CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Effluent is defined as overflowing of water or gas from a natural body of water and from manmade structure (Spiller *et al*., 2012). It also serves as liquid waste flowing out of a factory, farm, commercial establishment and household into a water body such as a river, lake, lagoon, sewer system and reservoir (Baum *et al*., 2013).

Industrial wastewater is one of the important pollution sources in pollution of water environment. During the last century, a huge amount of industrial wastewater was discharged into rivers, lakes and coastal areas. This resulted into serious pollution problems in the water environment and caused negative effects to the eco-system and human lives (UNESCO, 2016). Pollution is the introduction of contaminants into the natural environment that causes adverse change. Pollution can take the form of chemical substances or energy, such as noise, heat or light (Vikas and Dwarakish, 2015).

Water pollution is the contamination of water bodies for example, lakes, rivers, oceans, aquifers and groundwater. It occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. It affects plants and organisms living in these bodies of water. In almost all cases, the effect is damaging not only to individual species and populations, but also to the natural biological communities (Cao and Ikeda, 2005).

Water pollution is a major problem, which requires ongoing evaluation, and revision of water resource policy at all levels –starting from international to individual aquifers and wells. It has been suggested that it is the leading worldwide causes of deaths and diseases, and it accounts for the deaths of more than 14,000 people daily (Dasgupta, 2004). An estimate of 580 people in India die of water pollution related illness everyday. 90% water in the cities of China was polluted, and as of 2007, half a billion Chinese had no access to safe drinking water. In addition, to the acute problems of water pollution in developing countries, developed countries continue to struggle with pollution problems as well. (Dwight *et al.*, 2005).

A cost of illness framework was applied to health and income data to quantify the health burden from illnesses associated with exposure to polluted recreational marine waters. Urbanisation, intensive agriculture, recreation and the manufacturing industry are affecting water quality throughout the world (Esoka and Umaru, 2006). Available literature on environmental monitoring of surface water indicates that streams and rivers in the country are showing increasing trend of water pollution due to increased population, industrialisation and urbanisation. Waste generations by the industries and households have continued to increase (Adebayo *et al.*, 2007). These wastes are indiscriminately disposed-off into the water bodies. This has led to pollution of inland water bodies and coastal waters which subsequently increase water quality parameters such as heavy metals, nutrients and organic matter, soluble ions, oil and grease and organic chemicals such as pesticides, volatile organic compounds and poly-nuclear aromatic hydrocarbons (PAHs) (Jaji *et al.*, 2007).

Urgent attention is therefore necessary to mitigate water pollution problems in Nigeria through monitoring as well as enforcement of emission standards by industries (Ekiye and Zejiao, 2010).

1.2 Sources of water pollution

Water pollution is the contamination of water bodies (e.g. lakes, rivers, oceans, and groundwater). This may be defined in terms of the undesirable changes in the chemical and physical properties of water, which are not favorable to all living things utilizing water for their lives. There are two basic forms of water pollution.

(1) Changing the types and amounts of materials carried by water, and

(2) Altering the physical characteristics of a body of water (Gupta *et al*., 2009).

Water pollution occurs in many forms, from a wide range of sources. Agriculture may contribute to water pollution from feed lots, pastures, and croplands. Mining, petroleum drilling and landfills may also be major sources of water pollution. Other water pollution sources related to men are sanitary sewers, storm sewers, industry and construction (Dongbin *et al*., 2007).

According to a report published from the Environmental Protection Agency (EPA), greater than 50% of the water pollution of streams and rivers occurred due to leaching and mixing of chemicals from the agriculture practices (Wang *et al*., 2016). The next highest source is municipal sources (about 12%).

Water pollution occurs when a body of water is adversely affected due to the addition of large amounts of materials to the water. The sources of water pollution are categorised as being a point source or a non-point source of pollution.

(a) ***Point source pollution:*** Point source (PS) pollution refers to contaminants that enter a water way through a discrete conveyance, such as pipe or ditch (Jalan and Somanathan, 2008; Klein *et al*., 2007). Examples of sources of this category include discharges from a sewage treatment plant, a factory or a city storm drain. Point source also included municipal storm sewer systems, as well as industrial storm water, such as from construction sites (Flora *et al*., 2008).

