least in December 2014 (0.43 mg/L), with a mean of (1.40 mg/L). These results are close to that obtained in Malawi by Phiri, *et al*; (2005). The readings obtained were all below the FMEnv and WHO set allowable standards of 50.0 mg/L. The phosphate ion concentration was highest in February 4.75 mg/L and least in January 0.894 mg/L, a seasonal mean of 2.47 mg/L. This result fell below the acceptable phosphate concentration for surface water (FMEnv 1991) of 250 mg/L.

The acidity was highest in the month of January 67.8 mg/L and lowest in November, 27.1 mg/L, with a seasonal mean of 47.1 mg/L. The was lowest in January, (11.2 mg/L) and highest in February,38.10 mg/L, with mean alkalinity of 24.08 mg/L. These results are similar to Bhagirathi *et al*; (2012) and is below FMEnv and WHO limit for surface water (100 mg/L). The Total organic carbon was highest in January, (38.5 mg/L) and least in February, (14.6 mg/L), with seasonal mean of 28.32 mg/L. Chemical oxygen demand (was highest in November, (325 mg/L) and least in December, (96.0 mg/l). The mean concentration was 202.60 mg/L. This result was above FMEnv and WHO limit of 10 mg/L. The biological oxygen demand was least in December, (62.0 mg/L) and highest March (88.0 mg/L), with a seasonal mean of 74.0 mg/L. These results are above FMEnv and WHO value of 6.0 mg/L. Dissolved oxygen ion concentration was least in November,(15 mg/L) and highest in March,

(122 mg/L) with a seasonal mean of 82.20 mg/L. These results are above FMEnv and WHO value of 7.5 mg/L. Turbidity ranged from 0.90 NTU value in November to 24.0 NTU in February, a seasonal mean of 12.38 NTU. This result was within the 50.0 NTU recommended by FMEnv and WHO for surface water. This result is similar to results obtained by Adekunle (2009).

The Total Suspended Solids (TSS) was highest in January, (38.7.mg/L), least in November (4.7 mg/L) with a seasonal mean of 21.36 mg/L. These results are close to outlined by Phiri, *et al*; (2005) and which was within the FMEnv and WHO limits for surface water of 30 mg/L . The Total Dissolved Solids (TDS) were highest in December, (88.0 mg/L) and least in November (3.6 mg/l), with a mean of 45.84 mg/L. These results were below the standards by FMEnv and WHO of 500 mg/L. The electrical conductivity (EC) value was least in November (0.04 µS/cm) and highest in March, 1.58 µS/cm, with a seasonal mean of 1.15 µS/cm and was below FMEnv and WHO limit of 500 µS/cm. The pH value was least in February, 4.85 and highest in November 5.98, with a mean of 5.26. These results were close to that obtained by Phiri, *et al*; (2005) . These results are acidic and can be detrimental to aquatic life. The Total Hardness (TH) of the site was least in February 32 mg/L and highest in Novenber 174 mg/L with a mean of 75.6 mg/L. Total hardness results were within the acceptable limits of 500 mg/L by FMEnv and WHO .

Table 4.9: Physicochemical   Properties of Water Sample for Aba River(ABT) 2014/15 Dry Season

Parameters	NOV	DEC	JAN	FEB	MAR	MEAN
Temp (°C)	28.3	28.5	28.5	28.8	27.4	28.3
Cl(mg/L)	119	139	141	166	162	145.4
NO_3^-(mg/L)	6.82	0.67	0.74	0.382	0.361	1.79
PO_4^{-3} (mg/L)	1.479	0.81	0.564	1.75	1.632	1.25
Acidity(mg/L)	242;6	93.2	95.3	60	63.1	110.84
Alkal(mg/L)	`10	16.5	16.7	53.1	52.5	29.76
TOC(mg/L)	51.8	40.1	42.1	42	43	43.8
COD(mg/L)	323	106	108	190	192	183.8
BOD(mg/L)	7.5	44	46	67	69	46.7
DO(mg/l)	25.2	35	34	78	76	49.64
Turb(NTU)	2.8	12	16	9	11	10.16
TSS(mg/L)	3.4	46.6	46.8	11.7	12.1	24.12
TDS(mg/L)	3.6	88	87	26.1	25.6	46.06
EC(us/cm)	0.02	1.61	1.56	3.11	3.09	1.88
pH	5.21	5.27	5.25	5.56	5.65	5.48
Hardn(mg/L)	83	66	64	30	28	54.2

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400ʊSC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010), FMEnv, 1991)

In Table 4.9 the temperature of the effluents at the ABT site ranged from 27.4 ^0C *in March to* 28.8 ^{0}C in February, and a mean value of 28.3 ^{0}C, this report is close to

that by Al-Musharafi *et al;* (2014), which result was below the WHO guide lines of (30-32 ^{0}C) for surface water and will be hazardous to the aquatic animals and plants. The chloride ion concentration ranged between 119 mg/L in November and 166 mg/L in February. The mean concentration of chloride ion was 145.41 mg/L for the season. These results are within the Federal Ministry of Environment (FMEnv, 1991) and WHO stipulated guide lines of 250 mg/L. The nitrate ion concentrations ranged from 0.361 mg/L in March to 6.82 mg/L in November, with a mean concentration of 1.79 mg/L. These results are within (FMEnv 1991) standards of 50 mg/L. The phosphate ion concentration ranged from 1.632 mg/L in March to 0.564 mg/L in January, with a mean of 1.25 mg/L for the season. PO_4^{-3}Total phosphate decreased from Nov to Jan, 1.479 mg/L to 0.564 mg/L, the low concentrations PO_4^{-3} indicates that the river was slightly disturbed at this station.

Alkalinity was observed to be lower than 100mg/L WHO set standard, and ranged from 10.0 mg/L in November to 53.1 mg/L in February with a mean of 29.76 mg/L**.** Acidity values ranged from 63.1 mg/L in March to 242.60 mg/L in November with a mean of 110.84 mg/L. The total organic carbon in the season at this site ranged from 40.1 mg/L in December to 51.8 mg/L in November, with the seasons mean of 43.8 mg/L. The values for the chemical oxygen demand was very high as compared to the accepted levels of 10mg/L. The COD results ranged between 323.0 mg/L in November to 106 mg/L in December. The mean for the season was 183.8 mg/L. These are within 120 mg/L limit by FMEnv 1991/WHO The biological oxygen demand had the highest value of 69 mg/L in March and the least value of 7.5mg/L in November with mean of concentration of 46.7 mg/L.These values were above WHO set standard of 6.0 mg/L. The turbidity values ranged from 2.8 ntu in October to 16 NTU in January. The mean turbidity in the season was 10.16 NTU. This result is

similar to some sites in that by Adekunle (2009).The results for the Total suspended solids was highest in January at (46.8 mg/L) and least in November at (3.4 mg/L). The seasons mean (TSS) was 24.12 mg/L and is above 10 mg/L limit set by FMEnv 1991/ WHO. The Total Dissolved Solids (TDS) had the highest value of 88.0 mg/l in December and the least value of 3.6 mg/L in November. The dry season average for (TDS) was 46.06 mg/L. as against 100 mg/L limit of FMEnv 1991/WHO.The TDS values were high in the months of December 88 mg/L and January 87 mg/L, if this water was used for irrigation it would ferment salinity problems similar results were recordedd by Shah,1999.

The Electrical Conductivity (EC) had the highest value of 3.11 µS/cm in February, while the least conductivity value was in November (0.02 µS/cm) with a seasonal mean of 1.88 µS/cm. The pH was least in the month of November (5 .21). This pH is strongly acidic and could cause stress to the aquatic life . The highest pH was 5.65 in the month of March and is above WHO/FMEnv limit of 6.5-8.5 safe a quatic sustenance of life. The pH at all the months for the season were outside the permissible limits, the effluents from the Abattoir having the highest pH in the month of March of 5.65 , this range of pH will adversely affect aquatic life due to its acidic nature. The highest total hardness for the river at the site was in the month of November of 83.0 mg/L and a least value of 28.0 mg/L in March. The seasonal mean hardness was 54.20 mg/L. The result is within the WHO limits of 500 mg/L .

Table 4.10 showed the result for physicochemical parameters in Aba river in the dry season at the DSAR site.

Table 4.10: Physicochemical Properties of Water Sample for Aba River (DSAR) 2014/15 Dry Season

Parameters	NOV	DEC	JAN	FEB	MAR	MEAN
Temp(^{o}C)	27.3	27.4	27.3	27.6	27.5	27.42
Cl (mg/L)	106	101	103	157	158	12.5
NO_3^-(mg/L)	21.3	21.5	21.3	1.88	3.54	13.9
PO_4^{-3}(mg/L)	1.45	1.54	1.56	3.48	3.47	2.3
Acidity(mg/L)	160.3	95	93	67.8	67.5	96.72
Alkal(mg/L)	32	10.3	10.5	10.75	10.81	14.87
TOC(mg/L)	35.6	43.5	43.2	23.8	23.7	33.96
COD(mg/L)	232	115	113	132.1	130.02	144.42
BOD(mg/L)	8.36	51	52	92	93	59.27
DO(mg/l)	25	42	43	103	102	63
Turb(NTU)	1.1	16	14	33	32	19.22
TSS(mg/L)	3.95	56.9	56.8	22.9	22.7	32.65
TDS(mg/L)	3.8	87	88	26	25.6	46.08
EC(us/cm)	0.02	1.34	1.33	1.96	1.94	1.32
pH	5.8	5.99	6	6.03	6.05	5.97
Hardn(mg/L)	50	50.9	50.8	59.4	59.2	54.06

(WHO)Temp=25^0C,.0,Turb=50.0ntu,pH=6.58.5,Cl=250Acidity=mg/L,TOC=mg/L,NO_3=45 mg/L,PO_4=250,COD=10mg/L,BOD=6.0mg/L,DO=6.0mg/L,TDS=1000mg/L,EC=1400$_U$SC m[1], T/Hardn=500mg/L, Alkan=30mg/L, (WHO, 2008, EPA (2010), FMEnv, 1991).

The temperature at this site was least in the months of November 27.3 ^{0}C with highest in the month of February at a temperature of 27.6 ^{0}C with a seasonal mean temperature of 27.42 ^{0}C. These results were below the acceptable temperature for surface water set by Federal Ministry of Environment (FMEnv 1991) at 30-31 ^{0}C. This temperature range was abnormal for sustenance aquatic life. The results are close to that by Al-Musharafi et al;(2014); Bhagirathi et al; (2012). The chloride ion

concentration was highest in the month of March (158 mg/L) and least in December at 101 mg/L. The mean chloride concentration for the season was 125.0 mg/L. The nitrate ion concentration had the highest concentration in the month of December, (21.5 mg/L) and the least in February, 1.88 mg/L with a mean of 13.9 mg/L.The results obtained were all below the FMEnv and WHO standards of 50.0 mg/L. The phosphate ion concentration was highest in February,3.48 mg/L and least in the month of November 1.45 mg/L with a seasonal mean of 2.30 mg/L. These results are close to that by Phiri, *et al*; (2005).The results are within the standards by Federal Ministry of Envirosultnment (FMEnv 1991) of 250 mg/L .The acidity value was recorded highest in the month of November (160.3 mg/L) and lowest in March (67.5 mg/L), a seasonal mean of 96.72 mg/L. The alkalinity was lowest in December 10.30 mg/L and highest in November 32.0 mg/L, with a seasonal mean alkalinity of 14.87 mg/L, which value is below FMEnv and WHO limit for surface water at 100 mg/L.

The Total organic carbon was highest in Dec 43.5 mg/L and least in March 23.7 mg/L, with a seasonal mean of 33.96 mg/L. Chemical oxygen demand was highest in October 232 mg/L and least in January 113 mg/L. The mean concentration was 144.42 mg/L. The results at this site were above FMEnv and WHO set limit of 10mg/L for the season. The biological oxygen demand was least in November 8.36 mg/L and highest February 92.0 mg/L, with a seasonal mean of 59.27 mg/L. These results are above FMEnv and WHO set value of 6,0 mg/L. Dissolved oxygen ion concentration was least in November (25.0 mg/L) and highest in February (103 mg/L), with a seasonal mean of 63.0mg/L, (which results are above FMEnv and WHO set value of 7.5mg/l). Turbidity ranged from 1.10 NTU least value in November to 33 NTU in February, with a seasonal mean of 19.22 NTU. This result was within 50 NTU the FMEnv and WHO limit for surface water (50.0NTU). The Total Suspended Solids

(TSS) was highest in January,56.9 mg/l and least in November 3.95 mg/L, with a mean of 32.65 mg/L. These results are close to that obtained in Malawi by Phiri, *et al*; (2005). These results are within limit by FMEnv and WHO limit of 30 mg/L. The Total Dissolved Solids(TDS) were highest in January(88.0 mg/l) and least in November (3.8 mg/L),with a mean of 46.08 mg/L. These results were below the limits set by FMEnv and WHO of 500 mg/l.The electrical conductivity was least in November (0.02 µS/cm) and highest in February (1.96 µS/cm) with a seasonal mean of 1.32 µS/cm. The results are below FMEnv and WHO limit of 500µS/cm. The EC in this station was observed low, it seems the run off did not bring in much ions from the fertilized farms such as : NO_3^{-1},PO_4^{-3},Cl^{-1} as compared to that in the rainy season.

The pH was least in November 5.8 and highest in March 6.05, with a mean of 5.97. These results were below FMEnv and WHO limit of 6.5-8.5. This pH is abnormal for healthy life of the aquatic animals and plants. The total hardness of the site was least in November 50.0 mg/L and highest in February 59.40 mg/L with a mean of 54.06 mg/L. These results were within the acceptable limits 200 mg/L and 500mg/L set by FMEnv and WHO respectively. The values in total hardness followed a common trend which did not vary much at the stations over the period.

The pollution index of physicochemical parameters for raining season are shown in table 4.11 while that of dry season are shown in table 4.12.

Table 4.11: Pollution Index of water from Aba River (Rainy Season)

Site/Time	March	April	May	June	July	August	September	October	Mean
USAR	2.4562	5.833	2.443	2.0057	2.1755	2.5105	2.5262	3.3997	2.9195
NBL	1.9747	0.9902	1.9455	2.0043	1.7789	2.2128	2.2228	2.4818	1.9513
PZ	2.6138	2.0591	2.112	2.0507	2.0596	2.3943	1.5352	3.9968	2.3527
ABT	2.6353	2.5059	2.5026	3.1544	3.1264	2.9573	2.9803	1.3764	2.6548
DSAR	1.8233	2.8696	2.8489	2.0185	2.5687	2.4621	2.4407	1.0656	2.3247

The pollution index of physicochemical parameters at the USAR site for the rainy season ranged from the highest in the month of April (5.833) to the least in June (3.0057), with a seasonal mean of 2.9195. The pollution index of the river was about six times the accepted WHO/FMEnv standard of 1.0. The river was near dead and was not suitable for healthy living as surface water. The results are within WHO/FMEnv, standards.

At the NBL site in this season of the rain, the pollution index ranged from (0.9903) in April the least to the highest in October (2.4818) with a seasonal mean of 1.9513. The pollution index indicated a healthy water body at this site for the of April, but the river deteriorated with passage of months and climaxed in decay by the month of October. With this result the river was not safe for human consumption. The seasonal value points to the possible recovery of river down stream.

The pollution index of the river at the PZ site was highest in the month of October (3.9968)to the least in September (1.5352), with seasons mean of 2.3527, which indicates that the river was not recovering as the pollution index doubled within a two month interval (September to October,2014).

The ABT site had the highest pollution index in the month of June (3.1544) and the least in the month of October (1.3764) with a seasonal mean of 2.6548. The mean pollution index was pointing at a river in the recovering trend, as was confirmed by the pollution index in October. Should the river continue with this trend the water body would have an index within the WHO/FMEnv standards 1 or <1.

