CHAPTER ONE

1.0 INTRODUCTION

1.1 GENERAL STATEMENT

The physical/chemical variability in rivers and estuaries is enormous, but causes and interaction are not clearly defined. Variations forced by weather and climate appear to be very important, but we don't yet understand how riverine-estuarine systems operate on very short and moderately long time scales. (USGS, 2014)

Project objectives are to better understand the variability of the physics (circulation) and chemistry (primarily oxygen, carbon, nitrogen and phosphorous dynamics) in riverine and estuarine environments, and to discriminate between natural due to atmospheric/oceanic forcing and human caused impacts.

To develop and implement an effective plan for a comprehensive estuarine monitoring network, it is important to understand the nature and dynamics of estuaries in general, and also to understand the details of the particular estuary, embayment, harbor, or river to be monitored. These details include the bathymetry, tidal range, circulation patterns, and pollution problems that are being encountered. (EPA, 2012)

Furthermore, the effect of anthropogenic activities also may be important. Without such kind information we cannot understand and predict how these system respond to variations in the amount, toxic- waste, sediment and plant-nutrient inflows to these environments.

Monitoring water quality in estuaries produces different results to monitoring freshwater (WEG, 2012). The estuarine environment is a complex blend of continuously changing habitats. Unlike fresh water rivers and lakes, estuaries can produce a wide range in the values of physical and chemical parameters that will be recorded, and frequent changes occur in these values both with tidal cycles and meteorological events. In streams, rivers, and lakes, water quality parameters are more likely to fluctuate within a well-defined range largely determined by rainfall and season, and these values are often homogenous throughout the water body. In an estuary, in contrast, these parameters can change abruptly in time and space, are dependent on the measurement location, and may or may not reflect general environmental conditions throughout the estuary. (EPA)

1.2 AIMS AND OBJECTIVES

The aim of this study is to investigate and assess the water physiochemical and sediment chemical properties spatial distribution from Aiyetoro river waterways to Abereke estuary with the objectives as follows:

- Determining and comparing the water physiochemical parameters in the rivers and estuary.
- Determining the depths along the waterways to the ocean mouth
- Determining and comparing the concentration of heavy metals in the rivers and estuary sediment.
- Correlating result with standards and limits.

1.3 THE STUDY AREA

The coastal region of Ondo State at the Ilaje Local Government area of the south western part of Nigeria between Lat. 5˚50’ – 6˚ 20’N and Long. 4˚40’ – 5° 05’ E as represented in Fig 1 below was the study area. The surveyed catchment has a total area of over 500km^2 and watershed of over 2500km transverse by river tributaries (Ondo State Surveys, 1998). The general climate is tropical humid condition of the Koppen-Geiger Am classification (Kottek et al., 2006). The mean annual rainfall is about 2,721mm, mean annual number of rain days around 170, mean monthly rainfall around 229mm and mean annual temperature of about 27.80C (Fasona, 2007).

The mud beach coast evolved from the growth of the Niger Delta into the gulf of guinea following gradual retreat of the sea after a short-lived Paleocene transgression (Wright et al., 1985). Major geological formations include general alluvium, lagoonal marshes, abandoned beach ridges and coastal plains sand. The exposures on the general alluvium reveal coarse, clayey, unsorted sands with clay lenses and occasional pebble beds which are lithologically indistinguishable from typical coastal plains sand strata (Jones and Hockey, 1964). These formations produce generally swampy soils on the nearly level coastal plains sand on alluvium, and very deep, well drained soil, with very dark brown to dark brown surface sands from the nearly level coastal plains on coastal plain sand (Federal Department of Agriculture and Land Resources, 1985). Elevation rises from about 1m along the coastline to between 35 and 55m in the upland (Fasona and Omojola, 2009; Iyun and

Source: Lawrence, 2014.

Figure 1. Map of Ilaje Local Government, Ondo state

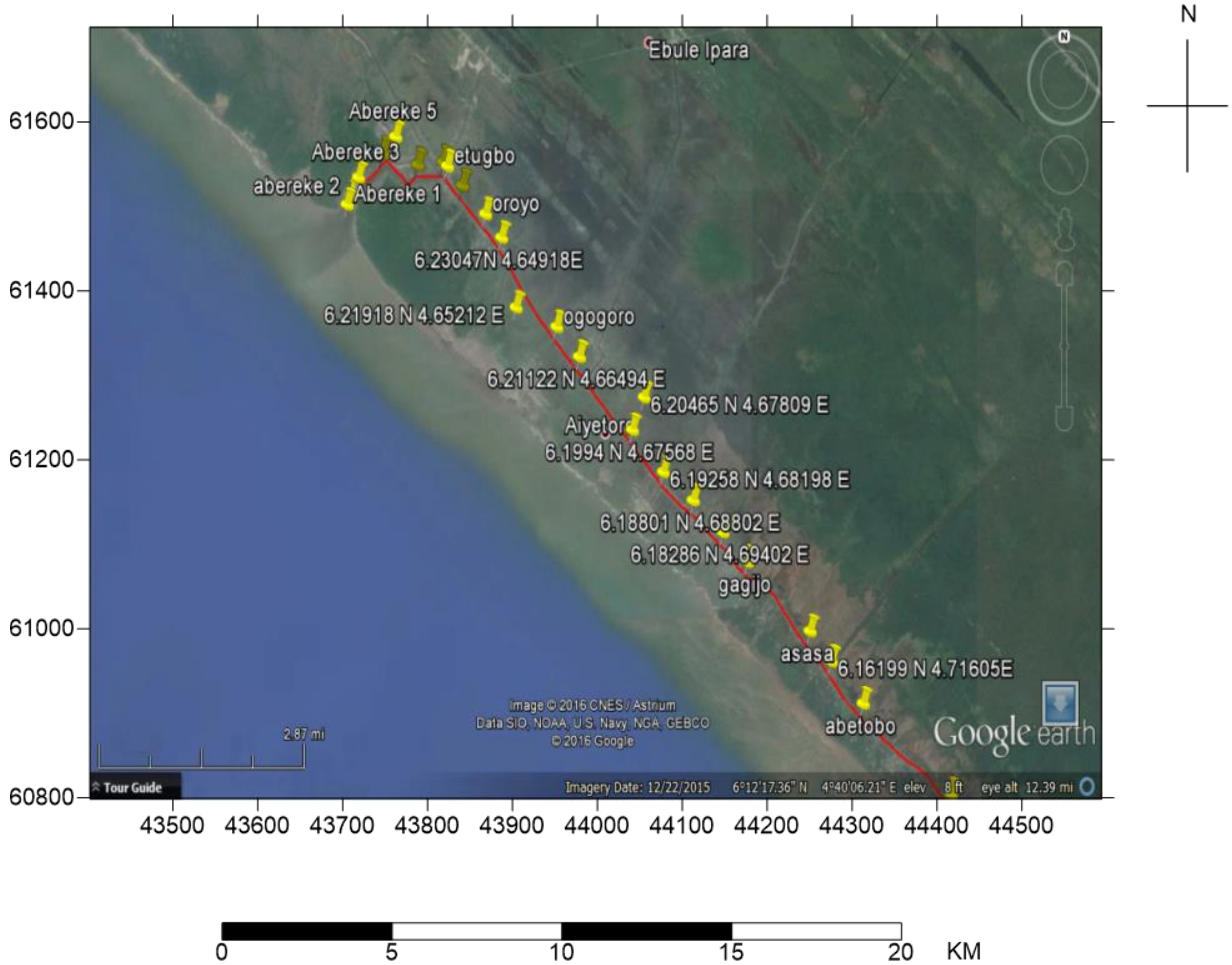

Figure 2. Map of study area

Oke, 2000). Although the firm upland area in the north is dissected by some seasonal rivers of the western littorals, surface drainage is sparse around the coast. (Omojola & Soneye, 2011) Topography and Drainage

At the axis of the Niger Delta, there is more burying of the sands by silts. The occurrence of sand and mud deposits is related to the river outflows. The silt muds are deeper at the axis of the Niger Delta off the kulama river. These muds grow progressively shallower westward, and wests of mahin flats (Ondo state) sand deposits are dominant (Fisheries and Aquaculture Department, 1985). The numerous lagoons in the coastal area have all disappeared due to silting and spread of aquatic weeds; the only survivor is the Mahin Lagoon. All the creeks and rivers in the area drain into Benin River. It is only here that the sandy beach materials of the Nigerian coastal plain are replaced by mud and lacustrine deposits. Olorunlana, 2013.