(b) ***Non-point source pollution:*** Non-point source (NPS) pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often the cumulative effect of small amounts of contaminants gathered from a large area. The leaching out of nitrogen compounds from agricultural land, which has been fertilised, is a typical example. Nutrient runoff in storm water from "sheet flow" over an agricultural field or a forest is also cited as examples of NPS pollution (Hung and Shaw, 2004). Contaminated storm water washed off parking lots, roads and highways, called urban runoff, is sometimes included under the category of NPS pollution. However, this runoff is typically channeled into storm drain systems and discharged trough pipes to local surface waters, and is a point source. However, where such water is not channeled and drains to ground is a non-point source (Mazumder, 2008).

1.3 Causes of water pollution

(a) Oil spillage: Oil spills are a common event in Nigeria and occur due to a number of causes, including: corrosion of pipelines and tankers (accounting for 50% of all spills), sabotage (28%), and oil production operations (21%), with 1% of the spills being accounted for by inadequate or non-functional production equipment. The largest contributor to oil spill that is corrosion of pipes and tanks is the rupturing or leaking of production infrastructures that are described as very old and lack regular inspection and maintenance (Ekubo and Abowei, 2011).

(b) Pathogens: Pathogen discharges may also be caused by poorly managed livestock operations. Coli form bacteria are commonly used bacterial indicator of water pollution, although not an actual cause of disease. Other microorganisms sometimes found in surface waters, which have caused human health problems, include Burkholderia pseudomalleis cryptosporidium parum, Giardic lamblia, salmonella, Novo virus and other viruses (Young and Loomis, 2014).

(c) Chemical and other contaminants: Contaminants may include organic and inorganic substances.

1.4 Effects of water pollution

Oil spillage has a major impact on the ecosystem into which it is released. An estimated 5 to 10% Nigerian mangrove ecosystems have been wiped out either by settlement or oil. The rainforest, which previously occupied some 7400km^2 of land has disappeared as well (Ekubo and Abowei, 2011).

Spills in populated areas often spread out over a wide area, destroying crops and aquacultures through contamination on the groundwater and soils (Young and Loomis, 2014).

The specific contaminants leading to pollution in water include a wide spectrum of chemicals, pathogens, and physical or sensory changes such as elevated temperature and discoloration (Maduka, 2006). While many of the chemicals and substances that are regulated may be naturally occurring (calcium, sodium, iron, manganese etc) the concentration is often the key in determining what is a natural component of water, and what is a contaminant. Oxygen-depleting substances may be natural materials such as plant matter (e.g. leaves and grass) as well as fabricated chemicals. Other natural and anthropogenic substances may cause turbidity (cloudiness) which blocks light and disrupts plant growth, and clogs the gills of some fish species (Reddy and Behera, 2006).

Many of the chemical substances are toxic. Pathogens can produce water borne diseases in either human or animal hosts (Prabodaine and Raffensperger, 2010). Alteration of water’s physical chemistry includes acidity (change in pH), electrical conductivity, temperature and eutrophication. Eutrophication is an increase in the concentration of chemical nutrients in an ecosystem to an extent that it increases the primary productivity of the ecosystem (Paudel *et al*., 2005). Depending on the degree of eutrophication, subsequent native environmental effects such as anoxia (oxygen depletion) and severe reduction in water quality may occur, affecting fish and other animal populations (Paudel *et al*., 2005).

1.5 The Ilorin Environment: A case study

Ilorin has been described as one of the fastest growing urban centres in Nigeria, with a population of forty thousand, nine hundred and ninety in 1952, two hundred and eight thousand, five hundred and forty-six (208546) in 1984 (Ajadi *et al*., 2011). By 1991 census, the city’s population has increased to five hundred and fifty-two thousand and eight (552,008) while in year 2005 it was seven hundred and eighty thousand, seven hundred and seventy-one (780771) (Aderamo, 2004).

According to National Population Commission (2012), it was reported that during 2006 census, Ilorin had a population of seven hundred and eighty-one thousand, nine hundred and thirty-four (781934) while a population projection of nine hundred and eight thousand, four hundred and ninety (908490) was observed in March 2011.