The pollution index at the DSAR site in the rainy season ranged from the highest in the month of April (2.8696) to the least in October (1.0656) with a seasonal mean of 2.8696. The seasonal mean is pointing at this site of a recovering river and this proved by the pollution index of month October. Taking a look at the pollution index values down the river from October at the (DSAR) site suggesting to a river near complete recovery as the pollution index is pointing towards 1.0 or < 1.0. A trend of decreasing potential index was observed: USAR> PZ >ABT>DSAR >NBL. The potential index values are: USAR=2.0057; NBL=0.9902; PZ=1.5352; ABT=1.3764 and DSAR=1.0656>1.0 These results differed from the reports of Ekiye *et al., (*2010); Aleksander-Kwaterczak and Ciszewski (2012).

Table 4.12:Pollution Index of water from Aba River (Dry Season)

Site/Time	November	December	January	February	March	Mean
USAR	3.4283	2.6066	1.3969	2.4724	2.4562	2.471
NBL	2.4732	3.361	3.3788	2.2803	1.9747	2.6936
PZ	4.003	2.3489	2.3661	2.6016	2.6138	2.7867
ABT	1.5775	2.613	2.5747	2.7608	2.6353	2.4323
DSAR	2.4291	2.2556	2.2708	2.7055	1.8232	2.2968

The pollution index of physicochemical parameters at the USAR site for the dry season ranged from the highest in the month of November (3.4283) to the least in January (1.3969), with a seasonal mean of 2.471.The pollution index of the river was about three and half times the accepted WHO/Env standard of 1.0. The river was not suitable for use as surface water. These results are not within WHO/ Env, standards. The mean pollution index at this site indicating a state of decay with a possibility of early recovery as the January pollution index points.

At the NBL site in this dry season, the pollution index ranged from (1.9747) in March the least to the highest in December(3.361) with a seasonal mean of 2.6936. The pollution index indicated a slightly healthy water body at this site in the of March but the river deteriorated rapidly with passage of months and climaxed in decay by the month of December. The mean seasonal pollution index indicated a tendency to this effect which was confirmed by December results. With this result the river was not safe at this site for human consumption and aquatic life will be badly affected.

The pollution index of the river at the PZ site ranged least in the dry season by the month of December (2.3489) to highest in November (4.003), with a seasons mean of 2.7867. The pollution index of the river at this was observed as about four times the WHO/FMEnv standards for surface water. The seasons' mean indicating that the river was deteriorated at this site. The river though heavily polluted was recovering as the pollution index halved within a two month interval (November to December).

The dry season pollution index of the river at the ABT site was highest in the month of February (2.768) and least in the month of November (1.5775) with a seasonal mean of 2.4323. The pollution index of the river had exceeded the

WHO/FMEnv standards by about two and half times. The pollution index of this river at this site has a strong indication of possible early recovery as the pollution index decreased appreciably considering the results of February and November.

The pollution index at the DSAR site in the dry season ranged from the highest in the month of February (2.7055) to the least in March (1.8232) with a seasonal mean of 2.2968. The seasonal mean is pointing at this site of a recovering river and this proved by the pollution index of month March. Taking a look at the pollution index values down the river over the period of the dry season presented a trend of decreasing pollution index values PZ=4.003>USAR=3.423>NBL=3.361> ABT=2.768>DSAR= 2.7055 . The river was healing from decay as the pollution index rightly suggests. The dry season pollution index values exceeded the rains due to the possibilities of some factors which may have direct effects on the pollutant. The case of industries releasing high oxygen demanding wastes into the river at or near time of sampling. The case of heavy storm washing away the industria l wastes released by the factory that contain the pollutants. These results differed from the reports of Indeksciniri *et al;* (2012).

Concentrations of heavy metals in water samples from Aba River are outlined on tables 4.13 to 4.18.

Table 4.13 Concentration of Heavy Metals in Water Samples from Aba River: June/July 2014

Metal/Site	USAR	PZ	NBL	ABT	DSAR
Cu(mg/L)	0.026	0.01	0.01	0.025	0.08
Cd(mg/L)	0.129	0.011	0.001	0.001	0.01
Fe(mg/L)	0.329	0.365	0.092	8.725	1.947
Cr(mg/L)	0.036	0.044	0.302	0.128	0.068
Zn(mg/L)	0.001	0.032	0.0026	3.7414	0.015
Ni(mg/L)	0.01	0.074	0.039	0.106	0.028
Pb(mg/L)	0.112	0.24	0.14	0.14	0.001
Mn(mg/L)	0.038	0.039	0.095	3.173	0.215

(WHO)Cu=10.0,Cd=0.02,Fe=0.3,Cr=0.05,Zn=5.0,Ni=0.02,Pb=0.05,Mn=0.5mg/L

The concentration of heavy metals in the months of June/July 2014 were at maximum for Cu (0.08 mg/L) at DSAR, Cd (0.129 mg/L) at USAR, Fe (8.725 mg/L) at ABT, Cr (0.302 mg/L) at NBL, Zn (3.744 mg/L) at ABT, Ni (0.106 mg/L) at ABT, Pb (0.24 mg/L) at PZ, and Mn (3.173 mg/L) at ABT; minimum values of Cu (0.01 mg/L) at PZ,Cd (0.001 mg/L) at ABT,Fe (0.072 mg/L) at NBL, Cr (0.036 mg/L) at USAR,Zn (0.001 mg/L) at USAR, Ni (0.01 mg/L) at USAR, Pb (0.001 mg/L) at DSAR, Mn (0.038 mg/L) at USAR. These results are similar to the reports in China by Yongzhong *et al* (2010).

Table 4.14: Concentration of Heavy Metals in Water Samples from Aba River Aug/Sept 2014

Metal/Site	USAR	PZ	NBL	ABT	DSAR
Cu(mg/L)	0.019	0.071	0.032	0.026	0.058
Cd(mg/L)	0.025	0.024	0.02	0.018	0.001
Fe(mg/L)	0.01	0.01	0.001	0.01	0.119
Cr(mg/L)	0.372	0.001	0.001	0.84	0.001
Zn(mg/L)	0.001	0.0314	0.0028	0.0106	0.0118
Ni(mg/L)	0.013	0.061	0.021	0.1	0.025
Pb(mg/L)	0.118	0.27	0.19	0.06	0.12
Mn(mg/L)	0.001	0.001	0.001	0.001	0.001

(WHO)Cu=10.0,Cd=0.02,Fe=0.3,Cr=0.05,Zn=5.0,Ni=0.02,Pb=0.05,Mn=0.5mg/L.

The concentration of heavy metals in the months of Aug/Sept 2014 were at maximum for Cu (0.071 mg/L) at PZ, Cd (0.025 mg/L) at USAR, Fe (0.119 mg/L) at DSAR,Cr (0.84mg/L) at ABT, Zn (0.034 mg/L) at PZ, Ni (0.061 mg/L) at PZ, Pb (0.27 mg/L) at PZ, and Mn (0.001 mg/L) at all sites. Minimum values were obtained for Cu (0.019 mg/L) at USAR, Cd (0.001 mg/L) at DSAR, Fe (0.001 mg/L) at NBL, Cr (0.001 mg/L) at NBL/DSAR, Zn (0.001 mg/L) at USAR, Ni (0.01 mg/L) at ABT, Pb (0.06 mg/L) at ABT, Mn (0.011 mg/L) at all the sites. These results are similar to the reports by Yongzhong *et al* ; (2010); Rossmann and Barres (1992).

Table 4.15: Concentration of Heavy Metals in Water Samples from Aba River Oct/Nov 2014

Metal/Site	USAR	PZ	NBL	ABT	DSAR
Cu(mg/L)	0.019	0.01	0.01	0.01	0.01
Cd(mg/L)	0.106	0.001	0.001	0.001	0.001
Fe(mg/L)	2.039	0.01	4.4	3.125	5
Cr(mg/L)	0.001	0.001	0.001	0.001	0.0116
Zn(mg/L)	0.1	0.318	0.003	0.0108	0.0116
Ni(mg/L)	0.019	0.051	0.003	0.1	0.089
Pb(mg/L)	0.529	0.329	0.125	0.215	0.235
Mn(mg/L)	0.224	0.175	0.179	0.22	0.217

WHO)Cu=10.0,Cd=0.02,Fe=0.3,Cr=0.05,Zn=5.0,Ni=0.02,Pb=0.05,Mn=0.5mg/L

The concentration of heavy metals in the months of Oct/Nov 2014 were at maximum for Cu (0.019 mg/L) at USAR, Cd (0.106 mg/L) at USAR, Fe (4.42mg/L) at NBL, Cr (0.116 mg/L) at DSAR, Zn (0.002 mg/L) at NBL, Ni (0.089 mg/L) at DSAR, Pb (0.529 mg/L) at USAR, and Mn (0.224 mg/L) at USAR. Minimum values were obtained for Cu (0.01 mg/L) at PZ,Cd (0.016 mg/L) at all the sites, Fe (0.435 mg/L) at USAR, Cr (0.15 mg/L) at USAR, Zn (0.01 mg/L) at NBL; Ni (0.09 mg/L) at PZ, Pb (0.13 mg/L) at NBL, Mn (0.038 mg/L) at NBL. These results are similar to the reports by Yongzhong *et al;* (2010).

Table 4.16: Concentration of Heavy Metals in Water Samples from Aba River Dec2014/Jan 2015

Metal/Site	USAR	PZ	NBL	ABT	DSAR
Cu(mg/L)	0.052	0.01	0.01	0.01	0.055
Cd(mg/L)	0.119	0.059	0.018	0.034	0.071
Fe(mg/L)	11.928	7.218	7.069	10.946	10.366
Cr(mg/L)	0.359	0.018	0.018	0.145	0.164
Zn(mg/L)	0.01	0.018	0.0163	0.014	0.01
Ni(mg/L)	0.01	0.023	0.01	0.018	0.011
Pb(mg/L)	0.11	0.16	0.32	0.44	0.291
Mn(mg/L)	0.249	0.119	0.157	0.301	0.216

(WHO)Cu=10.0,Cd=0.02,Fe=0.3,Cr=0.05,Zn=5.0,Ni=0.02,Pb=0.05,Mn=0.5mg/L

The concentration of heavy metals in the months o f Dec2014/Jan 2015 were at maximum for Cu (0.0550 mg/L) at DSAR, Cd (0.1190 mg/L) at USAR, Fe (11.9280 mg/L) at USAR, Cr (0.3590 mg/L) at USAR, Zn (0.0118 mg/L) at PZ, Ni (0.0230 mg/L) at PZ, Pb (0.440 mg/L) at ABT, and Mn (0.2490 mg/L) at USAR. Minimum values were obtained for Cu (0.01 mg/L) at all sites, Cd (0.018 mg/L) at NBL, Fe (7.069 mg/L) at NBL, Cr (0.018 mg/L) at PZ/NBL, Zn (0.01 mg/L) at USAR/DSAR; Ni (0.01 mg/L) at NBL, Pb(0.11 mg/L) at USAR, Mn (0.119 mg/L) at PZ. These results are similar to the reports in Yongzhong *et al* ; (2010).

Table 4.17: Concentration of Heavy metals in Water Samples from Aba River Feb/Mar 2015

Metal/ Site	USAR	PZ	NBL	ABT	DSAR
Cu (mg/L)	0.0760	0.0100	0.0030	0.0100	0.0100
Cd(mg/L)	0.2650	0.0680	0.0140	0.0190	0.0100
Fe(mg/L)	0.8200	0.7640	1.1180	2.0790	2.6510
Cr(mg/L)	0.1000	0.1000	0.1100	0.1160	0.1810
Zn(mg/L)	0.1718	0.0280	0.0160	0.0391	0.0531
Ni(mg/L)	0.0240	0.0280	0.0030	0.0290	0.0160
Pb(mg/L)	0.3400	0.1700	0.1800	0.1900	0.1850
Mn(mg/L)	0.1110	0.1380	0.0310	0.1540	0.1250

WHO)Cu=10.0,Cd=0.02,Fe=0.3,Cr=0.05,Zn=5.0,Ni=0.02,Pb=0.05,Mn=0.5mg/L

The concentration of heavy metals in the months of Feb/Mar 2015 were at maximum for Cu (0.0760 mg/L) at USAR, Cd (0.2650 mg/L) at USAR, Fe (2.6510 mg/L) at DSAR, Cr (0.1810 mg/L) at DSAR, Zn (0.1715 mg/L) at USAR, Ni (0.0290 mg/L) at ABT, Pb (0.3400 mg/L) at USAR, and Mn (0.1380 mg/L) at PZ. Minimum values were obtained for Cu (0.01 mg/L) at ABT/DSAR, Cd (0.0100 mg/L) at DSAR, Fe (0.7640 mg/L) at PZ, Cr (0.1000 mg/L) at USAR/PZ, Zn (0.0160 mg/L) at NBL; Ni (0.0030 mg/L) at NBL, Pb (0.1700 mg/L) at PZ, Mn (0.0310 mg/L) at BL.These results are similar to the reports by Yongzhong *et al.,*(2010).

Table 4.18: Concentration of Heavy Metals in Water Samples from Aba River Apri/May 2015

Metal/Site	USAR	PZ	NBL	ABT	DSAR
Cu(mg/L)	0.035	0.01	0.03	0.022	0.048
Cd(mg/L)	0.13	0.06	0.016	0.016	0.075
Fe(mg/L)	0.435	0.46	0.913	1.925	1.874
Cr(mg/L)	0.1	0.15	0.125	0.119	0.104
Zn(mg/L)	0.15	0.09	0.019	0.043	0.082
Ni(mg/L)	0.015	0.09	0.011	0.018	0.014
Pb(mg/L)	0.26	0.38	0.134	0.175	0.138
Mn(mg/L)	0.114	0.15	0.038	0.151	0.121

WHO)Cu=10.0,Cd=0.02,Fe=0.3,Cr=0.05,Zn=5.0,Ni=0.02,Pb=0.05,Mn=0.5mg/L

The concentration of heavy metals in the months of Apr/May 2015 were at maximum for Cu (0.0480mg/L) at DSAR, Cd (0.13000 mg/L) at USAR, Fe (1.9250 mg/L) at USAR, Cr (0.1000 mg/L) at USAR, Zn (0.1500 mg/L) at USAR, Ni (0.0110 mg/L) at NBL, Pb (0.3800 mg/L) at PZ, and Mn (0.1510 mg/L) at ABT. Minimum values of Cu (0.01mg/L) at PZ, Cd (0.0600 mg/L) at PZ, Fe (0.4350 mg/L) at USAR, Cr (0.1500 mg/L) at USAR, Zn (0.0190 mg/L) at NBL; Ni (0.0900 mg/L) at PZ, Pb (0.1340 mg/L) at NBL, Mn (0.031 mg/L) at NBL. These results are similar to the reports by Widdelkoop (2000).

4.2 POLLUTION INDEX OF HEAVY METALS

The pollution index of heavy metals from Aba River water for the Rain and Dry season 2014/2015.

Table 4.19 Pollution index of heavy metals from Aba River water for the Rainy

Site/Time	MAR	APR	MAY	JUNE	JULY	AUG	SEPT	OCT	MEAN	Stdev
USAR	2.4988	3.3904	2.4327	1.3203	1.3182	1.5528	2.5059	3.9886	2.3760	2.0765
PZ	2.5986	2.2397	2.4324	1.3500	1.3178	2.2874	2.2297	4.0626	2.3148	1.5197
NBL	2.206	2.5212	2.6312	1.9193	1.4184	3.9506	3.9868	2.4247	2.8230	2.1469
ABT	2.6921	2.7602	2.7725	2.2651	2.1807	2.8847	2.9272	2.6807	2.6454	0.5975
DSAR	4.2921	4.4028	4.0966	1.7407	1.6761	2.6067	2.4735	2.3839	2.9591	2.7680

season 2014/2015

USAR: The least pollution index value at this site for the rainy season was 1.3182 in the month of July. The pollution index was slightly above the WHO set standard of 1.0 by 0.318it of 2 which could be as a r esult of influx of heavy rain that carries pollutants to the site .The highest value was 3.9886 in the month of October. The high values could result from high concentration of pollutants reaching the site from near pollutant sources such as construction sites, abattoirs or even hot water from processing plants. The pollution index value exceeded WHO set standard by about four times. A seasonal mean pollution index of 2.3760 and standard deviation of 2.0765 was obtained in the period.