The major vegetation of the landscape is majorly open grassland, few trees and mangroves in many areas, some areas had plantations like plantain trees planted by people settling there.

The coastal soil is majorly fine grained muddy sand, usually dark or darkish-grey and organic in nature. This shows that the energy of deposition is low and erosional speed is slow.

The soils are hydromorphic. The older sand ridge complexes develop brown and orange sand soils while the more recent one near the coast bear light grey sand soils. Where there are depressions on the ridge complexes, the soils can be described as poorly drained light grey sands. The swamps flats are characterized by swampy ‘organic’ soils which in the major part consist of decomposed and partly decomposed matter, while areas affected by tides bear saline soils.

The economic activities includes in the area include agricultural practices, fishing, oil prospecting and commercial activities carried out by motorboat transportation. The coast is close to the Bright of Benin in the Atlantic Ocean and is in-between Lagos coast and Delta Coast, which are highly populated.

1.4 LITERATURE REVIEW

Many analytical work has been carried out on natural water bodies, both fresh water and marine water, throughout the globe and as such a voluminous literature is available on the subject. In view of the objective of the present research, a critical survey of literature was carried out to gather information on various relevant aspects such as physicochemical features, heavy metals concentrations and their bioaccumulation.

1.4.1 Physiochemical parameters

Seasonal variations in water temperature of various aquatic bodies have been recorded by Welch (1952), Hannan and Young (1974) and Harshey et al. (1982). Jolly and Chapman (1966) made a preliminary study on effects of pollution on Farmers Creeks and Cox's river with respect to temperature. pH variations in water are widely studied worldwide. Impact of addition of sewage and industrial effluents on pH levels has been observed by Oswald (1960) while Hannan and Young (1974) and Chapman and Kimstach (1992) recorded effects of industrial discharges on the pH level of water. Wanganeo (1984), Khalique and Afser (1995), Islam (1996) and Sithik et al. (2009) recorded changes in pH values with addition of sewage and agricultural effluents. Dissolved oxygen which is a parameter of primary importance in the aquatic ecosystem by virtue of its role in both chemical as well as biological reactions, has been recorded in various water bodies throughout the world by Hutichinson (1957), Reid (1961), Ray et al. (1966) and Kara et al. (2004). The changes in dissolved oxygen levels in water with addition of domestic sewage, various industrial wastes and agricultural run-off have been investigated in different water bodies by Gonzalves and Joshi (1946), George et al. (1966), Jolly and Chapman (1966), De Smet and Evens (1972), Cairns et al. (1975), King (1981), Woodword (1984), Meybeck et al. (1992), Jameson and Rana (1996) and Jameel (1998) and Otieno (2008).

1.4.2 Temperature: Temperature is a commonly measured water quality parameter, and is a critical factor influencing chemical and biological processes in an estuary. For instance, increased temperature decreases the level of oxygen that can be dissolved in the water column. Water temperature influences the rate of plant photosynthesis, the metabolic rates of aquatic organisms, and the sensitivity of organisms to toxic wastes, parasites, diseases, and other stresses. Temperature is recorded in degrees Celsius (Centigrade) or Fahrenheit.

Olatayo (2013) assessed temperature from four coastal towns (Ayetoro, Idiogba, Bijimi and Asumogha) in Ilaje local government area of Ondo State using standard methods with the view of determining the level of pollution through anthropogenic activities and state of the aquatic ecosystem. The results of the analyses of the water samples showed that temperature had minimum mean value of 29.42^{o}C in both Bijimi and Idiogba and maximum mean of 29.75^{o}C recorded in Asumogha.

1.4.3 Suspended Material Concentration and Turbidity: Suspended material concentration is the amount of material that is suspended in the water column and is measured as the amount of material retained in a filter. Smaller particles are considered dissolved solids. The sum of suspended and dissolved solids is referred to as total solids. All three measures are recorded in terms of mg/l. Turbidity is a measure of water clarity, that is, the ability of water to transmit light, and is influenced by the level of suspended material in the water column. Turbidity is often measured visually using a Secchi disk**.**

TDS is a convenient measure of the total ionic concentration in water. Large amounts of dissolved solids can lead to increased mineralization of the receiving waterway with the consequence of dissolved oxygen depletion (Akpan 1991; Essien-Ibok et al. 2010).

Concentrations of total dissolved solids (TDS) or non-filterable residue was measurecd in Eastern Obolo estuary showed highly significance ($P<0.001$) and wide spatial variations between the sampling Stations with the lowest values recorded at Okorombokho (4266.7 mg/l) and the highest (15966.0 mg/l) recorded seaward at Iko, a settlement hosting an oil flow Station. Udoh et al. 2013.

1.4.4 Dissolve oxygen: Oxygen is a key parameter of interest in water quality monitoring, because nearly all aquatic life needs oxygen to survive. DO is the level of oxygen in the water column in molecular form that is available to support life and is reported in milligrams per liter (mg/l). The DO level is controlled by mixing at the air/water interface, temperature and salinity, the level of photosynthesis (which produces oxygen), and decomposition of organic material (which depletes oxygen). Coastal waters typically require a minimum of 4.0 m g/l and also do better with 5.0 mg/l of oxygen to provide for optimum ecosystem function and highest carrying capacity (UNESCO/WHO, 1978). Main source of oxygen is aquatic plants also provide atmosphere, but much during photosynthesis, oxygen may fall to unhealthy levels if water is polluted. Example if sewage and other wastes (e.g. from food processing) with high Biological

Oxygen Demand (BOD) are discharged into the sea (Clark, 1996). Generally, DO levels of greater than 4 mg/l indicate an adequate supply of DO to support marine species growth and activity, while levels from 1-3 mg/l indicate hypoxic conditions, which are detrimental to marine life. DO below 1 mg/l indicates anoxia, a condition in which no life that requires oxygen can be supported.

Abowei (2009) measured Dissolved oxygen from four Stations in Nkoro River using Dissolved oxygen meter of the model: Oxy-Guard Handy MK II. Dissolved Oxygen values ranged from 3.2±0.1 mg/l (Station 3) to 7.3±0.16 mg/l (Station 1).

1.4.5 Salinity: Salinity is a measure of the salt content of water. Salinity levels vary along an estuary depending on the mixing of freshwater and saltwater at a site. Generally, salinity increases along a coastal stream as it gets closer to the river mouth, where tidal influences are strongest.

A freshwater stream generally has an electrical conductivity (EC) of 200–300 µS/cm. Estuaries have a much higher electrical conductivity than freshwater (typically from 20,000 to 40,000 µS/cm). As salinity increases, conductivity also increases. Seawater typically has a conductivity of 51,500 µS/cm. Many aquatic species can survive only within certain salinity ranges, so changes in salinity levels may result in changes to the variety and types of species present. In coastal areas, salinity can be viewed as the major factor limiting species distributions as these vary significantly in relation to the level of salinity.