Ilorin is a typical traditional African city which is located on latitude 8^o10’N and longitude 4^o35’ E marking a divide between the Southern forest zone and the Northern grassland of Nigeria (Agbola *et al*., 2012). The eastern part is generally steeper than the western part with height ranging from 900-1200 feet in some part and peaking at an isolated land forms, which is Sobi hill and about 1300 feet high (Ifabiyi and Omoyosoye, 2011). The occupation of Ilorin populace is classified into traditional occupation (farming, various crafts and petty trading) and modern occupation (professional positions and service positions). Scattered tall trees such as baobab, locust beans, shea butter, and acacia characterise the vegetation. The dominant streams are Asa, Aluko, Okun, Amule and Agba. The Asa River is of particular influence on the direction of growth of the city (Olorunfemi and Raheem, 2013). The River Asa catchments basin is about 1040km in area and lies between latitude 8^0 24^1 and 8^0 36^1 N and between 4^0 10^1 and 4^0 36^1E (Figure 1). The city experiences a tropical wet and dry climate each lasting for about six months with mean annual rainfall of 1200mm. Its temperature varies between 25^oC to 30^oC in March which marks the hottest month (Oguntunde *et al*., 2011).

1.6 Justification of the study

Industrial wastewater is one of the important pollution sources in pollution of water environment and is often the groundwork of studies on water quality or pollution. Availability of potable water in developing countries is a major problem due to the strong craves for industrialization to cater for unemployment problems.

Due to increasing globalisation, many industries have been established in Ilorin metropolis, Kwara State in recent times. Hence, a comprehensive study on the industrial effluents, discharge channels outside the company as it flows to Asa River at different distance intervals was studied.

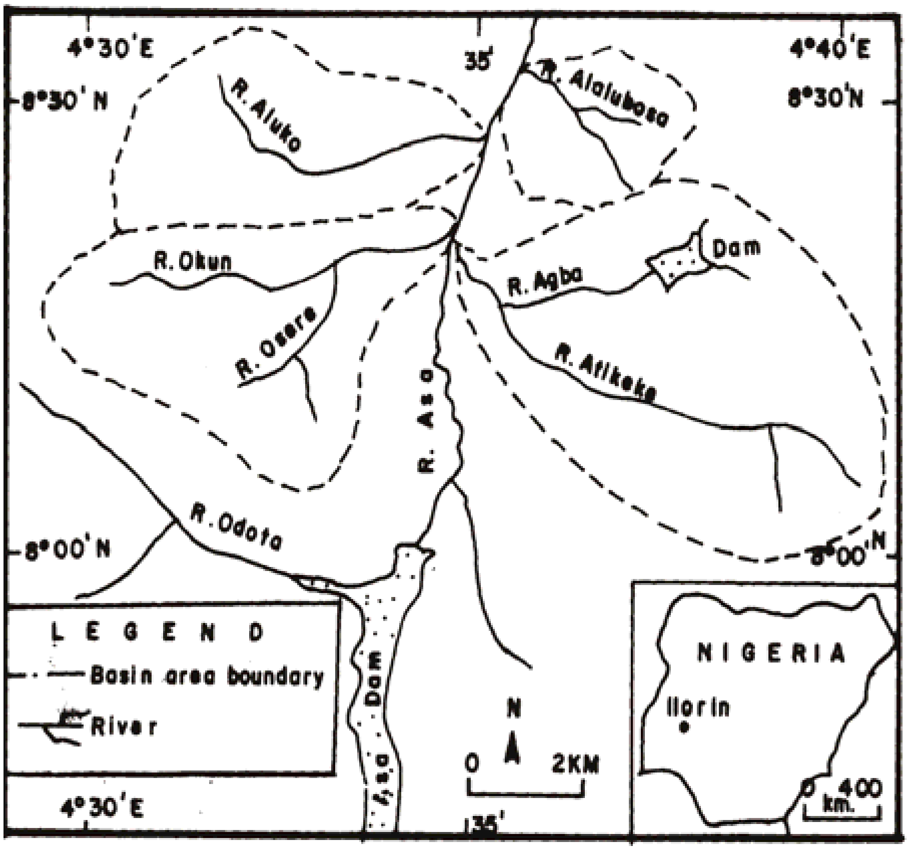


Fig. 1.1: River Asa and parts of its tributaries
Source: Author's fieldwork

Previous studies on the pollution status of the river were focused on sediment and water samples from few locations, in spite of intense urbanisation and industrial activities within its catchment. Hence, there is a need to ascertain the current pollution status of the river. Therefore, this study was designed to determine the impact of industrial activities on, and establish the pollution level of, water and sediments of Asa River using Overall Pollution Index, Contamination Factor, Geo-accumulation Index and Pollution Load Index.