PZ: The pollution index of heavy metals on Aba river water was highest at the PZ site in the month of October with a value of 4.0626 **.** This high value was about four times

WHO set standard. This may result from poorly treated industrial effluents, pollutants reaching the river through industrial waste waters and the effects of toxic/ hazardous wastes discharged into the river indiscriminately. The least value of the pollution index of 1.3178 was recorded in the month of July. This value indicates that industrial effluents entering the river may have received a better treatment to have brought the value to near WHO set limit of 1.0 for surface water. A seasonal mean of 2.3148 was recorded with a standard deviation of 1.5197 for the period.

NBL: The highest recorded pollution index value of 3.9868 was obtained at this site in month of September. This may be reflection of the ill treated industrial wastes reaching the river from the industries. Pollutants which may include particles of food, solutions of reagents discarded at end research analyses, blood samples used as specimen. This low pollution index 1.4184 recorded can attributed to some factors which may include improved effluent discharge treatment plants installed. This value indicates a recovering river. A seasonal mean of 2.8230 and a standard deviation of 2.1469 was recorded at this site.

ABT: At this station the highest pollution index value of 2.9272 in the month of September while the lowest pollution index was 2.1807 for the month of July, with a seasonal mean of 2.1807. A standard deviation of 0.5975 was obtained for the rainy season. The high index value may have come around by the undiminished presence of pollutants generated from washings of meat slaughtered.

DSAR: The pollution index of the river was highest in the month of April with a value of 4.4028 and lowest value of 1.6761 for July. A seasonal mean of 2.9591 and a standard deviation of 2.7680 was recorded in the season. The high index value recorded may have been brought about by the influx of anthropogenic activities that

heralded the season. Such activities may have come from much car washes , home washings, dredging activities and toxic /hazardous chemicals from phaemacetical operations. The high pollution index value was in excess of the WHO/FMnEnvr set standard by about four and half times. This is an indicate on of heavy impartation of the river by the effluents that were discharged uncontrolled and indiscriminately. This study is not similar to that by Alcubugwo *et al;* (2012).

Table 4.20 Pollution index of heavy metals from Aba River water for the Dry season 2014/2015.

SITE/TIME	NOV	DEC	JAN	FEB	MEAN	STDev
USAR	1.9814	2.5128	1.4226	2.4532	2.0925	1.5619
PZ	4.0768	2.3107	2.3396	2.5268	2.8135	2.5267
NBL	2.4003	3.2111	3.3788	2.2534	2.8109	1.9362
ABT	2.7960	2.5772	2.6828	2.6952	2.6878	0.2313
DSAR	2.3088	2.1844	2.2624	4.2313	2.7468	2.9091

USAR: The least pollution index value at this site for the dry season was 1.4226 in the month of January. The pollution index was slightly above the WHO set standard of 1.0 by 0.4226 units. The highest value was 2.5128 in the month of December. The high values could result from high concentration of pollutants reaching the site from near pollutant sources such as dump sites, meat shop washings or even cold water from processing plants and hospitals. The pollution index value exceeded WHO set standard by about two and half times. A seasonal mean pollution index of 2.0925 and standard deviation of 1.5619 was obtained in the period.

PZ: The pollution index of heavy metals on Aba river water was highest at the PZ site in the month of November with a value of 4.0768. This high value was about four times WHO set standard. This may result from poorly treated industrial effluents, pollutants reaching the river through industrial waste waters and the effects of toxic/hazardous wastes discharged into the river indiscriminately. The least value of the pollution index of 2.3107 was recorded in the month of December. This value indicates that industrial effluents entering the river needed a better treatment to bring down the value to near WHO set limit of 1.0 for surface water. A seasonal mean of 2.8135 was recorded with a standard deviation of 2.5267 for the period.

NBL: The highest recorded pollution index value of 3.3788 was obtained at this site in month of January. This may be reflection of the industrial wastes reaching the river from the industries. Pollutants may involve solutions of reagents, discarded solutions. This least pollution index 2.2534 was recorded for the site in the season. None installation of waste treatment plants leads to poor quality effluents discharged into rivers. This value indicates a recovering river. A seasonal mean of 2.8109 and a standard deviation of 1.9362 was recorded at this site.

ABT: At this station the highest pollution index value of 2.7960 in the month of November while the lowest pollution index value was 2.5772 for the month o f December, with a seasonal mean of 2.6878. A standard deviation of 0.2313 was obtained for the rainy season. The high index value may be caused by the undiminished presence of pollutants generated from washings of meat slaughtered, and animal feed / washings.

DSAR: The pollution index of the river was highest in the month of February with a value of 4.2313 and lowest value of 2.1844 for December. A seasonal mean of

2.7468 and a standard deviation of 2.9091 was recorded in the season. The high index value recorded may have been brought about by the influx of anthropogenic activities that heralded the season. Such activities may have come from much car washes, home washings, dredging activities, painting of homes and toxic /hazardous chemicals from hospital operations. The high pollution index value was in excess of the WHO/FMnEnvr set standard by about four times. This is an indication of heavy impartation of the river by the effluents discharged into it. The water quality reports ar e similar to Amadi (2012); Akpabio and Ekpo (2013).

4.3 BIO-CONCENTRATION FACTORS OF TRACE METALS IN TISSUES OF *Eichhnor crassipes* (Water Hyacinth)

Bio-accumulation Factor on *Eichhnor crassipes* (Water Hyacinth) leaf

The bio-accumulation of metals on water hyacinth leaf from Aba river are outlined in Tables 4.21-4.25 for the months of June 2014 to May 2015.

Table 4.21: Bio-concentration of heavy metals on *Eichhnor crassipes*leaf (Water hyacinth) leaf in Aba River June/July 2014

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	12.957	2.508	0.3145	0	167.737	3897.9	1	2.3577
NBL	66.8043	0	3.3	0.7143	48.5368	121.154	1.4872	1.02
PZ	18.9808	0	1.2364	0.5	125.4359	37.9063	0.4459	7.35
ABT	0.3053	0	8.2	2.4285	0.6313	1.3402	0	1.548
DSAR	31.1315	0	0.95	300	10	234.43	3.1785	1.76

The bio concentration of heavy metals on *Eichhnor crassipes* leaf (Water hyacinth) among the sites investigated in months of Jun/July 2014 (Table 4.21), showed that Chromium metal was most bio accumulated at the ABT site on the plant leaf, with variance value of 1.2580 and 7.3871 respectively. The analysis of variance between sample with F calculated 1.0207 and F critical 2.7141. F calculated within sample test analysis 1.2084 and F critical of 2.3593 respectively (Appendix VI). The concentrations of heavy metals on the leaf are in appendix A2A. The above results were accepted as true values. Product moment correlation coefficient analysis on metal to metal bio concentrations proved that Cr had positive correlations with Mn and Zn of 0.7417, 0.9986 respectively. Ukiwe *et al.,* (2008) had similar results.

The bio-concentration activities at ABT had no positive correlations with the bio-concentration activities at the other four sites. Bio-concentration trend of heavy metals on *Eichhnor crassipes* leaf, at the ABT site followed the trend. Zn>Fe>Cu>Cr>Cd>Ni>Mn>Pb.

Zn = 9695 > 0.0535 mg/kg; Fe = 365.6 > 0.2757 mg/kg, Cu = 342 > 0.0294 mg/kg; Cr = 194 > 0.00 mg/kg; Cd = 143 > 0.486 mg/kg, Ni = 45.0 > 0.00 mg/kg; Mn = 26.43 > 0.0678 mg/kg; Pb = 6.8667 > 0.2159 mg/kg. Aerosols cause heavy metal contamination of Cr, Cd, Pb, Zn, Ni in soil through atmospheric deposition, which are consequently absorbed and bio-accumulated by plants or get adsorbed on aerial surfaces of the plants (Temmerman and Hoenig, 2004). Using the metal-accumulating plants to remove metals from contaminated soils has been proposed because of environmental-friendliness and cost benefits of phyto-remediation (Cunningham *et al*., 1995).

Table 4.22: Bio-concentration of heavy metals on *Eichhnor crassipes*leaf (Water hyacinth) leaf in Aba River Aug/Sept 2014

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	2675.1	4.4252	9.32	0	7418	804.8	71.8462	7.2842
NBL	4113	0	0.005	1.4737	4715	37.446	5.333	1.3063
PZ	591.8	131.5	0.3875	0.5025	3675	19.8758	4.7541	0.5281
ABT	365.6	0	0.4861	0.6667	2643	181.519	0	2.3923
DSAR	171.554	0	8.1	1.25	3621	104.613	0	0.4931

Of all the heavy metals investigated in the month of Aug/Sept 2014, Pb was the most prevalent heavy metal that bio accumulated on the leaf at the ABT station with variance of 7.2144 and 838911.5164 respectively. The analysis of variance between samples gave F calculated as 2.0785 and F critical as 2.7141. Soleimani*et a.,l*(2009; and Ukiwe,*et al* (2010) had similar results, whereas Wislocka (2006) demonstrated bio-concentrations of varied heavy metals in three plants (*Salix caprea L., Betula pendula Roth*.) and a shrub (*Rubus idaeus L.*). For this study, within samples calculation gave F as 17.1294 and F critical as 2.3593. With this result the analysis was rejected for within samples**.**

Product moment correlation co−efficient analysis indicated that the bio-accumulation of Pb on the leaf had no positive correlations with the other metals, (Table 4.28). ABT had appositive correlation with the activities at the DSAR site with a correlation of 0.9955 (Appendix VII). Heavy metal bio-concentration profile on *Eichhnor crassipes* leaf at ABT

site followed the order Zn>Fe>Cu>Cr>Cd>Ni>Mn> Pb which is Zn=9695>0.0535mg/kg; Fe=365.6>0.2757mg/kg; Cu=342>0.0294mg/kg; Cr=194>0.00mg/kg; Cd=143>0.486mg/kg; Ni=45.0>0.00mg/kg; Mn=26.43>0.0678mg/kg and Pb= 6.8667>0.2159mg/kg respectively. Pb accumulation by plants depends on Pb phyto-availability in soil. Phyto-availability of heavy metals is also depending on soil characteristics (Jesper and Jensen, 1998). The amount of accumulated Pb in shoots could be related to plant type, soil properties and soil Pb content (Begonia *et al*., 2005). In a related study the Correlation coefficient of Pb in roots vs. shoots of r = 0.93 was obtained by Soleimani *et al;* (2009).

Table 4.23: Bio-concentration of heavy metals on *Eichhnor crassipes*leaf (Water hyacinth) leaf in Aba River Oct/Nov 2014

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	12.055	766.6	2.481	0.529	34.7254	4138.9	472	26.31
NBL	1.2402	0	26	86.667	24.391	115	0.733	258
PZ	2.316	256	63	0.1829	18.3943	1841.4	160	172
ABT	1.3162	194	143	4.1418	14.9364	9695	45	342
DSAR	15.6994	88	147	0.0043	1589.86	4594.7	0.1124	239

The bio-concentration on the plant leaf signified that NBL was most affected by the metal Fe with variance factor of 7971.596 and 46.8817 for the PZ site and metal Fe respectively.The plant was most affected by the metal Fe at NBL site. Fruzinska (2011); Hernández-Castro *et al.,*(2015) had similar results showing the bioaccumulation of heavy metals in plant tissues.

This result when considered with analysis of variance upon the calculation of F for the between samples were F calculated was 1.0788 and critical F was 2.7141 which made for the acceptance of the result. This again was considered for within samples and the F calculated was 5.6967 while F critical was 2.3593. The result was rejected for the within samples.

Some level of relationships were observed to have existed with the element to element as investigated on the product moment correlation.Fe correlated with Mn of value 0.7552. On site to site analysis no correlations were observed between the leaves at NBL site and the other sites. Heavy metal bio-concentration profile on *Eichhnor crassipes* (water hyacinth) leaf at NBL site were Fe>Cr>Mn>Cu>Zn>Cd>Ni>Pb. The heavy metal concentrations are shown in order of decreasing magnitude per heavy metal.

Fe = 591.8 > 0.1288 mg/kg; C r= 256.0 > 0.035 mg/kg; Mn = 125.4309 > 0.034 mg/kg; Cu = 172 > 0.112 mg/kg; Zn = 37.9063 > 0.0063 mg/kg; Ni = 4.75 > 0.107 mg/kg ; Cd = 2.066 > 0.3875 mg/kg; Pb = 4.25 > 0.00 mg/kg. The work of Hernandez-Castro *et al.,* (2015) are similar to this study. The accumulation ratios of Mn in the leaves of *B. pendula* (1.04–9.56) from t he investigated areas were higher than the mean value (0.1) for various species of plants reported by kabata-Pendias and Pendias, (1993), which result was similar to this report. Relatively high concentrations of Mn (182 to 949 mg

/kg-1d.w.) and accumulation ratios (1.24 to 3.62) were noted in the leaves of *R. idaeus*. However, the leaves of S. caprea contained a low level of this metal 26.7 to 286 mg kg/d.w. Alvarez, *et al*; (2003) and Vandecasteele, *et al*., (2004) observed that *Salix atrocinerea* and *Salix cinerea* were capable of accumulating Mn at contaminated sites.

Table 4.24: Bio-concentration of heavy metals on *Eichhnor crassipes*leaf (Water hyacinth) in Aba River Dec 2014/Jan. 2015

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	2.4533	0.5263	0.3826	0	0.0265	0.0076	0.026	0.1238
NBL	0.2032	0.0543	1.125	20	0.0411	0.0053	0.0446	0.041
PZ	1.0721	0.0277	1.4048	4	0.0244	0.0067	0.1411	0.0163
ABT	1.2976	0.0526	0.2429	1.375	0.0977	0.0535	0.0526	0.0294
DSAR	0.8205	0.7922	0.5548	0.7073	0.0691	0.0044	0.0571	0.2381

Dec. 2014/Jan 2015 months analysis of variance of the water hyacinth leaf gave an indication that heavy metal Zn was the most bio accumulated metal on the tested leaf (Ukiwe *et al* 2008., Lawal *et al*; 2011) at DSAR site with variance value of 0.0005 and 0.1227 for the metal and site respectively. This result was considered for acceptability with the F calculated for between sample variations of 0.8536 and F critical of 2.7141. For within sample analysis of F calculated of 1.717226 and F critical of 2.3593, these results were accepted. On further analysis of the result the product moment correlation coefficients indicated that Zn had no positive correlations. The product moment correlation coefficient analysis on site to site gave an indication of no positive correlation between DSAR and the other sites. Heavy

metal bio-concentration on water hyacinth leaf at DSAR site had the order Zn>Mn>Pb>Cu>Fe>Cd>Cr>Ni,which is Zn=234.43>0.0043mg/kg; Mn = 1589.86 > 0.0393 mg/kg; Pb = 300 > 0.0043 mg/kg; Cu = 239 > 0.0833 mg/kg; Fe = 171.554 > 0.2232 mg/kg; Cd = 147 > 0.0833 mg/kg; Cr = 88.00 > 0.0.0186 mg/kg; and Ni = 3.1785 > 0.05 mg/kg. As leafy vegetables have a higher tendency for uptake and accumulation of heavy metals, these can be conveniently used for the removal of toxic heavy metals from polluted agricultural fields. Singh and Kumar (2006) showed that higher uptake of Zn, Pb, Cr, Cu,Ni and Cd in vegetables grown on sewage sludge amended soil more than those grown on un-amended soil.

Table 4.25 showed the bio-concentration of heavy metals on *Eichhnor crassipes* (Water hyacinth) leaf in the months of Feb/Mar 2015.