1.4.6 Alkalinity and pH: are two additional parameters that provide insight into changing water quality conditions in an estuary. Both can be determined by simple tests. Although these parameters are generally not as critical as DO and nutrients, they are important to ecosystem health because most aquatic plants and animals are adapted to a specific range of pH and alkalinity. Sharp variations outside of this range can be detrimental. In addition, pH and alkalinity influence the estuarine carbon cycle, which involves the movement of carbon from the atmosphere into plant and animal tissue and into water bodies. The pH of water is the measure of how acidic or basic it is. A pH level of 1 to 7 indicates degrees of an acidic solution, while a level of 7 to 14 indicates degrees of a basic solution. Alkalinity is a measure of water's capacity to neutralize acids and is influenced by the presence of alkaline compounds in the water such as bicarbonates, carbonates, and hydroxides. Alkalinity is reported as mg/l of calcium carbonate ($CaCO_3$). The livable pH range is from 5.5 to 10 (Moyle, 1993). A low pH can result in death as well as a variety of more subtle effects.

Ahiarakwem et al. (2012) collected a total of 30 water samples from Oguta Lake and 24 water samples from the associated rivers and analyzed using the AAS (atomic absorption spectrophotometer), digital meters and membrane filters. Their results of the analyses showed that the pH of Oguta Lake water varied from 5.1 to 6.5 with a mean value of 5.92, while the pH value of Rivers Utu, Awbana, Orashi and Njaba was 6.35, 6.30, 6.20 and 6.40

1.4.7 Geochemical survey

Many studies indicated that levels of metals were higher in sediment than in water. Krauskopf (1955) suggested the heavy metal concentration increases in the sediment due to the adsorption of cations by organic matter present in the sediment layers. Similarly Curits (1966) and Singer (1977) suggested that metals interact with organic matter in aqueous phase and settle down resulting in high concentrations in sediments. The role of sediments in adsorption of cations has been demonstrated in a study on rivers by Moriarty and Hanson (1988).

Many studies conducted on metal accumulation in sediment showed increase in metal levels in sediment with addition of sewage, industrial effluents and agricultural wastes (Vivian and Massie, 1977; Nolte, 1988; Fernandez et al., 1994; Barlas, 1999; Thari et al., 2005; Pradit et al., 2009; Uluturhan, 2009 and Wang et al., 2009). Bhuvana et al. (2014) assessed Kortalaiyar River in Tamilnadu, India for heavy like Cr, Ni, Cu, Mn, Zn, Ti, Co, Pb and Cd. The concentrations of the Co, Pb and Cd were below detectable levels in few locations, the other heavy metals exhibit their existence in significant levels.

The coastal area of Ondo State has 50 settlements dispersed within 2 local government area close to the coast and there is none existence of any pollution monitoring programme in the area. All domestic waste are directly discharged untreated into the coastal area by agricultural practices, atmospheric precipitation, roof and urban runoffs, soil leaching, seawater intrusion, water transportation means and oil exploration. With such discharge into the coastal system the amount of toxic contaminants entering estuaries has greatly increased. These contaminants include heavy metals (such as mercury, lead, cadmium, zinc, chromium, and copper), petroleum hydrocarbons, and synthetic organic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticides (e.g., dichlorodiphenyl-trichloroethane). Many of these toxic contaminants are persistent, can be incorporated into sediments, and can be concentrated in the food chain, so that they pose a magnified threat to animals at higher trophic levels and to humans. They are generally measured through laboratory analysis (which can often be complex and time-consuming), although field test kits are available for some heavy metals and other contaminants. The contaminant concentrations are usually reported in mg/l.

CHAPTER TWO

2.0 MATERIALS AND METHODS

2.1 DATA ACQUISATION AND FIELD PROCEDURES

Collection of environmentally relevant information involves a series of steps going from site selection, sampling, sample pre-treatment, and analysis (including quality control) to data handling, storage, and interpretation (Chapman, 1996). Even when state-of-the-art laboratory facilities are available close to the location of the field course, it is recommend that priority is given to simple basic parameters that can be measured directly in the field (Wetzel and Likens, 1991; Chapman, 1996).

2.1.1 MATERIALS USED ON THE FIELD

Various materials used on the field are listed below;

- Sampling bottles: water samples is been stored into the sampling bottles for laboratory analysis.
- Survey Boat.
- Echo sounder (FURUNO LS-6100): it is used for measuring the depth of subsurface water at a particular location.
- Multi – meter water analyzer (HANNA HI 9828): it is used in taking and recording the physico-chemical parameters of the water. It consist of a probe which is dipped inside the water and a meter which takes records and stores the various data gathered.
- pH meter: it is used to measure the acidity and alkalinity of the water, and it ranges from 1-14.
- GPS (global positioning system)
- Tapes and maker: used to label and identify water samples taking at different location'
- Field note for recording.

2.1.2 FIELD PROCEDURE

The water surface physiochemical parameters at each sampling points were detected and recorded by the multi-meter probe and analyzer directly in contact with the river and estuary from the mouth of the Atlantic Ocean at Abereke estuary to the river at Ilape about 19km along Aiyetoro waterway. The water depth was determined at each sampling point by the echo sounder erected at the side of the boat.

Surface water sample were obtained at 4 Stations in the estuary with distance of 10m separating each point, while at the river 19 water samples were obtained at 19 Stations. Twenty three 1litre of sampling bottles were used to collect the water samples for further laboratory analysis on nutrients.

Sediments from the bottom of river and estuary were obtained using the van veen grab, sixteen sediments were collected in total in polythene bags for laboratory heavy metal test.

2.2 LABORATORY ANALYSIS AND METHODS

2.2.1 MATERIALS USED IN THE LABORATORY

Various materials used in the laboratory are listed below;

- Aqua Regia Reagent
- Conical flask and beaker
- Atomic Absorption spectrophotometer
- Distilled water
- Funnel
- Filter paper

2.2.2 DIGESTION METHOD

Samples collected were sun dried, grounded and sieved to grain size of < 200 µm. 1 grams of each sediments was measured and digested with volume of 5 ml mixture of 16 M HNO_3 (J.T Baker) and 11.5 HCL (Fisher trace metal grade) in a ratio 2:1 into a conical flask. The whole mixture was boiled at temperature of 150 °C at which the sample was boiled for almost 2 hours until the solution is almost dry, then interior walls of the flask were washed with a little distilled water and stirred by stirrer and filtered with filter paper through funnel into a beaker. The resulting digests (filtrate) were made up in 100 ml volumetric flasks with distilled water. The metals obtained were regarded and analysed as pseudo-total metal because not all the silicate phase present in the sediments were dissolved but filtered out with an acid washed filters (45 µm pore size).

The analyses of Fe, Pb, Cr, Zn and Cu in the digested samples were done using Flame Atomic Absorption Spectrometer (AAS) AA320N model with direct air-acetylene flame method. The laboratory used is Geomodels Nigeria Limited located at Ola-Oluwa Crescent, off Awojulugbe Street, off FUTA Road, Akure.