1.7 Aim and scope of the study

River Asa water is used for household and irrigation purposes and it receives wastes from both municipal and industrial sources therefore, the aim of this study was to carry out environmental monitoring and assessment of industrial effluent discharge into Asa River and its impact on surface water, sediment quality and groundwater.

The research objectives include the impact of pollution based on:

i. determination of physicochemical parameters in industrial effluents, river water and groundwater, which include water pH, turbidity, conductivity, colour, total solids, total hardness, total alkalinity, nitrate, phosphate, ammonia, chloride, sulphate, Chemical Oxygen Demand etc.

ii. quantitative analysis of the levels of heavy metals in (a) industrial effluents, surface water and groundwater [Na, Ca, Mg, Fe, Cu, Cr, Cd, Zn and Pb] (b) Asa River sediment [Cu, Pb, Co, Cr, Ni, Zn, Al, Fe and Mn].

iii. analysis the relationship between organic pollutants in industrial effluent and surface water.

iv. analysis the relationship between organic pollutants in both surface water and sediment.

v. Assessment of socio-economic impacts of the people by administering questionnaire so as to ascertain the perception of industrial activity on their socio-economic well being using three factors
    (I) Domestic purpose factor
    (ii) Health impact factor
    (iii) Environmental impact assessment factor

vi. Assessment of the contaminant level of Asa River sediments and water using pollution indices.

vii. Modelling of experimental data to describe the dispersion of pollutants mathematically along the river network.

CHAPTER TWO

LITERATURE REVIEW

2.1 Background review of Asa River

Asa River is a major river for economic, environmental and agricultural significance in Ilorin the capital city of Kwara State, Nigeria. The River receives direct runoff of effluents from industries along its course, a part from domestic wastes and other activities carried out along it that contribute to its pollution (Adekunle and Eniola, 2008).

Eletta *et al*., (2005) pointed out that the river is subject to high level of eutrophication due to the organic matter and industrial discharge into it. The pollution of Asa River through flood effects on human have been reported by Jimoh, (2008a) which revealed factors that causes river erosion and the modes of house location. Sand materials are loose in disposition and thus yield readily to the forces of erosion studies on rainfall, runoff engine and stream flow characteristics. Asa River catchment basins had shown that the incidence of flood has been on the increase and these indicated that the basin size and land use has profound influence on the explanation of discharge in the river catchment basins (Jimoh and Iroye 2009 & 2010). Ilorin has been experiencing flood disaster on annual basis due to high river discharge of Asa River during extreme precipitation periods of wet season amongst other non-climate driven or anthropogenic reasons (Olayemi, 2007).

Adekunle and Eniola, (2008) affirmed the impact of constant pollution from effluent of soap and detergent industries into Asa River. The indiscriminate point pollution of Asa River from industrial, domestic, agricultural, commercial activities in the environs have been associated with the river overflowing its bank in the rainy season. (Kolawole et al., 2008; Akiwumi and Eletta, 2013) have reported several other investigations on the discharges of waste and storm water runoff into rivers in Ilorin during rainy season. The little attention being paid to runoff studies in Nigeria are daily manifesting in water and water-related problems being experienced in Nigeria (Akoteyon *et al.*, 2011; Jimoh, 2008b&c).

From the work of (Jimoh and Alao, 2009), Asa River Catchment was found to have a very high precipitation and sediment yields when analysed yearly for a period of seven years. The high amount of sediment yields is directly related to the amount, duration and intensity of rainfall, as well as stream discharge, which often increase the river water level and finally causes flooding in the basin area of Ilorin. This calls for preparative actions by water resource management operatives against such occurrence.