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	0.185	0.014	0.8229	0	0.012	0.159	0.089	0.142
NBL	0.126	0.058	0.5882	1.3534	0.008	0.009	0.026	0.012
PZ	0.128	0.033	2.0606	4.25	0.034	0.003	0.107	0.112
ABT	0.277	0.045	0.0813	0.2159	0.068	0.313	0.141	0.032
DSAR	0.222	0.016	0.0833	0.8571	0.033	0.028	0.069	0.083

From two factor without replication analysis of variance it was indicated that the element Zn (Ukiwe *et al*, 2008; Lawal *et al*, 2011; Radulescu *et al*; 2013) was bio-accumulated on the leaf at the DSAR site among the sites tested. This had a variance value of 0.00045 and 0.1227 for the metal and site respectively. These

results are similar to that of Ukiwe *et al.,* (2008); Lawal *et al.,* (2011); Radulescu *et al.,* (2013). Further more when the result was considered on the analysis of variance between samples F calculated was 1.6504 and F critical was 2.7141. For within sample, F calculated was 2.6267 and F critical was 2.359. With these results between sample result was accepted while that for within samples result was rejected. . With these results it showed that the bIo-accumulation of this metal was not directly related to the presence of industries.The product moment correlation coefficient analyses on the metal to metal correlations with the heavy metal Cr bio- accumulations gave no indications at those other four sites. The product moment correlation coefficient analysis on site to site gave no positive correlation between ABT and the other sites (APPENDIX X). Bio-concentration of heavy metals on water hyacinth leaf at the ABT site was $Zn > Fe > Cu > Cr > Cd > Ni > Mn >$ Pb. Which gave, $Zn = 9695 > 0.0535$ mg/kg; $Fe = 365.6 > 0.2757$ mg/kg; $Cu = 342 > 0.0294$ mg/kg; $Cr = 194 > 0.00$ mg/kg; $Cd = 143 > 0.486$ mg/kg; $Ni = 45.0 > 0.00$ mg/kg; $Mn = 26.43 > 0.0678$ mg/kg. $Pb = 6.8667 > 0.2159$ mg/kg. The concentration of heavy metals (mg/kg) in edible portions of vegetables including *spnacia oleracea , solanum melongena, lycopersicon esculentus* and cabbage of late autum ranged between 0.55 and 10.30 for Cu,29.35 and 469.45 for Zn,1.55 and 6.90 for Cd(Sharma *et al*; 2006). This result compared well with the results of this study.

Bio-accumulation Factoron *Eichhnor crassipes* **(water hyacinth) STEM**

The bio-accumulation of metals on water hyacinth from Aba River are outlined on Tables 4.26- 4.30 for the months of   June 2014 to   May 2015.

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	1527	1.21	0.04	1.667	78.54	29441	0	0.535
NBL	226.7	0	2	1.0714	20.895	276.15	0	0.91
PZ	188.1	0	2.091	0	767	51.609	0	10.484
ABT	2.245	0	4.1	0	0.3769	3.7414	1.45	0.804
DSAR	26.58	0	1.2	0	0.3271	246.41	3.18	1.25

Table 4.26 depicted the concentration of heavy metals on *Eichhnor crassipes* (Water hyacinth (Stem) for June/July 2014. The result of the two factor without replication on the bio-accumulation of the water hyacinth stem indicated that the metal Cr was most bio accumulated at all the sites especially at ABT site The   variance value of 0.2933 and 2.6456 for the metal and site respectively were obtained (Ukiwe *et al*, 2008; Lawal *et al*; 2011). From the analysis of variation F calculated was   0.7026 and F critical   was 2.7141 for between samples.   This   result was accepted. Results for within sample gave F calculated as 1.1084 and F critical as 2.359 and this result was also accepted. From the product moment correlation coefficients,   it was seen that Cr had positive correlation with metals like Pb and Zn with values 0.8033 and 0.9955 respectively. Based on site to site possible correlations, it was observed that site ABT had positive correlations with DSAR site with variance value of 0.7393. The concentrations of heavy metals on the stem are in appendix A3A. Bio-concentration of heavy metals on water hyacinth stem at the ABT site followed the trend in the heavy

metal concentrations: Zn>Fe>Mn>Cu>Cd>Pb>Ni>Cr . Specific metal concentration values followed the trend Zn= 9930.8 > 0.0113 mg/kg; Fe = 3833.4 > 0.0905 mg/kg; Mn = 1157 > 0.140 mg/kg; Cu = 1.173 > 0.0598 mg/kg; Cd = 83 > 0.1538 mg/kg; Pb = 9.5 > 5.7894 mg/kg; Ni = 1.4521 > 0.5556 mg/kg and Cr = 0.0741 > 0.0562 mg/kg.Vegetable samples collected were influenced by seasonal variations in concentrations for there is more release of heavy metals in soil solutions for uptake by plants (Agrawal *et al*; 2007) in rainy season, with higher concentrations in dry season, this was because of high decomposition rate of organic matter during the dry seasons.

Table 4.27 showed the bio-concentration of heavy metals on *Eichhnor crassipes* (Stem) in Aug/Sept 2014.

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	4606	8.145	3.297	5.3097	3494	717.3	0	2.0053
NBL	38926	0	0.004	0	1315	314.04	0	1.3719
PZ	4241	449	0.204	0	1650	12.895	0	0.6577
ABT	3833	0	0.244	0	1157	166.31	0	1.173
DSAR	585.3	0	14	0	1813	124.18	0	0.6586

The analysis of metals for bioaccumulations to the stem of the plant indicated that the metal Pb was most bio accumulated. At DSAR site the bio-accumulation had   a variance value of 5.6386 and 405791.993 for the metal and site respectively.

This result is similar to the results of Lawal *et al*, (2011); Nagajyoti *et al*; (2010). This result was considered on the analysis of variance for between samples with F calculated as 0.9600 and F critical as 2.7141. This result was accepted as a true

result. The results for within samples were F calculated as 2.0446 and F critical as 2.3593. This result was also accepted as true.A product moment correlation coefficient of the elements indicated Pb had a positive correlation with Mn, Zn and Cu with values 0.9612, 0.9192 and 0.8279 respectively . Site inter-actions gave an indication that DSAR site had nopositive correlations with the actions at the other four sites. Bio-concentration of heavy metals on water hyacinth stem profile at the DSAR site gave the trend: Zn>Mn>Cd>Fe>Cu>Pb>Ni>Cr. Specific metal, concentration values followed the trend. Zn = 2817.6 > 0.441 mg/kg; Mn = 1813 > 0.0987 mg/kg; Cd = 1277 > 0.5556 mg/Kg ; Fe = 585.328 > 0.0998 mg/kg; Cu = 133 > 0.061 mg/kg ; Pb = 89 > 10 mg/kg; Ni = 89 > 0.3571 mg/kg and Cr = 11 > 0.0833 mg/kg. In a related study the Correlation coefficient of Pb in roots vs. shoots of r = 0.93, higher amount of soil Pb caused higher accumulation in plant shoots by bio-accumulation (Soleimani *et al*; 2009).

Table 4.28 showed the bio-concentration of heavy metals on *Eichhnor crassipes* (Water hyacinth (Stem) in OCT/NOV 2014.

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	35.54	91	0.321	0.0946	13.376	147.63	83	6
NBL	39.6	0	16	0.0078	15.844	0	0	232
PZ	37.77	73	15	26	12.674	1069.7	26	203
ABT	21.73	0	83	0	5.25	9930.8	0	111
DSAR	15.72	11	35	89	8.7419	2817.6	89	133

The two factor without replication analysis of variance on the bio accumulation of heavy Fruzinska (2011) was most bio-accumulated of the eight elements investigated. The most affected were the USAR site elements with a variance factor of 2954.3337 and 17.4784 for the site and metal respectively. This result when viewed for between sample F calculated was 0.9813 and F critical was 2.7140. This was accepted as a true result. Testing the result within sample, the F calculated was 2.1967 and F critical was 2.3592. This result was equally accepted as true result. Among the metals identified as bio-accumulating on the stem, Mn had no positive correlation with the other seven heavy metals bio-accumulating on the stem. On site to site interaction analyses, it was seen that positive correlations existed between USAR with PZ,ABT and DSAR, having correlation values of 0.7262,0.7428 and 0.7393 respectively . Bio-concentration of heavy metals on water hyacinth stem at the USAR site followed the trend: Fe>Mn>Zn>Cr>Cu>Ni>Pb>Cd. Specific metal concentration values followed the trend: Fe = 4606 > 0.0403 mg/kg; Mn = 78.5842 > 0.035; Zn = 2940 > 0.0086 mg/kg; Cr = 91.00 > 0.0377 mg/kg; Cu = 6.00 > 0.472 mg/kg; Ni = 983 > 0.0mg/kg; Pb = 5.3097 > 0.0946 mg/kg; Cd = 3.2971 > 0.3207 mg/kg. 78.5842 > 0.035; Zn = 2940 > 0.0086 mg/kg; Cr = 91.00 > 0.0377 mg/kg; Cu = 6.00 > 0.472 mg/kg; Ni = 983 > 0.0 mg/kg; Pb = 5.3097 > 0.0946 mg/kg ; Cd = 3.2971 > 0.3207 mg/kg.

Table 4.29 Bio-concentration of heavy metals on *Eichhnor crassipes* Stem (Water hyacinth) in Aba River DEC 2014/JAN 2015.

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	0.522	2.331	1.082	0	0.0863	0.0086	0	0.4727
NBL	0.031	0.06	0.237	0	0.122	0.0111	0	0.035
PZ	0.031	0.089	0.683	0	0.0925	0.0091	0	0.0321
ABT	0.091	0.056	1.097	5.7894	0.2532	0.0113	0.56	0.0599
DSAR	0.1	0	2.219	10	0.1292	0	0.48	0.3198

The two factor analyses without replication on the metals bio-accumulation of water hyacinth stem on the sites were found to have the metal Zn at the NBL site as the most bio-accumulated. Zn at this site had a variance of 2.16E-05 and 0.0088 for the site and metal respectively. The analyses of variance between samples had F calculated as 1.3208 and F critical as 2.7140. For within sample F calculated was 2.0059 and F critical was 2.3592. These result were accepted as true from the hypothesisThe product moment correlation coefficient revealed that the heavy Zn had no positive correlations with the other seven heavy metals tested . Based on site to site correlations, it was observed that NBL had a positive correlation value of 0.8780 with PZ.

Bio-concentration of heavy metals on water hyacinth stem at the NBL site followed the order:Fe>Mn>Zn>Cu>Cd>Pb>Cr>Ni. The metal to metal concentration trend are Fe = 38926 > 0.0313 mg/kg; Mn = 1335 > 0.023 mg/kg; Zn = 314.035 > 0.0111 mg/kg; Cu = 232 > 0.0139 mg/kg; Cd = 16.0 > 0.04 mg/kg; Pb = 1.0714 > 0.0078 mg/kg; Cr = 0.0943 > 0.06 mg/kg and Ni 0.00 mg/kg. Zinc was one of the most available nutrients

which can be accumulated by cabbage and then translocated in different parts of this vegetable as was highlighted by Radulescu*et al;* (2013).

Table 4.30 Bio-concentration of heavy metals on *Eichhnor crassipes* Stem (Water hyacinth)in Aba River FEB/MAR 2015

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	0.04	0.038	2.227	0	0.035	1.0584	0	0.7108
NBL	0.011	0.094	0.526	0	0.023	0.0139	0	0.0139
PZ	0.011	0.036	3.091	0	0.1009	0.0014	0	0.4968
ABT	0.091	0.074	0.154	9.5	0.1403	0.0785	0	0.0598
DSAR	0.1	0.083	0.556	0	0.0987	0.441	0.36	0.061

The two factor analyses without replication on the bio- accumulating metals and sites revealed that site NBL was most affected by the metal Mn with a variance value of 0.0322 and 0.0024 for the site and metal respectively. These results are similar to the reports of Ukiwe, *et al* (2008); Radulescu,*et al*., (2013).

The analyses of variance between samples had F calculated as 0.6366 and F critical as 2.7140, that for within sample F calculated as 0.9395 and F critical as 2.3593. These result were accepted based on the hypothesis. Product moment correlation coefficient indicated that no positive correlations existed between Mn and the other seven metals over the period. Site to site product moment correlation coefficient gave an indication that NBL had positive correlation of 0.971 with PZ. Bio-concentration of heavy metals on water Hyacinth Stem profile at the NBL site followed the

order: Fe>Mn>Zn>Cu>Cd>Pb>Cr>Ni. The metal concentrations followed the order,
Fe = 38926 > 0.0313 mg/kg; Mn = 1335 > 0.023 mg/kg; Zn = 314.035 > 0.0111 mg/kg; Cu
= 232 > 0.0139 mg/kg; Cd = 16.0 > 0.04 mg/kg; Pb = 1.0714 > 0.0078 mg/kg; Cr = 0.0943
> 0.06 mg/kg and Ni= 0.00mg/kg.

Eichhnor crassipes **(Water hyacinth)** ROOT

The bio-accumulation of metals on *Eichhnor crassipes* (water hyacinth) root from Aba
River are outlined on Tables 4.29-4.33 for the months of June 2014   to May 2015.

Table 4.31: Bio-concentration of heavy metals on *Eichhnor   crassipes* Root (Water
hyacinth) in Aba River **JUNE/JULY 2014**

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	159.7	0.1275	0.024	8.158	139.63	3125	0	1.385
NBL	224.1	0	6.8	1.5	66.2	0.07	2.85	1.17
PZ	179.7	0	0.473	0	64.513	36.53	0	6.7
ABT	1.995	0	5.8	2.714	0.7767	1.348	1.35	0.532
DSAR	39.11	0	0.23	180	19.27	288.5	0	2.76

Table 4.31 showed bio-concentration of heavy metals on *Eichhnor crassipes,* Water
hyacinth (Root)in June/July 2014.A look at the two factor without replication on   bio
accumulating heavy metals and   respective sites revealed that Ni was the most bio-
accumulating heavy metal   within the month of study and affected the ABT site most.
This is with a variance   value of 3.3110 and   1.5996 for the site and metal
respectively. This result was subjected to the analyses of variance between samples
with F calculated as 1.0815 and F critical as 2.7140. This value of the variance was

accepted for the between samples. For within sample analyses F calculated was 1.1991 and F critical was 2.3592 and this was accepted for the within sample analyses. These results are similar to the reports of Majeti (2005).

On product moment analyses of the heavy metal bio accumulation on the plant root indicated positive correlation coefficient of the metals. The metal Ni had no positive correlation with the other metals. The product moment correlation coefficient on bio accumulation on site interactions revealed that ABT had no positive correlation with the actions at the other sites (Carrasco *et al*; 2011).

The concentrations of heavy metals on the root are in appendix A4A. Bio-concentration o f heavy metals on water hyacinth root at the ABT site were in this order, Zn>Cr>Cd>Mn>Fe>Pb>Cu>Ni . The metal concentrations trend were: Zn = 8339.7 > 0.002 mg/kg; Cr = 77142 > 0.147 mg/kg; Cd = 4152.25 > 0.23 mg/kg; Mn = 4143 > 0.0287 mg/kg; Fe = 660.202 > 0.0422 mg/kg; Pb = 180 > 1.0 mg/kg; Cu = 47.5 > 0.0276 mg/kg and Ni = 2.4719 > 0.11136 mg/kg. These results are similar to the reports of *Nora et al; (1997)* on water fern (*Azolla filiculoides Lam).* Significant differences between Ni bioaccumulation by the plant roots in two soils were reported by Soleimani *et al*; (2009).