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CHAPTER THREE

3.0 RESULT AND DISCUSSION

3.1 Physico-chemical parameters at different Stations within the Ilaje estuary and river are shown in Table 1. The **temperature** of all the locations is generally high with the temperature highest at Station 24 having a value of 30.88°C and lowest at Station 17 having a value of 28.48°C (Figure 3). Oloruntegbe, K.O. (Ph D), Akinsete, M.A., and Odutuyi, M.O. in their observation on Ilaje waters suggests pollution as a causal factor, more so that there is marked difference in observed data between spill and non-spill areas. Though the observed temperatures fall within the acceptable limits for aquatic lives, 20°C‑33°C, however, such high records are capable of reducing the dissolved oxygen, which is another important factor influencing aquatic lives. High water temperature enhances the growth of microorganisms however the effect of changes in temperature on living organisms can be critical. Temperature controls the solubility of gases in water, and the reaction rate of chemicals, the toxicity of ammonia, and of chemotherapeutics to fish. Temperature is the most important physical variable affecting the metabolic rate of fish and is therefore one of the most important water quality attributes in aquaculture

From the estuary through the rivers the **pH** is majorly around 7 except for Station 21 which have a pH of 8.11, thus the pH ranges between 7.26 and 8.11. The mean pH values are were well within the acceptable range for drinking water (6.5 to 8.5), optimal aquatic productivity (6.5 to 9.0) and livable range of 5.5 to 10 (Wetzel 2001).

The amount of **dissolve oxygen** in the river is averagely higher than the amount in the estuary though the highest value of dissolve oxygen 4.37 mg/l was obtained in the estuary at Station 2 and lowest in the river at Station 16 with a recorded value 1.29 mg/l. As noted earlier high temperature reduces the dissolved oxygen in water. The amount of DO is generally too low in the water body, the desirable amount of DO in water is usually greater than 4 mg/l, as a general rule, concentrations of DO above 5 mg/L are considered supportive of marine life, while concentrations below this are potentially harmful. The water is in hypoxic condition, but high temperature is not the reason, as the water are highly polluted with organic substances that deplete DO in the water.

The total dissolve solid and conductivity follows same trends decreasing in concentration from the estuary to the river as they are both highest at Station 3 with value of 24090 µS/cm and 48040 mg/l in the estuary respectively, conductivity is lowest at Station 24 (1800 µS/cm) and TDS lowest at Station 23 (1252 mg/l), Figure 4. Turbidity is a measure of the amount of suspended particles, which includes fine sediments, in the water. Circulation within the estuary redistributes the suspended sediment and a turbidity maximum usually is located in the region of the estuary where fresh water from the rivers contacts the more saline coastal waters.

Most estuaries are very efficient at retaining dissolved and particulate matter. In this respect, estuaries are often thought of as filters or traps that are located between the land and the sea. Because these systems are so efficient at retaining these substances, they are very susceptible to pollutants that are washed into the estuary. Organic and heavy-metal pollutants typically have a long residence time in estuaries and tend to accumulate over time.

Salinity is higher in the estuary and reduces towards inland water, salinity influences the density of water, temperature is another parameter that influences water density. The density of water plays a major role in the movement of water in estuaries. Density, which is the weight per unit volume of water, increases with increasing salinity and decreasing temperature. In an estuary, the lighter fresh water mixes with the heavier salt water from coastal waters and creates a gradient in water density in the estuary. As the fresh water gains salt, becomes heavier, and sinks, the resulting movement of water is known as gravitational circulation, and is caused by density and elevation differences between the fresh-water runoff and saltier coastal waters. In some estuaries, large differences in water temperatures can also drive gravitational circulation. Figure 5 salinity, temperature and density data were plotted into a graph to show how water is driven by density and how saline and fresh water are mixed, the colder water with high salinity are the densest water, though salinity play more role in the stratification of the water, temperature also contributes to the water mass. In the region around temperature of 29.5°C and salinity between 15 and 30 the graph forms an antiform showing how serious mixing between the fresh and saline water is going on there. Figure 6 shows the density variation with location with the denser water in the estuary, also showing depth of the water body with the thickest area representing the deepest depth and smaller area representing the shallower depth of the water body.

Table 1. Physico- chemical parameter

Sample location	Location	lat N	long E	temp (°C)	pressure (mmHg)	conductivity (µS/cm)	TDS (mg/l)	salinity (‰)	density (g/cm^3)	DO (mg/l)	pH	depth (m)	
S1	O1	6.23582	4.61787	29.11	765.8	46850	23420	30.29	24.3	3.5	7.76	3.6	Abereke
S2	O2	6.23712	4.61873	28.92	766	47340	23230	30.13	24.8	4.37	7.75	2.1	
S3	O3	6.24021	4.62015	28.98	758	48040	24090	31.33	35.2	3.5	7.84	4.3	
S4	O4	6.24408	4.62511	28.96	759	46060	23030	29.77	23.8	3.28	7.76	4.4	
S5	O5	6.2468	4.62769	29.04	760.4	46840	23530	30.37	24.4	3.18	7.79	4.5	
S6	O6	6.24225	4.63219	28.99	761.2	46990	23500	30.42	24.4	2.96	7.75	4.5	
S7	O7	6.24268	4.6373	28.9	762.1	45100	22600	29.24	23.5	2.74	7.66	4.9	
S8	O8	6.24205	4.63819	29.47	762.5	48030	24000	31.16	25	3.35	7.8	4.8	Etugbo
S9	O9	6.2389	4.64125	29.57	762.4	47210	23620	30.58	24.5	3.14	7.77	5.6	
S10	O10	6.2343	4.64593	29.51	762.3	46810	23420	30.3	24.3	3.09	7.74	5.7	Oroyo
S11	OJ1	6.23047	4.64918	29.47	762.4	45740	22870	29.51	23.7	2.89	7.67	5.8	
S12	OJ2	6.21918	4.65212	29.32	762.5	45270	22630	29.19	23.4	2.65	7.64	5.8	
S13	OJ3	6.21606	4.66037	29.24	762.5	42778	21390	27.38	22	2.19	7.53	4.4	Ogogoro
S14	OJ4	6.21122	4.66494	29.11	762.1	40450	20230	25.75	20.7	1.71	7.48	4.5	
S15	OJ5	6.20465	4.67809	28.74	762.3	37200	18600	23.46	18.18	1.38	7.37	3.3	
S16	OJ6	6.1994	4.67568	28.53	762.3	34580	17310	21.69	17.4	1.29	7.33	2.6	
S17	OJ7	6.19258	4.68198	28.48	762.3	30240	15230	18.96	15.2	1.34	7.36	2.2	
S18	OJ8	6.18801	4.68802	29.58	762.3	22840	11990	13.13	10.3	2.76	7.4	1.8	
S19	OJ9	6.18286	4.69402	28.7	762.3	21420	10760	12.88	10.3	2.41	7.43	1.3	
S20	OJ10	6.17809	4.69901	28.94	762.4	27730	13930	16.89	12.9	3.08	7.41	1.1	Gbabijo
S21	OK1	6.16688	4.71171	30.41	760.9	7202	3470	3.4	3.1	3.99	8.11	1.7	Asasa
S22	OK2	6.16199	4.71605	29.99	761.8	5416	2707	2.9	2.2	3.65	7.96	1.5	
S23	OK3	6.15517	4.72249	30.43	762.5	2544	1252	1.27	0.9	4.08	7.37	1.3	Abetobo
S24	OK4	6.14053	4.74032	30.88	762.3	1800	1800	0.9	0.6	3.81	7.26	1.1	Ilape

Table 2. Physico- chemical parameters in correlation with standards

Parameters	Ranges	Mean	WHO Standard	USEPA
Temperature °C	28.48-30.88	29.3	25-29	-
pH	7.26-8.11	7.62	6.5-8.5	6.5-8.5
conductivity µS/cm	1800-48040	34770	1,400	-
TDS mg/l	1252-24090	17442.0417	1,500	500
DO mg/l	1.29-4.37	2.93	> 7.5	-
Salinity ‰	0.9-31.33	18.12		

Source: WHO (1996, 2004, 2006, 2011) and USEPA

From table 2, temperature and pH range falls within acceptable standard value, conductivity and TDS are far greater above standard, the WHO standard for TDS shown in table above is for 2006, 2011 TDS accepted standard is 500 mg/l. The DO is very low compare to standard that is suitable for marine life.