Kolawole *et al.*, (2011) focused on the risk assessment and suggested mitigable adoption options to river flooding which is common in Ilorin, a majority in North Central, Nigeria. Quality of water is increasingly being affected by anthropogenic activities through which natural waters are contaminated (Giwa *et al.*, 2008).

Eletta and Adekola, (2005) studied the physical and chemical parameters useful for water quality assessment has determined by the presence of both organic and inorganic compounds that are either suspended or dissolved in it. While, some of the compounds are toxic to the ecosystem, some constitutes nutrients to aquatic organisms and others are responsible for aesthetics of the water body.

Eletta, (2012) confirmed the impact of some activities carried out along the course of river on the concentration of some identified pollutants by randomly selecting locations in the various water bodies. Concentration of copper, lead, iron, nitrate in the water sample across the locations were found to be within allowable concentration levels by the World Health Organisation. Concentration of lead in the rain and surface water samples were determined across the locations. There was visibly, no significant change in the lead concentrations. Concentration of iron in the ground water sample was found to be below detection limits. However, the surface water samples concentration was found above the World Health Organisation allowable limits in location 3 and 5 with average concentration of 3.08 mg/L and 3.6 mg/L respectively and this happens because location 3 and 5 has a soap and detergent company emptying it waste into the water at this points. Concentration of nitrate was determined in the surface and groundwater, from the data collected; it was observed that the activities around the sampling points had direct influence on the nutrient loading. (Adekola and Eletta, 2007) have carried out studies on the heavy metal pollution of Asa River in Ilorin, Kwara State. The researchers reported metals in the concentration range of Manganese (179.9-469.4 mg/kg), Iron (1998.4-4420. 4mg/kg), Chromium (3.0-11.3 mg/kg), and Zinc (26.6-147.6 mg/kg). Enrichment factors (EFs) were calculated for Zinc, Chromium, Manganese and Iron in sediment samples and these values indicates anthropogenic source of contamination. (Eletta, 2007) also affirmed the determination of trace metal levels concentration in Asa River using Atomic Absorption Spectrophotometry (AAS) and X-ray Fluorescence (XRF), Statistical analysis showed there was no significant difference in the concentration of chromium, Zinc, lead and copper using two techniques but significant differences were observed at 5% probability level for manganese and Iron.

Okeola *et al*., (2010) carried out a comparative study between wells along the Asa River route to observe possible interactive effect of physical chemical parameters; sections of the River running through human settlement were selected along with three close wells. The result obtained showed that the temperature and pH of both bodies of water were closely related. The river samples in both seasons have relatively higher values in the following physical parameters color (33-36 ptco), turbidity (0.5-0.8 FAU), total dissolved solids (127-275 mg/L) and total suspended solid (0.8-0.9 mg/L), while electrical conductivity value was lower compared to each of the well samples. In addition, differences were observed in heavy metals with relatively higher results in the river sample. The result generally showed that the properties of the two bodies of water that is the river sample were distinct from that of the well, suggesting that the two bodies of water have little or no interaction. (Okeola *et al*., 2010) concluded in this report that the results and analyses suggest the distinct nature of different bodies of water. Their distinct nature however depends on geographical location, time zone and geological foundation of the water area.

Ajadi and Tunde, (2010) reported the waste management system by Kwara State environmental protection Agency within Ilorin metropolis and its essence on the river. Oshode *et al*., (2009) documented a report on the microbial load of fresh waters to elucidate the quality of water and to assess the potential health hazards inherent in them. A dearth of information exists on the effects of detergent effluents on microbial status of Asa River. However, (Adekunle, 2009) documented the effects of detergent effluent on sections of Asa River, Ilorin. The microbial load was reported to be $20.0* 10^4$-$17.4* 10^5$ cfu/mL and seventeen bacterial species of five families were isolated. In addition, the distribution of bacteria in water of Asa River was found to be in order of $20* 10^5$ cfu/mL and twenty bacterial species were isolated. (Adewoye, 2010) observed the distribution and diversity of fungal species along the tributaries of Asa River. The distribution of the micro biota was observed to depend on concentration of detergent effluent present in water.