Table 4.32: Bio-concentration of heavy metals on *Eichhnor crassipes* Root (Water hyacinth) in Aba River AUG/SEPT 2014

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	4003	2.2561	0.84	1.858	5768	339.4	0	5.421
NBL	38295	0	0.025	4.368	6458	576.6	5.33	1.409
PZ	6972	156.3	0.325	0	3704	30.63	0	0.528
ABT	3036	0	0.25	4	1968	120.3	0.37	7.058
DSAR	6602	0	4152	1	4143	98.45	0	1.452

Table 4.32 showed bio-concentration of heavy metals on *Eichhnor crassipes,* (Root) in AUG/SEPT 2014. Concentrations of metals on plant root when analysis of variance is applied on two factor without replication, it was confirmed that Pb metal was most bio-accumulating at the USAR site with variance of 3.5816 and 5229015.961 respectively. This value of the variance was subjected to between sample variation and F calculated gave 1.0939 while F critical gave 2.7140. This result was accepted. On testing the results for within sample, F calculated gave 2.2975 and F critical gave 2.3592 respectively. This test hypothesis was accepted as a true result. The product moment correlation coefficient analyses on the metal to metal bioaccumulation on the root indicated that Pb had positive correlation with Zn and Ni, with values of 0.6552 and 0.6731 respectively, and a significant correlation with Cu (of variance of 0.4715). When site to site inter actions was considered some correlation coefficients were observed: USAR correlated positively with NBL, PZ, ABT and DSAR with values 0.6231;0.8513; 0.8997 and 0.9856 respectively. Bio-concentration

of heavy metals on water hyacinth root profile at the USAR site had the trend: Mn>Fe>Zn>Cu>Cr>Ni>Pb>Cd.

The metal concentrations were: Mn = 5768 > 0.0227 mg/kg; Fe = 4002.6 > 0.0112 mg/kg; Zn = 3125 > 0.0027 mg/kg; Cu = 297 > 0.1948 mg/kg; Cr = 154 > 0.0361 mg/kg; Ni = 41 > 0.0213 mg/kg; Pb = 8.1578 > 0.3929 mg/kg and Cd = 4.25 > 0.0242 mg/kg. These results are similar to the reports of Hernández-Castro *et al*; (2015).

Table 4.33 showed the bio-concentration of heavy metals on *Eichhnor crassipes,* Water hyacinth (Root) in OCT/NOV2014

Table 4.33: Bio-concentration of heavy metals on *Eichhnor crassipes* Root (Water hyacinth) in Aba River OCT/NOV 2014

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	37.91	154	0.189	0.624	24.197	449.3	0	15.74
NBL	17.37	510	52	5.464	39.044	2066	41	297
PZ	41.1	261	24	0.031	21	28873	0	163
ABT	2.419	17	45	2.186	0.3404	9621	0	230
DSAR	17.48	77142	34	3.192	27.088	8340	2.47	47.5

Two factor without replication method of analysis was applied to bio-accumulating heavy metals and on the site to site interactions, results indicated that the metal Mn was most bio-accumulating at the USAR site. Mn had a variance value of 197.6971 and 24243.2524 for metal and site respectively.

Test of hypothesis of this result on the analysis of variance showed that F calculated was 0.9455 and F critical 2.7140 for the between samples and these results were accepted. For within sample, F calculated was 1.1195 while F critical was 2.359 and the result was accepted . The product moment correlation coefficient analyses on metal to metal bio-accumulation on the root indicated that Mn had positive correlation with Ni, with values of 0.6849. Site to site interaction analyses showed that positive correlation coefficient was observed between USAR and three other sites NBL,PZ and ABT with R values 0.9827; 0.9471 and 0.9438 respectively.

Bio-concentration of heavy metals on water hyacinth root at the USAR site followe the order:ZnCr>Fe>Mn>Cu>Pb>Cd>Ni. The specific metal concentrations were Zn = 449.27 mg/kg; Cr = 154 mg/kg; Fe = 37.91 mg/kg; Mn = 24.19 mg/kg; Cu = 15.73 mg/kg; Pb = 0.623 mg/kg; Cd = 0.1887 mg/kg and Ni = 0. These results are similar to the reports of Lawal *et al*; (2011).

Table 4.34 showed the bio-concentration of heavy metals on *Eichhnor crassipes,* (Root) in Dec 2014/Jan2015.

Table 4.34: Bio-concentration of heavy metals on *Eichhnor crassipes* Root (Water hyacinth) in Aba River DEC 2014/JAN 2015

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	0.153	0.9782	4.23	0.393	0.0511	0.003	0.02	0.195
NBL	0.08	0.0348	0.429	0.821	0.0202	0.006	0.1	0.035
PZ	0.103	0.0224	1.686	0.471	0.0435	0.003	0.07	0.089
ABT	0.138	0.0538	0.944	1.419	0.0618	0.006	0.03	0.054
DSAR	0.15	2	3.727	15.27	0.05	0.003	0.11	0.206

Analyses of variance in the two factor without replication on the bio-accumulating heavy metals at the sites on the plant root gave an indication that the metal Mn was the most accumulated on the NBL site. This was with a variance value of 0.0002 and 0.0836 for the metal and site respectively.

Further variation between samples gave F calculated as 1.6566 and F critical as 2.7140. Variation within sample indicated F calculated of 1.7434 and F critical of 2.3592. From the hypothesis, these results were taken as true results for between and the within samples. Mn had no positive correlation with any of the other metals tested within the period. NBL had a positive correlations with PZ, ABT and DSAR with values 0.5622,0.9859 and 0.9520 respectively. Bio-concentration of heavy metals on water hyacinth root at NBL site followed the trend:Pb>Cd>Ni>Fe>Cr>Cu>Mn>Zn (Table 4.40) The specific metal concentrations were: Pb = 0.8205 mg/kg; Cd = 0.4285 mg/kg; Ni = 0.1 mg/kg; Fe=0.0795mg/kg; Cr=.0348mg/kg; Cu=.0348 mg/kg; Mn=.0202 mg/kg; Zn = 0.0056 mg/kg.

Table 4.35 showed the bio-concentration of heavy metals on *Eichhnor crassipes,* (Root) in Feb /Mar 2015.

Table 4.35: Bio-concentration of heavy metals on *Eichhnor crassipes* Root (Water hyacinth) in Aba River FEB/MAR 2015

SITE/ELEM	Fe	Cr	Cd	Pb	Mn	Zn	Ni	Cu
USAR	0.011	0.0361	3.955	1.545	0.0227	0.036	0.07	0.291
NBL	0.134	0.0338	0.385	0.277	0.0053	0.006	0.27	0.016
PZ	0.012	0.0287	1.943	1.308	0.0252	0.004	0.06	0.119
ABT	0.029	0.0781	0.114	0.864	0.0319	0.025	0.04	0.06
DSAR	0.042	0.1471	0.278	1.059	0.0287	0.002	0.22	0.028

The analyses of variance on the sites indicated that site NBL was most affected by the heavy metal Mn with a variance of 0.0001 and 0.0226 on the metal and site respectively. The bio accumulation potentials of these metals were subjected to analysis of variance between and within sample which gave F calculated as 1.5051 and F critical as 2.7140 for between samples. For within samples F calculated was 3.9285 and F critical was 2.3593. Mn had no positive correlation with any of the other metals tested within the period. NBL had a positive correlations with PZ and DSAR with values 0.8040 and 0.5865 respectively.

Bio-concentration of heavy metals on water Hyacinth root at the NBL site followed the trend: Cd>Pb>Ni>Fe>Cr>Cu>Zn>Mn.(Table 4.41). The specific metal concentrations were: Cd = 0.3846, Pb = 0.2769; Ni = 0.27; Fe = 0.1335; Cr = 0.0338; Cu = 0158; Zn = 0.0059; Mn = 0053mg/kg.

4.4   Geo accumulation of Heavy Metals

Tables 4.36 to 4.50 showed the Geo-accumulation index (Igeo) of metals for sediments of Aba River for the period June 2014 to May 2015.

Table 4.36: Cu % Geo-accumukation Index (Igeo) of Sediment in Aba River June 2014 – May2015

Site	Jun/Juy	Aug/Sep	Oct/Nv	Dec/Jn	Feb/Mar	Apr/May	Range
USAR	1.5347	2.3066	1	0.5219	0.2892	1.0802	2.3066 - 0.5219
PZ	2.7512	0.3845	15.3888	2.5361	2.3959	3.7796	15.3888 .- 0.3945
NBL	4.012	3.3249	2.433	2.433	4.078	2.3908	4.078 - 2.3908
ABT	4.4699	6.8445	4.5484	4.5484	4.5484	4.2502	6.8445 - 4.2502
DSAR	2.2429	2.6042	0.0431	0.0451	2.263	0.1338	2.6042-0.0431

The % geo-accumulation index of Copper (Igeo Cu) on Aba River sediment for the period June 2014 to May 2015 are shown in (Table4.36) in the appendix.

The highest metal values in sediment recorded at Sites may be due to the fact that when metal pollutants are discharged into aquatic environment, they do not remain in aqueous phase but instead are adsorbed onto the sediment. Sediment here serves as a sink for pollutants, this could be the reason for the higher concentration of these metals in Aba River sediments. This is similar to the findings of Amoo, *et al*; (2005) where they obtained levels of these metals in sediments were higher than those in the water of Lake Kanji in Nigeria.

The heavy metal copper, had a variance value of 0.528781 at   USAR site and 1.491733 in the month of June/July 2014 when   Anova two factor without replications was applied. This   result was further considered at   between and   within sample analyzes, with an F calculated of 2.610135 while F critical of 2.866081 for between samples.   F calculated for   within   samples   was 0.601898   and   the F critical was 2.71089. Product moment   correlation coefficient   had a positive R on some periods of interaction and on the sites. There were   positive R in June/July periods   with   Aug/Sept, Dec/Jan, Feb/Mar and   Apr/May   (with values of 0.689076,0.8746636,975133 and 0.705929 respectively). Aug/Sept had positive R with Dec/Jan and Feb/Mar with values of 0.60774 and 0.635603 respectively. Oct/Nov had R of 0.689083 with Sept/Nov. Dec/Jan had R of 0.783573 and 0.941851 with Feb/Mar and Apr/May respectively. Feb/Mar   had R of 0.606237 with Apr/May. Site to site interactions gave a R   0.766103 between USAR and ABT. NBL and DSAR, R of 0.905689,ABT   R of 0.549253 with DSAR. With these results the values were accepted as true for   the Hypothesis H_1 ,that the geo-accumulation of heavy metals

were related to the presence of the industries. This was also accepted as a true value within the 0.05 confidence limit and 29 degrees of freedom.

Cu at SITE-USAR, had the maximum geo-accumulation of 34% in the month of Aug/Sept and 4% in Feb/Mar. The accumulation index ranged from 2.3066 to 0.5219 (Table 4.36).

At PZ site, the metal Cu had a maximum geo-accumulation of 57% in Oct/Nov while the least accumulation was 1% in Aug/Sept. The accumulation index ranged from 15.3558 to 0.3945 (Table 4.36).

At NBL site Cu had maximum geo-accumulated in Feb/Mar of 22% with a minimum value of 13% in three respective months of Apr/May,Oct/Nov and Dec/Jan. The geo-accumulation index ranged at this site from 4.078 to 2.3908.

SITE-ABT, Cu had a maximum geo-accumulation of 23% in the month of Aug/Sept while the least accumulation of 15% was observed in the months of Feb/Mar, Apr/May and June/July. The geo-accumulation range was from 6.8445-4.2502.

At SITE-DSAR, Cu metal had a maximum geo-accumulation of 35% in Aug/Sept and a least concentration of Zero in Oct/Nov.The geo-accumulation ranged from 2.6042 to 0.0431. (Table 4.36).These results differed from the work of Dzomba *et al* ;(2012).

The % geo-accumulation index of Cadmium (Igeo Cd) on Aba river sediment for the period june 2014 to May 2015 are shown in Fig 4.17 to 4.21, (Table 4.36).

The analyses of geo accumulation index on heavy metal Cadmium for the period of study and on the sites had a variance of 1.491733 in the month of June/July. Most geo - accumulation effect at the USAR had a variance value of

0.528781.Analyses of variance was applied to these results for between and within samples.

Between samples had F calculated of 2.610135 and F critical of 2.866081 while within samples gave an F calculated of 0.601898 and F critical of 2.71089. Product moment correlation coefficient revealed a positive R value for some of the periods and sites, June/Julyhad R values of 0.689076,0.874636,0.975133 and 0.705929 with Aug/Sept, Dec/Jan, Feb/Mar and Apr/May. Aug/Sept results had R of 0.60774 and 0.635603 with Dec/Jan. Feb/Mar to Oct/Nov had R value of 0.689083 with Apr/May. Dec/Jan results had R values of 0.783573,0.941851 with Feb/Mar and Apr/May while Feb/Mar had R value of 0.606237 with Apr/May. Site to site interactions at USAR had an R value of 0.766103 with ABT. NBL results had R values of 0.905689 with DSAR while ABT had R value of 0.549253 with DSAR.

With these results, the values were accepted as true for the Hypothesis H_1,that the geo accumulation of heavy metals were related to the presence of the industries for between and within samples   at the 0.05 confidence limit and 29 degrees of freedom.

Cd GEO-ACCUMULATION INDEX OF TRACE METALS ON SOIL SEDIMENTS ABA RIVER 2014/2015

Table 4.37: Cd Geoaccumulation Index (Igeo) in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	0.9703	0.7615	-2.5581	-2.5581	-4.1766	-1.4375	0.7615-0.9703
PZ	0.2775	-5.1688	4.000	-1.6095	-1.8145	0.2224	4.000-5.16
NBL	0.5849	-4.9083	3.737	2.306	-1.1415	-0.3219	3.7370-0.5849
ABT	3.3219	0.1699	4.3692	-0.3505	1.7078	-0.4475	4.3692-0.4475
DSAR	0,6789	2.415	3.2224	-2.4868	0.9508	0.737	3.2224-2.4868

At USAR site Cd had the maximum geo-accumulation in the month of June/July (8%) while the least was in Feb/Mar of (-36%). The geo-accumulation index ranged from 4.1766 to 0.9703(Table4.38) in the appendix.

The metal Cd at the PZ site had the maximum geo-accumulation of 31% in Oct/Nov and the least geo-accumulation index of -14% in Feb/Mar. A range of 4.00 to -5.1688 was observed for the site.(Table4.37).

The metal Cd at NBL site had its maximum geo-accumulation in Oct/Nov (29%) and a least value of -9% in Feb/Mar.A range of 4.00 to -0.5849 was observed for this site. (Table 4.37)

At sit-ABT, Cd metal had a maximum geo-accumulation of 42% in Oct/Nov and a least value of -4.3692. A range of 4.3692 to -0.4475 was observed at this site

(Table4.37). The metal Cd at DSAR site had a maximum geo-accumulation of 31% in Oct/Nov while a least geo-concentration of -24% was obtained in Dec2014/Jan2015.The range observed was from 2.4868 to 3.2224 (Table4.37). These results are similar to that by the Indian standard Awashthi of 3.6mg/kg in Orisakwe (2012) and the landfill result by Al-Musharafi *et al*; (2014) ; Resongles *et al* ; (2004).

Fe GEO-ACCUMULATION INDEX OF TRACE METALS ON SOIL SEDIMENTS ABA RIVER 2014/2015

Table 4.38: Fe Geoaccumulation Index (Igeo)in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	10.7705	11.63444	4.5785	1.0081	4.7364	6.5237	11.6344-1.0081
PZ	6.8254	11.8499	4.6423	1.768	4.8858	6.4883	11.8499-1.7680
NBL	8.8949	12.331	3.4759	1.7749	4.2445	4.6005	12.33-1.7749
ABT	2.2491	10.4304	4.0062	1.8829	4.3288	4.4431	10.4304-1.9829
DSAR	4.3579	8.7164	4.9893	1.8962	3.7141	4.4747	8.7164 -1.8962

The % geo-accumulation index of Iron (Igeo Fe) on Aba river sediment for the period June 2014 to May 2015 are shown in Fig 4.22 to 4.26, (Table4.38) in the appendix..

The geo accumulation index of Iron based on two factor without replications revealed that the metal Fe was most geo-accumulated within the months of Dec.2014/Jan 2015 at the DSAR site. This has a variance value of 0.138783 and 5.043162 for the period and site respectively. The results were tested for trueness using the analyses of variance for between and within samples.

Anova between samples for F calculated gave 2.105489 and F critical gave 2.866081. for within samples, F calculated gave 22.0779 and F critical gave 2.71089.