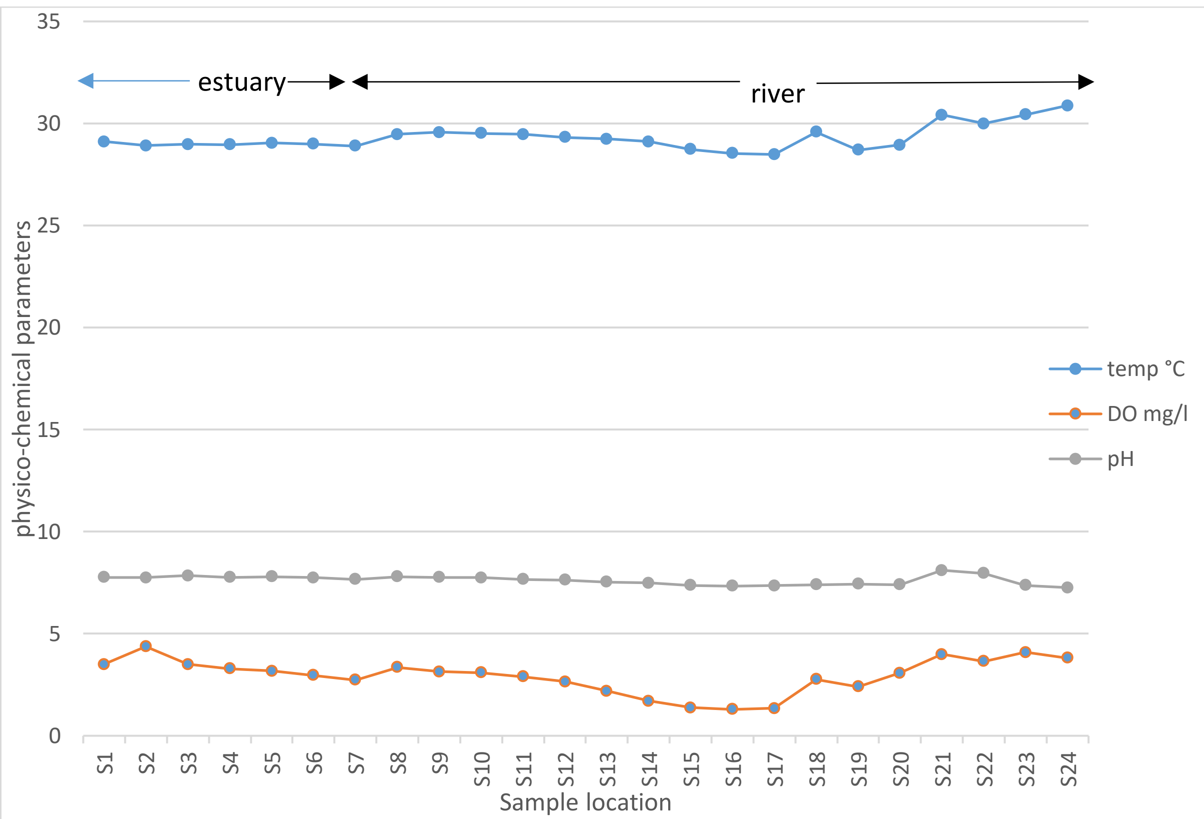

Figure 3. Temperature, DO and pH variation across sample locations

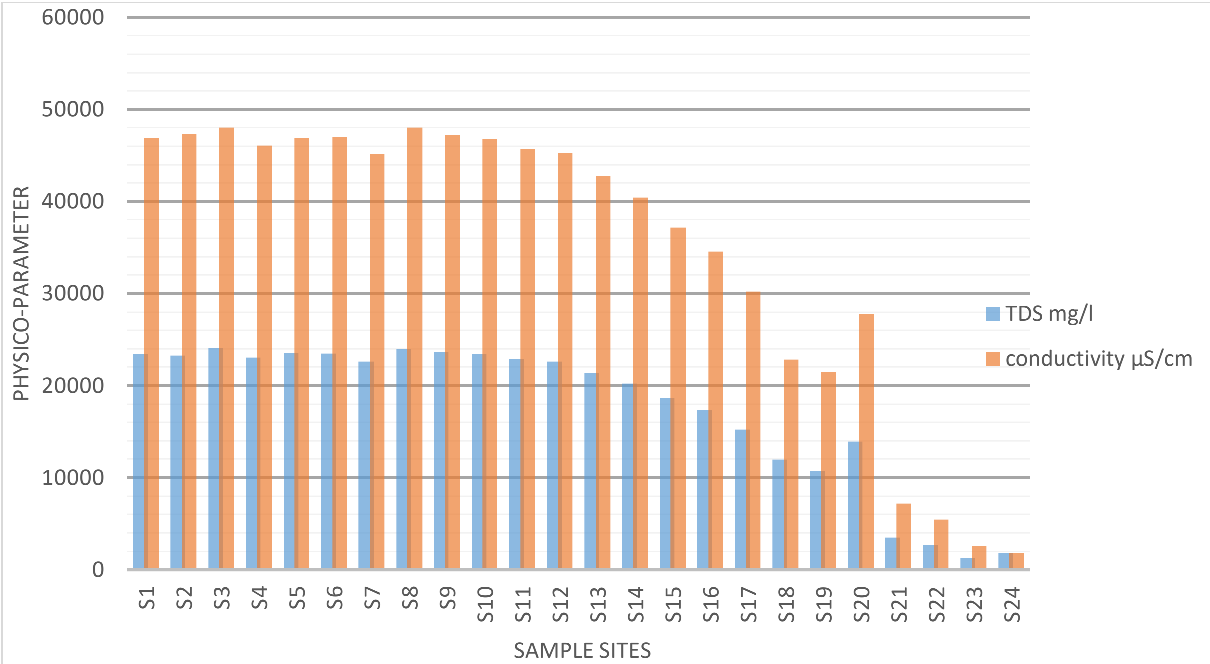

Figure 4. TDS and Conductivity

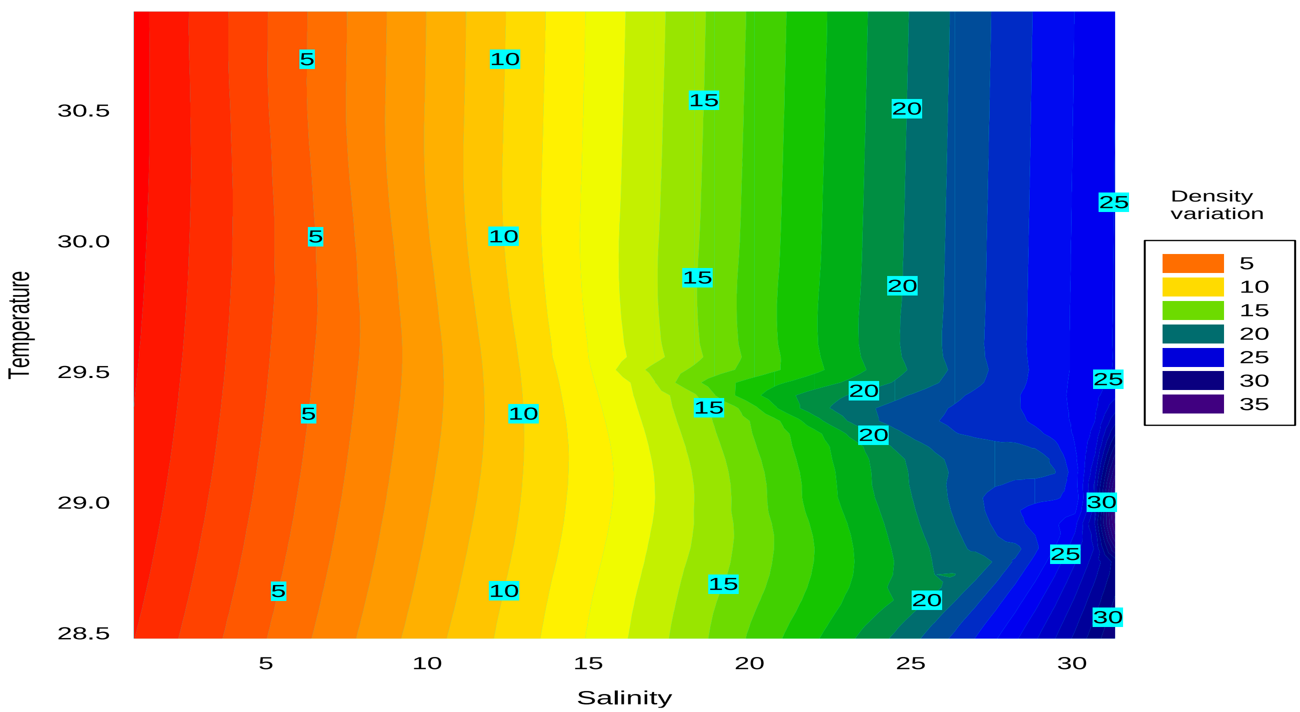

Figure 5. Salinity, temperature and density variation

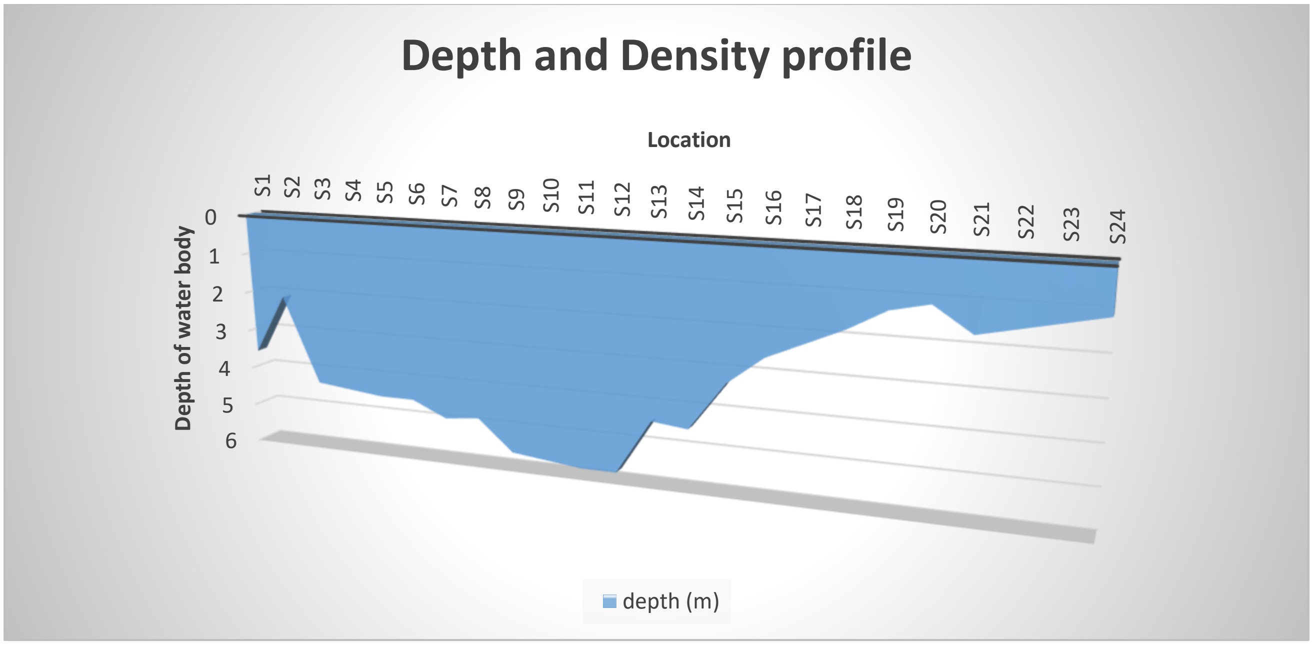

Figure 6. Depth profile

Table 3. Heavy metals in sediment

S. locate	sample site	Pb mg/g	Zn mg/g	Cu mg/g	Fe mg/g	Cd mg/g	
S1	O1	27.3056	21.9576	12.4768	674.7552	0	abereke
S2	O3	72.814	18.1048	8.4924	670.32	1.0472	
S3	O4	60.3008	21.4648	7.7504	763.3556	1.6688	
S4	O6	34.132	16.968	7.0728	704.368	0.9968	
S5	O7	48.9216	19.3032	7.9968	689.3824	2.5592	
S6	O8	71.6772	17.2508	2.6236	754.6028	2.436	etugbo
S7	O10	47.7848	21.8456	11.55	741.4148	0.2688	oroyo
S8	OJ2	32.9952	19.8128	7.6272	707.4872	1.8984	
S9	OJ4	80.78	20.118	1.7276	629.3168	2.2092	
S10	OJ6	44.3716	24.066	10.1892	776.1852	0.6636	
S11	OJ9	75.0904	21.0476	9.6656	771.3888	1.6268	
S12	OJ10	67.1272	21.3136	9.8196	781.4604	0.756	gagijo
S13	OK1	125.1516	22.946	12.9696	769.9496	1.6268	asasa
S14	OK2	91.0196	22.9264	10.4384	722.5932	1.8872	
S15	OK3	63.714	21.6916	10.962	761.3172	1.0668	abetobo
S16	OK4	120.5988	21.6916	9.1084	751.4864	1.2544	ilepa

3.2 Heavy metals in sediments

The sediment samples were analyzed for heavy metals namely Iron, Lead, Zinc, Copper and Cadmium. Sediments, generally regarded as sinks to heavy metals and other substances, accumulation of metals are good indicator of stress and pollution on the environment over time. Likewise, the metal concentration in sediments is attributable to the fact that metals generally have strong affinities for iron and manganese oxyhydroxides particulates thus, they absorb on such particles, which are commonly found in sediments. They also precipitate at high pH; form particles themselves or accumulate in biological particles found in sediments. (Kayode et al, 2009)