Adewoye, (2010) focused on seasonal influx of detergent effluent on microbial load and diversity in Asa River which stated the analysis of microbiological characterisation such as Escherichia coli, Proteus Vulgar is, Streptococcus Faecilis, Pseudomonas, Bacillus and Enterobacter species of water samples from three points revealed high microbial and faecal contamination with microbial load in the order of 10^5 and most portable number (MPN) of $\leq$ 1800.

2.1.1 Background review on other rivers within and outside Nigeria

Studies carried out in most cities in Nigeria had shown that industrial effluent is one of the main sources of surface water pollution in Nigeria (Ekiye and Zejiao, 2010). Industrial effluents when discharged directly into the rivers without prior treatment have capacity of increasing water quality parameters. (Wakawa *et al*., 2008) indicated that less than 10% of industries in Nigeria treat their effluents before being discharged into the rivers and this has lead to high load of inorganic metals such as lead (Pb), chromium (Cr) and Iron (Fe) in most water bodies. Table 2.1 reveals the results of physicochemical parameters of effluents collected from some industries in Lagos, Kaduna and Port-Harcourt. Most of the results were higher than the permissible limits set has observed by (Olugbuyiro, 2011). The resultant effects of this will be on the receiving streams and rivers. High phosphate concentrations in these effluents could result into nutrient enrichment of the receiving water bodies thereby leading to ecological disaster. Metal pollution of Warri River by industrial discharges has been reported by (Ayenimo *et al*., 2005) and the river was monitored for heavy metals such as Iron (Fe), Copper (Cu), Barium (Ba), Lead (Pb), Cadmium (Cd), Chromium (Cr), Nickel (Ni) and Cobalt(Co). Results showed elevated values of these metals and other water quality parameters at sampling point located near an industry. Correlation analysis of the metals also suggested common source. The activities of the oil industries in the Niger Delta region of Nigeria have impacted negatively on the surface water quality around the area. This has led to water scarcity, disruption of socio-economic activities and poor aesthetic quality of most water bodies polluted by oil spills (Wogus and Okaka, 2011). Pollution by crude oil has affected the treatment of drinking purpose in most rivers around the Niger Delta region of the country. The impacts of oil activities in these areas have done much havoc to the environment of this region most especially on the water resources (Taiwo *et al*., 2012).

Table 2.1 Effluent analysis of some industrial discharges in Nigeria

Effluent Parameters	Lagos (Adebayo et al, 2007)	Kaduna (Yusuf & Shonibare, 2004)	Port-Harcourt (Ajao & Anurigwo, 2002)	FEPA (1991)
pH	7.6	4.8		6-9
EC (μScm^{-1})	761	1156.6		
Turbid (NTU)	11.6	573.6		
Salinity (%)	0.1	0.5		
Alkalinity (mg/l)	766.6	445		
Chlorine (mg/l)		0.5		
Nitrate (mg/l)		4.0	362	20
Ammonia (mg/l)		1.0		
Phosphate (mg/l)		1.0	836	5
Total hardness (mg/l)		1233.3	4083.3	
TSS (mg/l)	320 833.3	400	3533	30
TDS (mg/l)		1100	2200	
Oil & Grease (mg/l)	20 0.0	7.0	2343	-
BOD (mg/l)	300	4374	30	
COD (mg/l)	850	2253	1800	
H_2S (mg/l)	17.2	130	0.6	

*Total effluent discharged from observed industries, TSS – Total suspended solids, TDS – Total dissolved solids, BOD – Biochemical Oxygen Demand, COD – Chemical Oxygen Demand, DO – Dissolved oxygen (Data adapted from Ekiye and Zejiao, 2010).