Product moments correlation coefficient analyses showed that positive R values were obtained for the Jun/July interactions with Aug/Sept and Apr/May giving values of 0.679971, and 0.623425 respectively. Aug/Sept had R of 0.757671 and 0.506587 with Feb/Mar and 0.506587 respectively. Feb/Mar hadR of 0.854311 with Apr/May. On site to site interactions, USAR had R of 0.907284; 0.955221; 0.586533 and 0.788129 with PZ,NBL,ABT and DSAR respectively. PZ had R of 0.940252; 0.867693; 0.948608 with NBL,ABT and DSAR respectively.NBL had R of value of 0.721614 and 0.8496 with ABT and DSAR. ABT had R of 0.925249 value with DSAR. With these results the null hypotheses H_O was accepted for the between samples as the F calculated was less than the F critical. The geo-accumulation of iron was not related to the presence of industrial establishments but may be through other anthropogenic factors.

The alternative hypotheses H_1 was rejected as F calculated was higher than the F critical, at the 0.05 confidence limit and 29 degrees of freedom.

The metal Fe at USAR site had a maximum geo-accumulation of 37% in Aug/Sept and the least geo-accumulation of 2% in Dec2014/ Jan2015. Fe had a range of 11.6344 to 1.0081 geo-accumulation index (Table 4.38).

Fe at PZ site was at a maximum geo-accumulation of 32% in Aug/Sept 2014 while the minimum of 5% was in Dec 2014/Jan2015.At this site a range of 11.8499 to 1.7680 was observed for this metal (Table 4.38).

At the NBL site, the metal Fe maintained the highest geo-accumulation of 35% in the months of Aug/Sept 2014 and the least value of 5% in Dec2014/Jan2015. A range

of 12.3310 to 1.7749 was observed for metal Fe at this site for the period (Table 4.38).

Fe maintained a maximum geo-accumulation of 38% in the months of Aug/Sept 2014 and a minimum of 7% in the month of Dec2014/Jan2015 at ABT site. A range of 10.4304 to 1.7749 was observed at this site for Fe (Table 4.38)

Fe at DSAR site had a maximum geo-accumulation of 31% in the months of Aug/Sept 2014 and a minimum of 7% in the month of Dec2014/Jan2015. A range of 8.7164 to 1.was observed at this site for Fe (Table 4.38). These results were below that reported by Uaboi - Egbenni *et al*; (2010).

The % geo-accumulation index of Chromium (Igeo Cr) on Aba River sediment for the period June 2014 to May 2015 are shown in Table 4.37.

Table 4.39: Cr Geoaccumulation Index (Igeo) in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	5.1452	0.644	-0.5849	-9.0398	-6.9658	1.8101	5.1452-9.0398
PZ	2.4831	-0.5819	-0.591	0.5849	-7.3574	0.4039	2.4831-7.3570
NBL	-1.1652	9.4972	9.4978	-0.5848	3.0352	-1.6126	9.4972-1.1652
ABT	-2	-0.8583	-0.8583	3.4764	1	-2.1966	3.47640.858
DSAR	-2.9714	8.0334	8.03 34	3.0233	-2.7691	-3.7704	8.0334--3.7704

Geo-accumulation index of the heavy metal Chromium, carried out on five respective sites over the period showed that the ABT site was the most affected

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site in the months of Apr/may of 2015.It showed a variance value of 4.607557 and 4.830609 for the site and period respectively based on two factor without replication analyses of variance. The result was further tested for trueness of value using the between and within sample variance which gave F calculated as 1.141389 while F critical was 2.866081.For within samples, the F calculated was 1.488798 and F critical was 2.71089.The F calculated values were less than the F critical in the two cases. This result suggests strongly that the geo-accumulation of Cr could be related to the presence of industrial establishments. Product moment correlation coefficient had R positive values for some test sites and periods. June/July had R of 0.981811 with Apr/May. Aug/Sept had positive R with Oct/Nov and Feb/Mar of values 0.994897 and 0.528901 respectively. Oct/Nov had an R of 0.56619 with Feb/Mar. USAR had a positive R of 0.564928 with PZ. With these results the null hypotheses H_O was accepted for the between samples since the F calculated was less than the F critical. The alternative hypotheses H_1 was rejected as F calculated was higher than the F critical, at the 0.05 confidence limit and 29 degrees of freedom. With these results it showed that the geo-accumulation of this metal was directly related to the presence of industries.

The metal Cr at USAR had a maximum geo-accumulation of 21% in June/July and the least geo-accumulation of -37% in Dec2014/ Jan2015. Cr had a rangeof 5.1452 to -- 9.0398 (Table 4.39)

Cr at PZ site was at a maximum geo-accumulation of 21% in June/July 2014 while the minimum of -61% was in Feb/Mar 2014 .At this site a range of 2.4831 to - 7.3570 was observed for this metal (Table 4.39).

SITE-NB, at the NBL site the metal Cr at NBL site maintained the highest geo-accumulation of 38% in the months of Aug/Sept 2014 and least value of -6% in Apr/May 2014. A range of 9.4972 to -1.1652 was observed for the metal at this site. (Table 4.39).

Cr at ABT site maintained a maximum geo-accumulation of 34% in the months of Aug/Sept 2014 and a minimum of -21% in the month of Apr/May 2014. A range of 3.3219 to -2.19631 was obtained (Table 4.39)

Cr at DSAR site had at maximum geo-accumulation of 28% in the months of Aug/Sept and Oct/Nov 2014 and a minimum of -13% in the month of Apr/May 2015. A range of 8.0334 to -3.7704 was observed at this site (Table 4.39). These results were above that reported of Davies *et al* ., (2006).

The % geo-accumulation index of Znic (Igeo Zn) on Aba River sediment for the period June 2014 to May 2015 are shown Table 4.39.

Table 4.40: Zn Geoaccumulation Index (Igeo) in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	10.2111	1.8875	1.2505	6.8031	2.385	2.8183	10.2111 1.8875
PZ	5.8076	3.7461	-0.8051	6.997	6.6406	6.503	6.9970--.8051
NBL	9.5796	9.0901	7.7504	5.4551	4.9048	7.5857	9.5796-4.9048
ABT	-1.0967	5.8233	8.7685	6.8956	4.8182	5.164	8.7685-1.0967
DSAR	7.7713	8.7091	7.4751	7.4008	4.6391	5.2576	8.7091-4.6391

The period Dec/Jan was observed as the maximum geo-accumulation of the heavy metal Zn at DSAR site. A product moment correlation coefficient on respective sites and period had positive R values for Aug/Sept and Oct/Nov,Apr/May of 0.793242 and 0.656904 respectively. Feb/Mar had positive R values for 0.791603 with Apr/May. On site to site interactions gave positive R values with NBL and DSAR of values 0.640768. This result was substantiated by taking the computation of the analyses of source of variation between samples and within samples .The results for between samples gave F calculated as 1.298756 and F critical as 2.866081 while for within samples F calculated gave 0.383188 and F critical gave 2.71089 respectively. With these results the null hypotheses H_O was accepted for the between samples as the F calculated was less than the F critical. The geo-accumulation of Zinc was not related to the presence of industrial establishments. The alternative hypotheses H_1 was rejected as F calculated was higher than the F critical, at the 0.05 confidence limit and 29 degrees of freedom.

The metal at USAR had a maximum geo-accumulation of 40% in June/July 2014 and the least geo-accumulation of 5% in Oct/Nov 2014. Fe had a range of 10.2111 to 1.8875 (Table 4.40) .

Some metals are known that may interact competitively for accumulation example of such being Zn and Ni in calamite and serpentine soils (Majeti, 2005). Zn at PZ site was at a maximum geo-accumulation of 23% in Dec 2014/Jan 2015 while the minimum of -3% was in Oct/Nov 2014 .At this site a range of 6.9970 to -0.8051 was observed for Zn (Table 4.40).

At NBL site the metal Zn maintained the highest geo-accumulation of 22% in the months of June/July 2014 and a least value of 11% in Feb/Mar 2014. A range of 9.5796 to -4.9048 was for the metal at this site (Table 4.40)

Zn at ABT maintained a maximum geo-accumulation of 27% in the months of Oct/Nov 2014 and a minimum of -3% in the month of Jun/July 2014/2015. A range of 8.7685 to -1.0967 was observed for Zn (Table 4.40).

Zn at DSAR site had at maximum geo-accumulation of 21% in the months of Aug/Sept 2014 and a minimum of 11% in the month of Feb/Mar 2014. A range of 8.7091 to -4.6391 was observed at this site (Table 4.40). These results are similar to the landfill result by Al-Musharafi *et al*; (2014); Adekunle and Akinyemi, (2004).

The % geo-accumulation index of Nickel (Igeo Ni) on Aba river sediment for the period June 2014 to May 2015 are shown in Table 4.41).

Table 4.41: Ni Geo-accumulation index (Igeo) in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	3.6323	4.941	-4.8323	-3.9062	-5.1687	2.9511	4.9510-3.9062
PZ	-6.7959	1.3852	0.2504	-5.1078	-5.1078	-1.5109	.2504-6.7959
NBL	2.3776	2.3625	-2.1701	-3.9061	-2.1701	3.7038	3.7038-3.9061
ABT	0.1134	-1.5851	-7.2216	-3.1418	-4.6439	2.5119	2.5119-7.2216
DSAR	2.3219	-5.227	-1.537	0.05526	5.4811	3.356	5.4811-(-5.227

For the geo accumulation of Ni over the period it was observed that NBL site was most affected with a variance value of 9.92446 in the month of Apr/Mar of 2015. with a variance value of 4.4958 for the period on the two factor without replication variation. The source of variation analyses on between sample gave a value of F calculated of 1.301002 , F critical of 2.866081 and F calculated of 2.167673 and F critical of 2.71089 for within samples. Product moment correlation coefficient analyses of the geo accumulation index gave positive R for some sites and periods. June/July had R of 0.964607 with Apr/May. Dec/Jan had R of 0.928342; 0.53302 with Feb/Mar and Apr/May respectively.Site to site variation showed that USAR had R value of 0.921268 with NBL. NBL had R value of 0.812667 with ABT. With these results the null hypotheses H_O was accepted for the between samples as the F calculated was less than the F critical. The alternative hypotheses H_1 was rejected at the 0.05 confidence limit and 29 degrees of freedom. The geo-accumulation of Nickel was not related to the presence of industrial establishments , but may be related to some factors prevalent in the area.

Ni at USAR site had the maximum geo-accumulation of 20% in the month of Aug/Sept and -20% in Feb/Mar. The accumulation index ranged from 4.9410 to -3.9062 (Table 4.41).

Ni PZ site had a maximum geo-accumulation of 7% in Aug/Sept 2014 while the least geo- accumulation was -34% in June/July 2014. The geo-accumulation index ranged from 0.2504 to -6.7959 (Table 4.41).

.At NBL site Ni geo-accumulated maximum at a 38% with a minimum value of --40% in the months of Dec 2014/Jan 2015. The geo-accumulation index ranged from 3.7038 to -3.9061. (Table 4.41)

Ni at ABTsite had a geo-accumulation maximum of 13% in the month of Apr/May while the least accumulation of -38% came in months of Oct/Nov2014 . The geo-accumulation range was from 2.5119 to 7.2216 (Table 4.41).

Ni accumulation at DSAR site had a maximum geo-accumulation of 30% in Feb/Mar 2014 and a least concentration of -8% in Oct/Nov. The geo-accumulation ranged from 5.4811 to-5.227 (Table 4.41). These results are similar to that by Al-Musharafi, *et al.*, (2014); Szarek-Gwiazda *et al.*, (2011).

The % geo-accumulation index of Lead (Igeo Pb) on Aba river sediment for the period June 2014 to May 2015 are shown in Table 4.42).

Table 4.42: Pb Geo-accumulation Index (igeo) in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	0.5734	0.7123	-9.5873	-7.357	-8.9658	-7.37	.7123--9.5873
PZ	-3.1701	-1.5324	-8.9658	-7.4548	-8.0023	2.5641	2.5641--8.9658
NBL	2.3219	3.0251	-7.5873	-8.8954	-8.0783	0.1474	3.0251--8.8954
ABT	3.1568	5.9925	-8.335	-3.1178	-8.1584	2.2224	5.9925-8.3335
DSAR	8.0589	3.618	-8.4804	-3.9062	-4.737	0.9625	8.0589--8.4804

The geo accumulation of heavy metal lead Pb over the period and at the respective sites indicated that the PZ site was most affected in the months of Oct/Nov of 2014 with a variance value of 20.27701 and 0.55476 for site and metal respectively, when

two factor without replication variation analysis is applied to the results . Product moment correlation coefficient of these parameters gave positive R values for June/July with Aug/Sept, Dec/Jan, and Feb/Mar of values 0.7344; 0.605183 and 0.767241 respectively. Aug/Sept had R values with Oct/Nov and Dec/Jan of value 0.565159and 0.664368. Dec/Jan had R values of 0.501667 with Feb/Mar. These results were further tested for trueness of value by analyzing between and within samples for the F calculated which gave 4.207319 and F critical was 2.866081. For within samples, F calculated was 33.90828 and F critical was 2.71089. The H_0 was rejected and H_1 accepted as F calculated was greater than F critical for between and within samples at the 0.05 confidence limit and 29 degrees of freedom (Ciszewski *et al.*, 2012).

The metal Pb at USAR site had the maximum geo-accumulation in the month of Aug/Sept of 3% while the least was -34% in Oct/Nov2014, the geo-accumulation index ranged from 0.7123 to 9.5873(Table 4.42).

The metal Pb at PZ site had the maximum geo-accumulation of 8% in Apr/May while least accumulation was -28% in Oct/Nov2014. A range of 2.5641-8.9658 was observed . (Table 4.42).

At NBL site, Pb had its maximum geo-accumulation in Oct/Nov (10%) and a least value of -30% in Dec2014/Jan2015.A range of 3.0251 -8.8954 (Table4.42).

Pb metal at ABT had a maximum geo-accumulation of 20% in Aug/Sept 2014 and the least value of -27% in Oct/Nov2014. A range of 5.9925 to-8.3335 was observed (Table 4.42).

Pb at DSAR site had a maximum geo-accumulation of 27% in June/July 2014 but had least geo-concentration of -27% in Oct/Nov2014. The range observed was from

8.0589 to-8.4808 (Table 4.42). These results are above that of Davies *et al*; (2006) and landfill by Al-Musharafi,*et al*., (2014).

The % geo-accumulation index of Manganesse (Igeo Mn) on Aba river sediment for the period June 2014 to May 2015 are shown in Table 4.43.

Table 4.43: Mn Geoaccumulation index (Igeo) in Aba River Sediment June 2014 – May 2015

Site	Jun/July	Aug/Sept	Oct/Nov	Dec/Jan	Feb/Mar	Apr/May	Range
USAR	3.5934	8.4235	1.6951	1.7848	4.6623	4.6623	1.6616-8.4235
PZ	3.83	9.0534	-8.0397	2.5646	2.9203	2.9203	8.0397-9.0524
NBL	4.5	12.0457	-2.5146	2.2676	4.7782	4.7782	2.5146-12.0457
ABT	-1.8699	13.1113	3.7658	2.6712	3.6385	3.6385	1.8699-13.1113
DSAR	2.1426	12.0618	2.4842	2.9286	3.6912	3.6912	2.1426-12.0618

Over the period of study the geo accumulation of the heavy metal Manganese Mn was indicated to have been at the peak in the in the months of Dec/Jan at the USAR with variance value of 0.191685 and 7.01351 respectively based on two factor without replication variations. The product moment correlation coefficient gave positive R values for Aug/Sept with Dec/Jan and Apr/May with values 0.628065 and 0.541656 respectively. Feb/Mar had R values of 0.503829 with Apr/May. On site to site analyzes USAR had positive R with PZ,NBL, ABT and DSAR of values 0.721094,0.821026,0.7554 and 0.90043respectively. PZ had R positive with values of 0.92689 and 0.640453 for NBL and DSAR. NBL had R of 0.609377 and 0.803955

with ABT and DSAR respectively. ABT had R of 0.937514 . These results were analyzed on source of variation for between samples which gave F calculated as 0.917528 F critical as 2.866081 For between samples Ho was accepted as the true result. For within samples F calculated was 11.66726 while F critical was 2.71089. This result was rejected for within samples. H1 was accepted as the true value for within samples results: This conclusion is because F calculated was greater than F critical within the 0.05 confidence limit and 29 degrees of freedom.