The concentration of the metals are represented in Table 2, the concentration of iron in sediment is higher compared to every other metal, from Figure 7, the maximum value of iron is recorded at Station 12 with concentration of 781.4604 mg/g and minimum at Station 9 with concentration of 629.3168 mg/g, this two Stations are found to be in the river, however the sediments in the estuary were rich in iron, they are averagely lower compared with the river, highest concentration of iron were recorded in the shallow waters where the residence time of Fe could be shorter as well as agricultural practice in this area could have also increased iron concentration in that region. Fe is far greater than standard revealing that the sediment has accumulated high proportion from runoff weathering of soil materials.

Cadmium has a concentration below detectable level in the sampling locations from the estuary and river, the maximum concentration 2.5592 mg/g was detected at Station 5, nothing was detected at Station 1 from Figure 8, correlated with standard WHO (6mg/g) and USEPA (0.6mg/g), the water body could have been contaminated by cadmium but not to a pollution level. Cadmium is one of the most dangerous pollutants due to its high potential toxic effects. The primary use of water high in Cd could cause adverse health effect to consumers such as renal disease and cancer. The presence of Cd in the sediments is attributed to the reasons of human activities such as discharge of industrial effluents of fertilizers industries and chemical industries along a river. The probable sources of Cd in the river water are from the catchment soils and runoffs from agricultural soils.