The metal Mn at USAR site had a maximum geo-accumulation of 39% in Aug/Sept 2014 and the least geo-accumulation of 8% in Apr/May, Oct/Nov and Dec2014/ Jan2015 consecutively. Mn had arange of 8.4235 to 1.6616 (Table 4.43).

Mn at PZ site had a maximum geo-accumulation of 32% in Aug/Sept 2014 and with a minimum of -28% in Oct/Nov 2014 .At this site a range of 9.0524 to -8.0397 was observed for this metal (Table 4.43).

At the NBL site , the metal Mn maintained the highest geo-accumulation of 38% in the months of Aug/Sept 2014 and a minimum value of -8% in Oct/Nov2014. A range of 12.0457 to 2.5146 was observed for Mn at this site (Table 4.43).

Mn at ABT site maintained a maximum geo-accumulation of 47% in the months of Aug/Sept 2014 and a minimum of -7% in the month of Jun/July 2014. A range of13.1113-1.8699 was observed (Table 4.43).

Mn at DSAR site had maximum geo-accumulation of 46% in the months of Aug/Sept 2014 and a minimum of 8% in the month of 2014 June/July. A range of 12.0618 to 2.1426 was observed at this site (Table 4.43). These results fell within the set limits in a similar work by Butu and Iguisi (2013).

4.5   Target Hazard Quotient of *Telferria occidentalis and Talinum trianglare*

The target hazard quotient (THQ) has been recognized as a useful parameter for evaluation of risk assiocated   with the consumption of heavy metal contaminated foods crops (Yongzhang *et al;* 2010).

*Telferria occidentalis:*The Target Hazard Quotient of *Telferria occidentalis* leaf for the period June 2014 to May 2015 are shown in Tables 4.44 to 4.48.   Also the International Standards for metal concentrations in vegetables is shown in Table 4.49.

In this study, two edible vegetables locally taken from the River side of Aba River in the South Eastern Nigeria, in Abia State,Nigeria ; *Telferria occidentalis and Talirum trianglare*   were studied for   the period June 2014 to May 2015.   Vegetables are known to   take up and accumulate heavy metals in quantities high enough to cause clinical problems to human after   consumption of the said   vegetables (Orisakwe,et al;2012). Various plants have been used as bio-indicators to assess the impact of pollution source on the vicinity which is due to high metal accumulation of plants(Lawal *et al.*, 2011).

Table 4.44: Target Hazard Quotients of Heavy Metals in *Telferria occidentalis* Leaf June/July 2014

METAL/SITE	USAR	PZ	NBL	ABT	DSAR
Cu	0.0691	0.0258	0.0029	0.0472	0.0496
Zn	0.0096	0.1102	0.0895	0.1287	0.0516
Cd	26.48	22.72	3.3045	3.9448	3.7176
Cr	2.478	3.0292	2.0791	8.8121	4.6814
Ni	0.5763	3.8209	2.0137	0.5473	1.4457
Pb	7.5728	5.5076	6.2717	7.1598	6.7467
Mn	28.029	28.767	70.073	23.383	15.859
Fe	0.0485	0.0518	0.1357	0.1287	0.0287

***Telferria occidentalis leaf* (Jun/July 2014)**

In this study the leaves of *Telferria occidentalis* bio-accumulated heavy metals over a range for Cu (0.0029 at NBL minimum and maximum 0.0691 at USAR). Zn and Fe were bio-accumulated through the mobility of heavy metals from soil through the plants to the food chain but their concentrations were below WHO and FMEnv standards. This leaf of *Telferria occidentalis* could be said to be a poor accumulator of the heavy metals Cu, Zn and Fe. From the sites metals had varied results which were above WHO and FMEnv set standards. For example Cd had these results: 26.48USAR; 22.72PZ; 3.3NBL; 3.945ABT; 3.7176DSAR; Cr had these values: 2.478USAR; 3.0292PZ; 2.0791NBL; 8.8121ABT; 4.6814DSAR Equally, Pb had the values: 7.5728 USAR; 5.5076PZ; 6.2717NBL; 7.1598 ABT; 6.7467DSAR while Mn had the values: 28.029USAR; 28.767PZ; 70.073NBL; 23.3825 ABT; 15.8588 DSAR .

This study has shown that THQ of heavy metals in vegetables varied depending upon the sources (sites) of heavy metal contamination and these reports are close to that of Singh and Kumar (2006) and similar to the report of Agrawal *et al;* (2007)**.**

Nickel metals identified at the sites where were with respective THQs and had the values: 3.82PZ; 2.013NBL. Some of the metals were at significant or trace level concentrations. For example, Ni had values: 0.576USAR; 0.547ABT; 1.45DSAR. These reports were observed to be similar to that by Adah *et al*.(2013). Again Pb 7.57USAR;5.50PZ; 6.27NBL;7.16ABT; 6.75DSAR. These results are found similar to those reported by Kara;(2008) and that by Lawal *et al;*(2011) with high THQ Pb in the leaf; Mn 28.03USAR;28.77PZ; 70.07NBL; 23.38ABT;15.86DSAR. The negative impact of heavy metals were demonstrated by Agrawal et al.,(2007) working on human health risk and consumption of vegetables from contaminated soil.the THQs of heavy from Telferria occidentalis leaf decreasing order of Mn> Cd> Pb> Ni>Cr>Fe>Zn>Cu. This result suggest

that Mn ingestion has the highest potential health risk of adverse effects and Cu ingertion has the minimum risk.

Table 4.45: Target Hazard Quotients of Heavy Metals in *Telferria occidentalis* Leaf Aug/Sept 2014

METAL	USAR	PZ	NBL	ABT	DSAR
Cu	0.049	0.1832	0.0826	2.6	0.1497
Zn	0.0003	0.1081	0.0096	10.6	0.041
Cd	7.2787	4.9568	0.1307	1.8	0.2065
Cr	2.56	0.0688	0.1033	8.4	0.0895
Ni	1.0327	3.1496	1.0843	10	1.2908
Pb	8.1236	8.3302	7.504	6	5.5905
Mn	0.0959	0.0738	0.1106	0.18	0.1475
Fe	0.0004	0.0002	0.0002	0.16	0.0176

In his study the results from the leaves of *Telfrria occidentalis* from Aba river side analyzed in Aug/Sept 2014, The THQ results on Cu, Zn and Fe are less than one indicating that the Aba River population will not confront with a significant potential health risk by the trace metal Cu, Zn, Mn, and Fe from consumption of *Telfrria occidentalis* leaf excepting at the ABT station. Cd results: USAR 7.22; PZ4.96; ABT1.8Cr values: USAR 2.56,ABT 8.4 with mean 0.0895. Ni values PZ 3.15; ABT10, with significant values at USAR1.03; NBL 1.08 and DSAR1.29 respectively. Pb exceeded set values at the test stations with values of USAR 8.12;PZ8.33;NBL7.5;ABT6.0;DSAR 5.59the THQs of trace metal from consumption of telferria occidentalis leaf is in order of increasing THQs the Zn>Ni>Cr>Pb>Cd>Cu>Fe>Mn. Our results suggest that Zn ingestion has the highest potential health risk of adverse effects and Mn ingestion the minimum risk. These results are similar to those reported by Kara;(2005) and that of Lawal *et al.*(2011) with

high concentrations of Pb in the leaf. This study indicated poor health possibility for the inhabitants of Aba River waterside from the consumption of *this* leaf.

Table 4.46 Target Hazard Quotients of Heavy Metals in *Telferria occidentalis* Leaf Oct/Nov. 2014

METAL	USAR	PZ	NBL	ABT	DSAR
Cu	0.0516	0.0258	0.0287	1.3	0.0387
Zn	0.0344	0.0344	0.0011	1.08	0.0004
Cd	21.893	0.2065	0.2891	0.14	0.3718
Cr	0.0689	0.0895	0.1033	0.12	0.0757
Ni	0.981	2.6333	0.1549	10	4.5954
Pb	36.42	22.581	8.812	21.5	37.108
Mn	16.523	12.796	13.088	22	15.867
Fe	0.0298	0.0279	0.0693	31.25	0.0066

The *Telferria occidentalis* leaf planted at the Aba river side by Oct/Nov2014 were observed to be of no health risks arising from toxic effects of Cu, Zn, Cr and Fe, at all the test stations within this periodbeing less than one excepting at ABT station . Cd had a maximum THQ of 21.893 USAR and minimum THQ 0.14 ABT.Ni values were:2.6 PZ;10 ABT; 4.595DSARwhile Pb values were (36.42USAR;22.58; 8.81NBL; 21.5ABT;37.11DSAR. Mn values were(16.523USAR;12.796 PZ;13.088NBL; 22.0ABT and 15.867DSAR. The THQ values are > 1.0, the THQ's of the trace metal from the consumpsion of *Telferria occidentalis* leaf is in increasing order Fe > Pb > Mn > Cd > Ni > Cu > Zn > Cr. These results suggest that Fe ingestion has the highest potential health risk of adverse effect and Cr igestion has the minimuim risk. These results are found similar to those reported by Nagajyoti*et al.*(2010), Agrawal *et al*. (2007) Lawal *et al*.(2011).The consumers of *Telferria occidentalis*leaf are by this report prone to high risks

associated with bio-concentrations of these metals Pb, Mn and Cd from the plant planted by Aba river side(Walling *et al*., 2004).

Table 4.47 Target Hazard Quotients of Heavy Metals in *Telferria occidentalis* Leaf Dec 2014/Jan 2015

METAL	USAR	PZ	NBL	ABT	DSAR
Cu	0.1342	0.0291	0.0364	1..62	0.0418
Zn	0.0039	0.0059	0.0064	1.68	0.0058
Cd	24.58	12.185	3.7776	3.4	7.0221
Cr	24.72	1.3149	1.1152	1.53	1.0533
Ni	5.23	11.8757	19.345	25.12	12.9703
Pb	8.1236	5.4318	4.9086	6.89	4.7433
Mn	17.112	8.7728	11.581	30.1	22.2023
Fe	0.0716	0.0107	0.0104	10.94	0.0161

The results from *Telferria occidentalis* leaf analyses in the months of Dec2014/Jan2915 gave an indication of bio-accumulation levels of the metals Cd as 24.58USAR,12.19PZ, 3.77 NBL , 3.4ABT,7.0221 DSAR andCr as 24.72 USAR,1.53 ABT, 1.1152 NBL, 1.053 DSAR is a significant value which today is not harmful but with continued consumption of the leaf may bio-accumulate to lethal level.THQ result's for Nihad values of 5.23USAR, 11.875PZ, 19.35 NBL, 25.12 ABT and 4.595 DSAR while Pb had valuesof (8.12 USAR, 5.432 PZ, 4.91 NBL, 6.89 ABT, 37.108DSAR;Mn had values of 17.11 USAR,8.778PZ, 11.58NBL, 30.1ABT and 15.86 DSAR. The THQ values exceeding one suggest that the inhabitants of Aba river side will confront a significant potential healthrisk by intake of trace metals Cd, Cr, Ni, Pb and Mn from consumption of *Telferria occidentalis* leaf. The THQ's values of the trace metals is in

increasing order Mn > Ni > Cr > Cd >Fe > Pb > Zn > Cu.These reports were similar to the report by Agrawal *et al*.(2007).

Table 4.48 Target Hazard Quotients of Heavy Metals in *Telferria occidentalis* Leaf of Feb/March 2015

METAL	USAR	PZ	NBL	ABT	DSAR
Cu	0.1962	0.0413	0.0077	0.16	0.0046
Zn	0.059	0.004	0.0039	3.91	0.0183
Cd	54.73	14.044	0.2272	0.18	0.2478
Cr	6.8844	0.0895	0.1928	0.31	0.241
Ni	1.2391	1.1876	0.1549	2	0.5163
Pb	23.407	11.704	12.392	19	12.392
Mn	8.1876	10.179	2.286	15.4	9.2202
Fe	0.121	0.1127	0.0165	20.79	0.0391

From the results of Feb/Mar2015, it was seen that metals like Fe, Cu and Zn were below or within safe limit, THQ < 1.0 except at ABT; other metals such as Cd[54.73USAR and 14.04 PZ),Cr (6.88USAR;THQ > 1.0 were above safe limits. Nickel had significant levels atUSAR, PZ and ABT:Ni(1.2USAR, 1.19PZ,ABT2.0), while Pblevels were 23.40USAR; 11.70 PZ; 12.39NBL;19ABT;12.39 DSAR and were above one. Mn values were 8.19USAR;10.19PZ; 2.28 NBL; 15.4ABT; 9.2DSAR),Tracemetals Cu,Zn, and Zn had THQ values not exceeding one which suggests no significant potential health risks by the intake of the trace metals from consumption of this leaf. The THQs from of the trace metals from consumption of Telferria occidentalis leaf is in increasing order Cd>Pb>Fe>Mn>Cr>Zn>Ni>Cu.This result suggesrs that Cd ingestion has the highest potential health risk of adverse effects and Cu ingestion had

the minimum risk.. These reports were observed to be similar to that by Orisakwe *et al*; (2012). By these results, the THQ confirmes that unsafe health condition may emerge in the near future following continued consumption of this leaf (*Telferria occidentalis)* from Aba river side.

Table 4.49. European Union Standards for Cd, Cr, Cu, Ni and Pb

Standard	Cd	Cr	Cu	Ni	Pb
European Union Standards (2002) for soil (mg/kg)	3.0	150	140	75	300
European Union Standards (2006) for vegetables (mg/kg)	0.2	0.3	40	2.3	0.3
Indian Standard for plant (mg/kg)	1.5	20.0	30.0	1.5	2.5
NAFDAC standards for fresh vegetables (mg/kg)	….	….	…..	2.7	2.0

Source: WHO/FAO 2007(Aweng *et al.,* 2011), Abdulmojeed *et al.,* (2011) 1mg = 1,000µg

4.6. Target Hazard Quotient of *Talinum trianglare* leaf

The Target Hazard Quotient of *Talirum trianglare* leaf for the period June 2014 to May 2015 are shown in Tables 4.50 to 4.54. .Also the International Standards for metal concentrations in vegetables is shown in Table 4.48 Heavy metals are extremely persistent in the environment because of their non-biodegradable nature, long biological half-lives, thermal stability and potential to accumulate to toxic levels in both plants and animals (Adah *et al*. 2013; Rantetampang and Mallongi 2013,2014).

Table 4.50 Target Hazard Quotients of Heavy Metals in *Talirum triangulare* Leaf Period of

June/July 2014

METAL	USAR	PZ	NBL	ABT	DSAR	MEAN
Cu	0.0749	0.0361	0.0441	0.0503	0.0769	0.0565
Zn	0.0138	0.1146	0.0975	0.1352	0.063	0.0848
Cd	27.097	23.751	3.9654	4.3991	3.8828	12.619
Cr	2.8915	3.3734	2.5817	9.2251	4.764	4.5671
Ni	0.6712	0.8055	0.726	0.6403	0.1342	0.5954
Pb	9.8447	5.7142	6.4783	7.3801	7.5453	7.3925
Mn	36.54	29.136	61.222	23.895	17.26	33.611
Fe	0.1229	0.143	0.1388	0.132	0.1452	0.1364

Target hazard quotient for *Talirum triangulare* leaf in Aba river side was analyzed for heavy metal concentrations . *Talinum trianglare* leaf was observed to have bio-accumulated heavy metals such as Cd,Cr and Pb at all the sites with respective elements had THQ values that were above one with a seasonal mean of 12.62,4.56 and 7.39 respectively. These reports for Cd and Pb were observed to be similar to that reported by Lakhande *et al*.(2011). Cr had THQvalues of [2.89 USAR, 3.37 PZ, 2.58 NBL, 9.23 ABT and 4.76 DSAR withmean of 4.5671 while Mn had THQvalues of 36.54 USAR, 29.14PZ, 61.22NBL, 23.89ABT, 17.26DSAR with mean of 33.611, which are above one.The metals Cu, Zn and Fe had the THQ not above one. Ni THQ values were below one. It was observed that the metal Ni had values which were significant though not a threat but can bio-accumulate with time to lethal dose.The THQs of trace metals from consumption of *Talinum triangulare* leaf with values for individual element exceeding one suggests that the Aba River side population will confront with significant potential health risk by intake of a single trace element Mn,Cd,Pb and Cr from *Talinum*

triangulare leaf.The THQs from trace metals from the consumption of by this month is increasing order Mn>Cd>Pb>Cr>Ni>Fe>Zn>Cu.The report suggests that Mn ingestion has the highest potential health risk of adverse effects and Cu ingestion has the minimum risk. These results were observed to be similar to that Adah *et al.*(2013).