Lead ranges from 27.3056 mg/g at Station 1 to 125.1516 mg/g at Station 13 in Figure 9, Pb is averagely higher than USEPA standard which is 40 mg/g. Pb concentration is high in some location, even at lower doses, it can cause anemia and kidney damage. Pb is introduced into this environments through fuel exhaust from boat, batteries, and paint pigment.

Zinc ranges from. 16.968 mg/g at Station 4 to 22.946 mg/g at Station 13 in Figure 19. It is evenly spread across the sample location from estuary to river and its concentration is displayed in an unpolluted degree compared with standard. Copper ranges from 1.7276 mg/g at Station 9 to 12.9696 mg/g at Station 13. Copper just like Zn displays its concentration in an unpolluted degree. Major anthropogenic sources of Cu include agrochemicals (fertilizers and pesticides), wood preservatives, electroplating, and antifouling paints.

Table 4. Heavy metal concentration compared with standard

Heavy metals mg/g	Ranges	Mean	WHO 2011	USEPA
Pb	27.3056-125.1516	66.4865	-	40
Cd	0-2.5592	1.3729	6	0.6
Zn	16.968-22.946	20.781775	123	110
Cu	1.7276-12.9696	0.3136	25	16
Fe	629.3168-781.4604	729.336475	-	30

Source: EPA 2012.

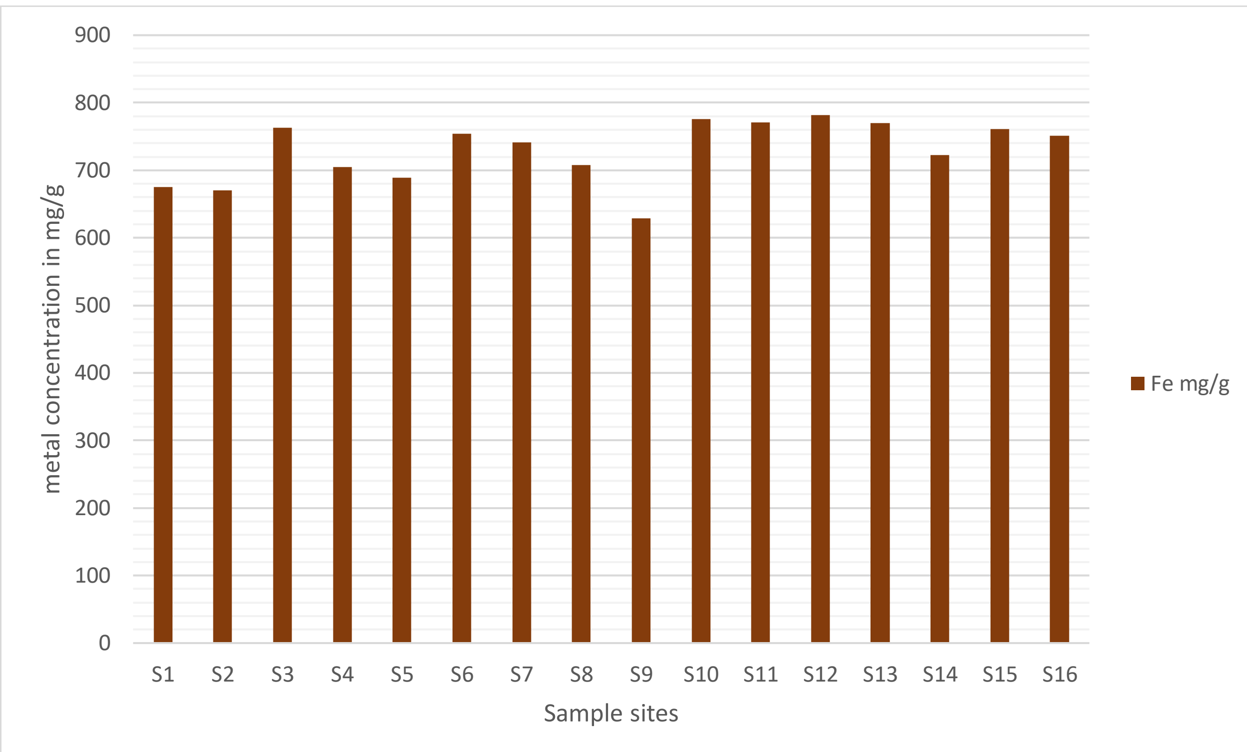

Figure 7. Iron concentration in different locations.

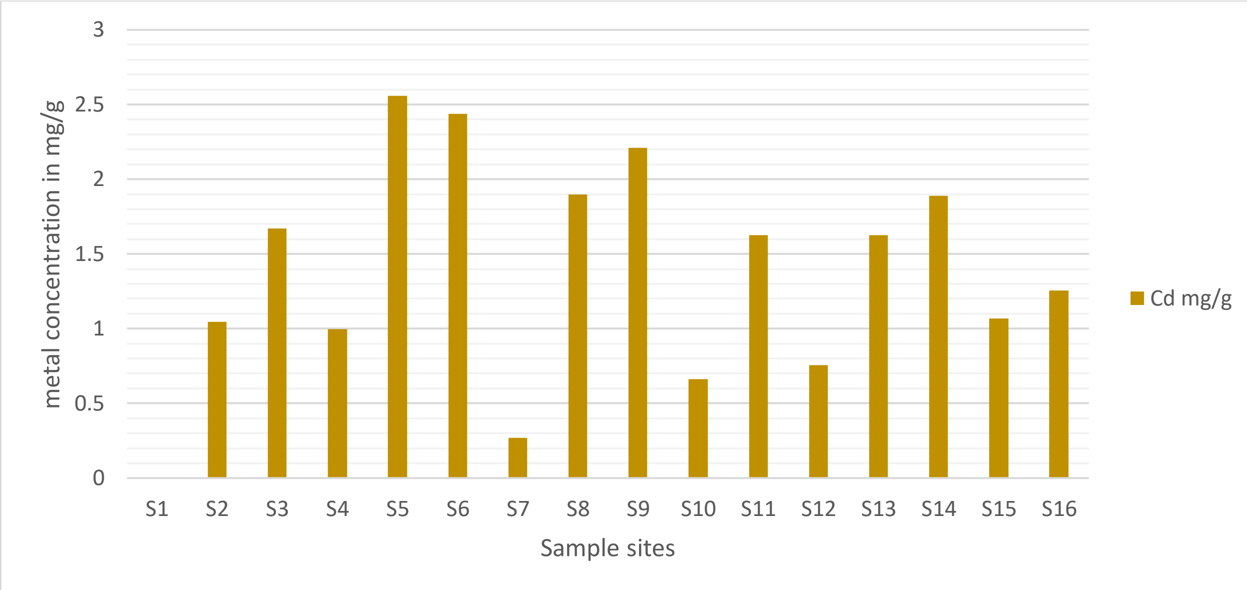

Figure 8. Cadmium concentration in different locations.

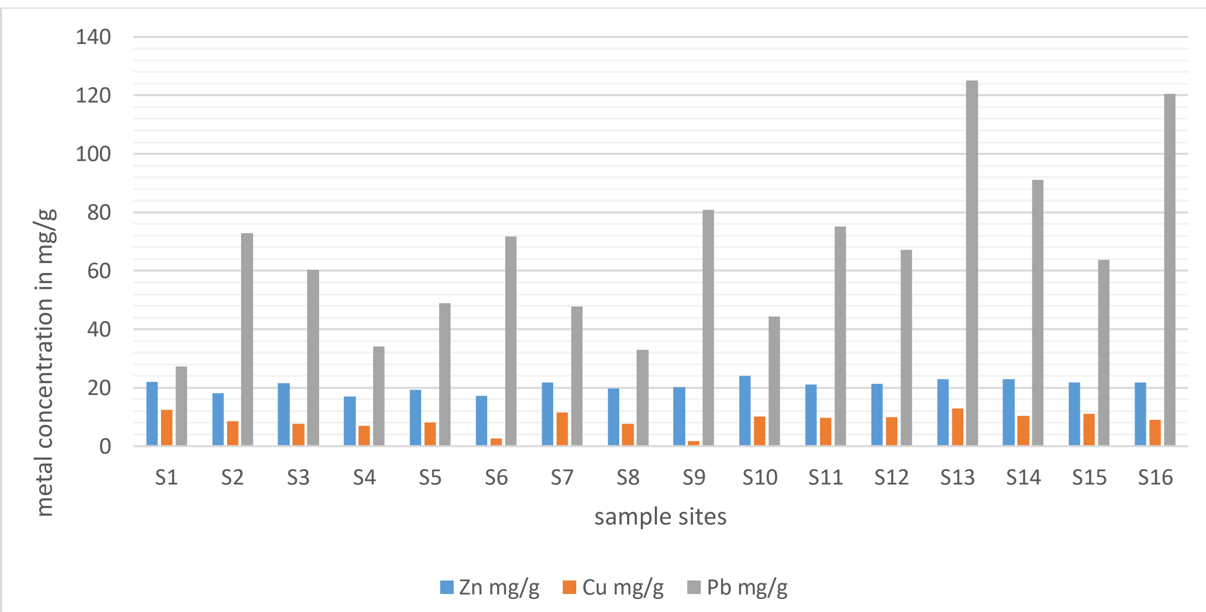

Figure 9. Lead, zinc and copper concentration in different locations.

CHAPTER FOUR

4.0 CONCLUSION AND RECOMMENDATION

4.1 SUMMARY

Aspects of the physicochemical parameters of Abereke estuary and rivers was investigated in a period of a single day, to assess the physico-chemical chemical parameter a multimeter-probe was used taking measurement of temperature, salinity, density, TDS, pressure, pH, DO, conductivity along the waterways. The physico-chemical behaviour was describe to see the spatial variation to use to evaluate the interaction between the river and estuary. Heavy metals in sediments were also evaluated, sediments sample were collected at some locations within the stretch of the exploration, to be able to visualize how copious heavy metals is in the estuary and rivers, and how human activities such as agricultural practice and transportation affects the concentration of heavy metal in various location.

4.2 CONCLUSION

From results of physico-chemical parameter of water, the temperature of water was too high and DO oxygen too low, the influence of fair climate condition and pollution by disposal of sewage and other organic materials could be perceived in this region. This in turn has adversely affected lives and living in the area. Visible signs of this can be perceived. These include decreased in fishing resources, damage to marine flora and fauna, loss of biodiversity, deforestation, coastal and marine erosion and flooding. Agricultural activities are also seriously affected, or almost practically impossible.

The amount of TDS is very high in the mix zones showing the accumulation of substance from inputs into the estuary, while TDS itself may be only an aesthetic and technical factor, a high concentration of TDS is an indicator that harmful contaminants, such as iron, manganese, sulfate, bromide and arsenic, can also be present in the water. This is especially true when the excessive dissolved solids are added to the water as human pollution, through runoff and wastewater discharges.

The geochemical cycle of trace metals in the riverine region is an important process to determine the present level of metal enrichment which interacts with the estuaries and other effluent input. The heavy metals play a major role in the ecotoxicology of the river ecosystem. The significance of anthropogenic metal enrichment and environmental effects in the Ilaje river sediments could be assessed through this study.

4.3 RECOMMENDATION

This project has lightened understanding about the spatial variation of the physico-chemical and geochemical properties of Ilaje waters, but has limitation on the part of reviewing the air-water interaction effect on the dynamics of the water and also temporal variation could not be achieved due to economic and time constraints. A regular monitoring of the point sources is suggested to minimize the effects of pollution in the near environments of the river.

There should be a constant monitoring of the physicochemical parameters in future because of the increase in anthropogenic activities around the area. It is further recommended that proper education, monitoring and clean up procedure be carried out promptly in these regions whenever they are stressed by pollutants generated from domestic, agricultural and industrial activities as well as effect of oil spills.

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Water Estuary Guide (WEG)

EPA and the Center for Marine Conservation (http://www.epa.gov/owow/estuaries/monitor)

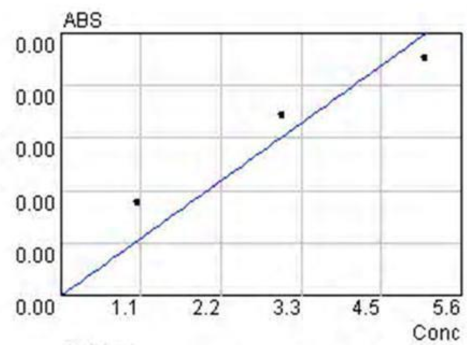
www.safewater.org Thursday, June 23, 2016, 2:07:48 PM

APPENDIX

Work Curve 6/25/2016 7:52:30 PM

No. Conc Abs SD RV

S1 0.0661-0.0006.0006.67%
S2 1.0661 0.0016.0046.67%
S3 3.0661 0.0029.0005.17%
S4 5.0661 0.0036.0028.53%



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Work Curve 6/26/2016 3:46:42 PM

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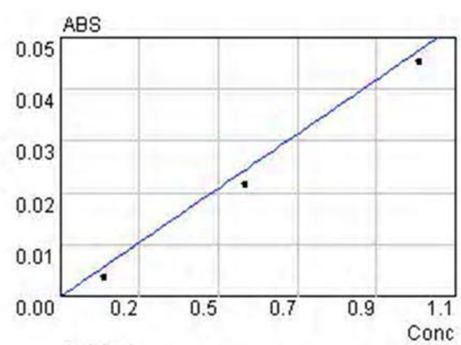

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Work Curve

7/2/2016 3:08:22 PM

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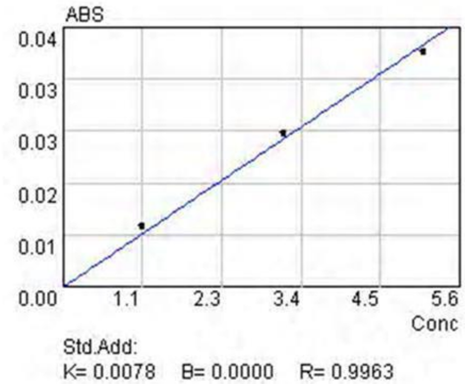

Work Curve

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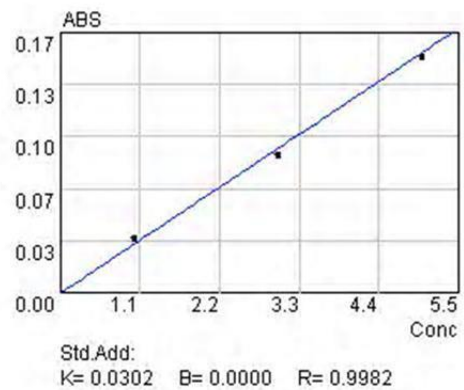
S3 3.0308 0.0882.0009.98%
S4 5.0308 0.1500.0027.78%



Work Curve

7/4/2016 2:31:59 PM

No. Conc Abs SD RV

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S3 0.5332 0.0526.0009.62%
S4 1.0332 0.0904.0034.78%