Table 4.51 Target Hazard Quotients of Heavy Metals in *Talirum triangulare* Leaf Period of Aug/Sept 2014

METAL	USAR	PZ	NBL	ABT	DSAR	MEAN
Cu	0.0980	0.1210	1.4770	3.050	0.989	1.147
Zn	1.0120	0.5680	0.0841	1.7638	1.2736	0.9403
Cd	23.834	1.0128	0.3718	0.9081	2.8915	0.5402
Cr	2.0859	0.3097	0.0785	0.1032	0.1239	2.6021
Ni	0.0567	0.0775	0.0929	0.1084	0.1601	0.3675
Pb	0.4131	0.5714	0.0778	0.3924	0.1583	0.3226
Mn	2.5743	0.0392	0.4363	0.8556	1.3425	1.0496
Fe	0.0395	0.0626	0.9034	0.0566	0.1026	1.0826

The THQs of individual trace elements through the consumption of *Talinum triangulare* leaves for the Aba River sidepopulation in Aug/Sept 2014 are listed in Table 4.51.The values of individual elements that exceeded one for the trace elements Cd 23.834 USAR, 1.0128 PZ, 2.8915 DSAR , with mean 0.5402, Cu 1.4770 NBL, mean 1.147, Mn 2.5743 USAR, 1.3425 DSAR, with mean 1.0496, Cr 2.0859 USAR, with mean 0.5402, Zn 1.7638 ABT, 1.2736 DSAR, 1.0120 USAR with mean 0.9408. The THQs values greater than one suggests that the Aba River population will confront significant potential health risk by ingestion of single trace metal Cd, Mn, Cr, and Zn from *Talinum triangulare*

leafconsumption.The trace elements Pb, Ni, and Fe with THQs value lessthan one will not suffer a significant potential health risk. The trend of THQs from the consumption of *Talinum triangulare* leaves are in decreasing order Cd > Cu > Mn > Cr > Zn > Pb > Ni > Fe. This report suggests that Cd ingestion has the highest potential health risk of adverse effects and Fe ingestion has the minimum risk. These results are similar to that by Adah *et al* ; (2013).

Table 4.52 Target Hazard Quotients of Heavy Metals in *Talirum triangulare* Leaf Period of Oct/Nov 2014

METAL	USAR	PZ	NBL	ABT	DSAR	MEAN
Cu	0.0516	0.0258	0.0287	1.3000	0.0387	0.2889
Zn	0.0344	0.0358	0.0011	1.0800	0.0004	0.0359
Cd	21.893	0.2065	0.2891	0.1400	0.3718	4.5801
Cr	0.0689	0.0895	0.1033	0.1200	0.0757	0.0915
Ni	0.981	2.6333	0.1549	10.0000	4.5954	3.6729
Pb	36.42	22.581	8.812	21.5000	37.1080	25.2842
Mn	16.523	12.796	13.088	22.0000	15.8670	16.0548
Fe	.0298	0.0279	0.0693	31.2500	0.0066	6.2767

The leaves of *Talinum trianglare* analysed in Oct/Nov 2014 indicated that metals Cu ,Zn, Pb and Fe did not pose health problems from the consumption of this leaf at all the sites excepting ABT, The THQ values being less than one suggests that consumption of the leaf at this station will not suffer significant potential health risk.The rest heavy metals had THQ values above one Pb 37.1080 DSAR, with mean 25.2842, Cd 21.8930 USAR, mean 4.5801, Mn 16.523 USAR, mean 16.054, Ni10.0000 ABT with mean 3.6792, Fe 31.2500 ABT,mean 6.2767.These results points that the consumption of this

leaf from this station will confront significant health risk from ingestion of single element Pb, Cd, Mn, Ni and Fe .The consumption of *Talinum triangulare* leaf in Oct/Nov2014 followed anincreasing order Pb > Cd > Mn > Ni > Cr > Fe > Cu > Zn.This result suggests that the ingestion of Pb,has the highest potential health risk while the ingestion of Zn has the least health risk These reports were similar to those of Kara (2005).

Table 4.53 Target Hazard Quotients of Heavy Metals in *Talirum triangulare* Leaf Period of Dec 2014/Jan2015

METAL	USAR	PZ	NBL	ABT	DSAR	MEAN
Cu	0.0028	0.0081	0.0072	0.0043	0.0044	0.0233
Zn	0.4017	0.369	3.0876	3.0876	0.6887	1.5269
Cd	0.2272	0.0454	0.005	0.064	0.0661	0.3548
Cr	0.0034	0.077	0.115	0.1225	0.0695	0.0774
4Ni	0.005	0.0155	0.0774	0.1858	0.0103	0.2858
Pb	0.1996	0.0068	0.0207	0.0143	0.0199	0.2454
Mn	2.1095	0.9525	0.9442	0.8778	1.2318	1.2232
Fe	0.3364	0.4219	0.5134	0.4396	0.3879	0.4198

The results of analysis of *Talinum trianglare* leaves in Dec. 2014/Jan2015 indicated that Mn exceeded one at the USAR 2.1095 but had significant values at PZ 0.9525, NBL 0.9442, ABT 0.8778, DSAR 1.2318 (El-Gendy *et al*., 2006 and Maine *et al.,* 2004). The THQs for Cu, Cd, Cr, Ni and Pb wereless than one suggesting that consumption of the leaf of *Talinum triangulare* by this month will not suffer significant health risks . Fe had THQ less than one but with a significant value that will bio-accumulate to lethal levels in the near future at the NBL 0.5134. Zn had THQ values greater than one at NBL3.0876; ABT 3.0876; with mean 1.5269 and a significant reading at DSAR 0.6887; Mn had THQ value greater than one at USAR 2.1095; DSAR 1.2318; with mean 1.2232 and a significant resultat NBL 0.9442. The THQs greater than one indicates that the

Aba river side population from the consumption of *Talinum triangulare* leaf will confront significant health risk from ingestion of single element Zn and Mn. These results are similar to that by El-Gendy *et al*; 2006 and Marie *et al*; 2004).

Table 4.54 Target Hazard Quotients of Heavy Metals in *Talirum triangulare* Leaf Period of Feb/March 2015

METAL	USAR	PZ	NBL	ABT	DSAR	MEAN
Cu	0.0028	0.0083	0.0056	0.0043	0.0042	0.005
Zn	0.5576	0.4626	2.485	1.7142	0.3855	1.12098
Cd	0.2457	0.0454	0.0392	0.1342	0.0371	0.1003
Cr	0.1824	0.1914	0.0703	0.0929	0.0026	0.1079
Ni	0.0002	0.0021	0.0465	0.0439	0.0145	0.0214
Pb	0.0021	0.0034	0.0056	0.1928	0.1446	0.0697
Mn	2.3213	0.9736	0.9921	0.8099	0.9342	1.2062
Fe	0.2998	0.3589	0.5275	0.339	0.3916	0.3834

The THQs of the individual elements from the consumption of *Talinum triangulare* leaves in Feb/Mar 2015 are listed in Table 4.56.The values for THQ that exceeded one are for trace elements Zn at NBL 2.485, ABT 1.7142 with amean of 1.1201, Mn at USAR 2.3213 with a mean of 1.2062. The THQs value greater than one suggests population confronting potential health risks from the consumption of this leaf. Zn values were less than one but of significant,values: 0.5576 USAR; Mn 0.9735 PZ; 0.9921 NBL ; 0.8099 ABT; 0.9342DSAR; Fe0.5275NBL with mean 0.3834. The significant values of THQ suggests that the ingestion of *Talinum triangulare* leaves will through bio-accumulation pose an health risk in the future. It is recommended that substantial attention be paid to the heavy metal levels in the water and fresh vegetables from the Aba river side. The implication of the results is that *Telferria occidentalis* leaf was a better bio-accumulator of heavy metals when compared to

Talinum trianglare leaf. On the other hand *Talinum trianglare* could be seen as a better filter of the heavy metals in that the tissues restricted the bio-absorption of some of those toxic heavy metals. It was further observed that the concentration of the heavy metals were higher in one plant(*Telferria occidentalis*) than in the other (*Talinum triangulare*). This difference was ascribed as a result of the physiological and morphological formations of the plants like variation in root interception of metal ions, variation in entry of the metal ions through mass flow and diffusion and translocation of metal ions from the root to shoot, their accumulation tendency and retention capacity (Carlton-Smith and Davis, 1983). Plants growing in metal-polluted sites exhibit altered metabolism, growth reduction, lower biomass production and metal accumulation. It is only when metals are present in bio-available forms and at excessive levels that they have the potential to become toxic to plants Eriyamremu *et al*; (2005), had similar results on some common vegetables like *Vernonia amygdalina* (bitter leaf),*Talinum triangulare* (Ceylon spinach or water leaf), and *Telferia occidentalis* (fluted pumpkin) being contaminated with varied concentrations of Cd and Pb ranging from 0.002 to 0.35 and 0.016 to 4.91 mg/kg respectively.

Threat to health did exist in this study from consumption of the leaves of *Telferria occidentalis* and *Talirum triangulare* following the bio-accumulating of heavy metals Cd, Cr, Pb, Mn and Ni which were observed to have risen from non-detectable concentration through to significant concentration to lethal concentration after prolonged bio-accumulation time. The concentrations of the heavy metals varied with the plant leaves as *Telferria occidentalis* bio-accumulated higher concentrations per element than *Talinum triangulare* (Marie *et al*; 2004; Rantetampang and Mallongi, 2013a, 2013b).

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

5.1 Summary

This work assessed the quality of water from Aba river in Aba, Abia State ,Nigeria from June 2014 to May 2015 on a bye monthly terms for the concentrations of trace metal pollutants and the Physicochemical parameters .The results revealed that temperature was within WHO set limits for drinking water.The results of mean Electrical conductivity (6.08-14.64 µS/cm); PO_4^{-3}(1.72-180.43 mg/L); Turbidity(4.78-16.11NTU) and Chloride (94.18-200.52 mg/L) were within the set limits by WHO. The pH ranged from (6.59 - 4.82), Dissolved oxygen (56.46-71.91 mg/L), Chemical oxygen demand (178-180.43 mg/L) and Biological oxygen demand (51.94-68.48 mg/L) were above the set standard limits by WHO. Alkalinity (14.84-34.14 mg/L),pH (5.54-5.85), TSS (29.79-41.31 mg/L), TH (43.37-75.42 mg/L), TDS (51.86-60.03 mg/L).The high values of DO,COD and BOD were indications that the water was not of good quality. The high TDS and TSS showed poor water quality.

The result of pollution index for these parameters DO,BOD,COD, Cd, Pb, Cr, Fe, Zn, Mn, Cu and Mn confirmed that pollution index for the river was greater than one (>1.0) indicating heavy contamination of the Aba river water for both the rainy and dry seasons.

Regression analyses on pollution indicators gave some linear equations relating the said parameters . Heavy metals (Fe, Pb, Zn, Cu, Mn ,Cr, Cd and Ni) were determined in sediment, water and plant tissues (*Eichhnor crassipes,Telferria occidentalis and Talirum triangulare*) from Aba river side. Vegetables planted by the river side consumed by the inhabitants of Aba river side when analyzed gave values of heavy

metal bioaccumulation factors for all the metals tested above WHO set safe standards except Fe, Cu and Zn on the two edible vegetables, *Telferria occidentalis and Talirum triangulare* leaves.These vegetables accumulate considerable amount of heavy metals in them and people indirectly injestthe the heavy metal contents(Ademorati,1996). The considerable variations in the levels of these contaminants among the different plant species indicates the important role of the physiological and ecological factors on the concentrating pollutants.

The Target Hazard Quotient test carried on the two edible vegetables indicated that *Telferria occidentalis* leaf had a THQ value above the permissible limit for Cd, Cr, Pb,Mn, and Ni which are possible cancer causing , while the THQ values for Fe,Cu and Zn were below the permissible limits is safe,no risk and hence non cancer causing.

The Target Hazard Quotient for the *Talirum triangulare* leaf had THQ values above safe limits for Cd,Cr,Mn and Pb which are possible cancer causing while the results for Fe,Cu,Zn and Ni were below the safe permissible limits hence are none cancer causing.

Eichhnor crassipes gave varied results of the bio-concentration factors on heavy metals for different parts of the plant, some metals such as Fe, Mn and Zn were bio-accumulated more in the leaf ,stem and root tissues, while others like Cd and Cu were bio-accumulated more on the stem and some also were bio-accumulated less on the roots like Ni, Cr and Cd.

The geo-accumulation index Igeo(x) of heavy metals on sediment gave the range of geo-accumulation index of the heavy metals; Cu:0.0431-15.3558; Cd:0.5849-4.5; Fe:1.0081-12.3310; Cr:1.1652-9.4972; Zn:1.0967-10.2111; Ni:0.2504-7.2216; Pb:0.7123-9.5873; Mn:1.6616-13.1113 Igeo (x).

Some heavy metals were discovered to have common source of origin from the correlation tests between metals such as Pb, Mn and Cu, while Fe, Ni, Cd, Zn, and Cr had negative correlations .

The summation of the above led to the conclusion that the Aba river water was not suitable for human consumption and therefore should be boiled and filtered before use for domestic purposes.

5.2 Conclusion

The Trace metals (Fe, Pb, Zn, Cu, Mn,Cr, Cd and Ni) tested were found to have varied bio-accumulation factors for the different tissues of *Eichhnor crassipes* (Leaf, Stem and Root). The geo-accumulation index for the heavy metals were found to vary with site and time.

The THQ results informed the unsafe health condition which may emerge in the near future following continued consumption of the *Telferria occidentalis* leaf from Aba River side. These results were observed similar to that by Orisakwe *et al.,* (2012).

Aba River from this work was confirmed heavily polluted by the industrial effluents discharged into it as the pollution index values were greater than 1.0.

5.3 Recommendations

From the results obtained in this work it is recommended that regulatory legislation controls be set up to control the treatment and discharge of the Industrial effluents into the river such as:

i. Consumers by the Aba river side should be cautioned of the associated dangers that may manifest in the near future as a result of bio-accumulation of these heavy metals in the body following prolonged use of the water and vegetables from the Aba river.

ii. Proper treatment of effluents prior to discharge into Aba River.

iii. Local government authorities should oversee activities near Aba River.

iv. There should be regular maintained monitoring and enforcement of the relevant policies concerning Aba river.

5.4   Contribution to Knowledge

This work has provided detailed information on the pollution status of Aba River due to industrial effluents. Such informationincludes the quality indices based on physicochemical parameters and of the heavy metals.

The study has provided foundational information which highlighted the effects of improper disposal and mismanagement of generated wastes from anthropogenic activities.

From this work the heavy metal distribution trend on the respective tissues of *Eichhnor crassipes*(leaf, stem and root)has been established.

This work showed that the leaves of *Telferria occidentalis and Talinum triangulare* were identified as viable plants for remediation of heavy metals (Byrne, 2012).

This study gave information on the geo-accumulation trend of heavy metal distribution on the sediments of Aba River.

The study adds to the data pool on health risks assessment base of the impact of industrial effluents on the inhabitants of the study area.

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ACRONYM

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