Indiscriminate disposal of municipal wastes remains a major threat to surface water pollution in Nigeria. In most cases, sewage and waste water from homes are routed into the rivers and streams. (Jaji *et al*., 2007) found elevated water quality parameters in some sampling locations of Ogun River. These were partly attributed to the activities of abattoir located close to the river at a notable market in Abeokuta metropolis. The work of (Arimoro *et al*.,2007) on the impact of sawmill activities on the water quality of River Benin reported high biochemical oxygen demand and low dissolved oxygen values at the discharge point of the wastes into the river. (Ogunfowokan et al., 2005) studied the impact of point source pollution from sewage treatment oxidation pond on a receiving stream. The researchers observed significant elevation of water indices such as pH, biochemical oxygen demand, nitrate, phosphate and total suspended solid. It is well known that oxygen depletion in water bodies could cause fish death while increase in biochemical oxygen demand signifies high load of organic matter. A study by (Ajibade, 2004) has shown high total suspended solid values in Asa River, Kwara State while (Osibanjo *et al*., 2011) has also reported similar findings for Rivers Ona and Alaro in Ibadan. Turbidity values reported for most rivers in Nigeria were far greater than 5.0 NTU limit given by (WHO, 2008) in Table 2.2. (Ajibade, 2004), (Adefemi *et al*., 2007) and (Wakawa *et al*., 2008) have reported elevated turbidity values in rivers in Nigeria. This could be linked to runoff effects as well as domestic and industrial discharges on the rivers. Low biochemical oxygen demand and chemical oxygen demand values have been reported in New Calabar River and Kubanni River in Kaduna. However, a high biochemical oxygen demand and chemical oxygen demand have been observed for Challawa River in Kano State with mean concentration ranging between 10-30 mg/L and 170-260 mg/L respectively by (Wakawa *et al*., 2008). Very low dissolved oxygen values (2.67 – 3.30 mg/L) were also observed in Challawa River. Pollution of the rivers was directly linked with the industrial effluent discharges. (Osibanjo *et al*., 2011) also reported high chemical oxygen demand values for the water samples from Rivers Ona and Alaro. The authors attributed these to leach ate from dumpsites, agricultural and urban runoffs.

Table2.2 Mean Concentration of water quality parameters of some rivers in Nigeria

Constituents	Ogun River(Jaji et al, 2007)				New Calabar River		Kubani River (Agbogu et al, 2006)		**FEPA (1991)**
	Wet Season		**Dry season**		(Abu and Egenonu, 2008)				
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	
Temp (oC)	27.0	0.47	30.03	1.17	25.8	0.92	22.71	0.62	
pH	7.12	0.17	7.09	0.40	5.38	0.41	6.72	0.03	6.5-8.5
DO (mg/l)	7.6	1.27	5.36	0.73	6.31	0.81			
BOD (mg/l)				2.24	0.41	1.83	0.28		
COD (mg/l)				6.4	2.72	224.08	9.38		500
EC (µScm-1)									
Salinity (%)	0.01	0.01							
Sulphate (mg/L)			22.95	7.47					<250
Turbd. (NTU)	43	15	15	5.94	106.4	21.11			<5.0
TSS (mg/L)				18.8	1.45				
TDS (mg/L)	156	39.6	443	900	1.26	0.22	26.2	1.76	<600
Cl- (mg/L)	16.6	4.8	262	733	5.44	3.19	29.02	2.12	250
Nitrate (mg/L)	3.80	5.27	3.64	2.86	0.32	0.12	1.86	0.09	11, 50
Phosphate (mg/L)	0.07	0.03	0.02	0.01	0.17	0.01	0.16	0.01	
Oil and Grease (mg/L)	147	71.7	71.3	72.6	0.02	0.01			
Pb (mg/L)	0.03	0.02	0.02	0.04	0.14	0.04	0.01		

SD – Standard deviation

The high values of coli form reported for some river water samples confirm faecal pollution from domestic sewages, dumping sites, abattoir activities etc. High coli form values are typical characteristics of many rivers in Nigeria. For instance, high population of faecal coli form counts has been reported in Ikpoba River, Edo State of Nigeria by (Awomeso *et al.*, 2010). Similarly, (Taiwo *et al.*, 2012) also reported coli form values in the range of 3100-150000 cfc/100 mL at Iddo area of Lagos Lagoon. The high population of these microbial pollutants was linked to contaminations from the dumpsites around the lagoon. Faecal pollution of rivers in Nigeria signifies poor sanitation management as well as unhygienic manner of living among people, especially those living close to the riverine areas. It has also been observed that pathogenic contamination of Nigeria's rivers comes from aqua culture practices involving fertilization of ponds with cow and poultry manures; and direct dumping of faecal matters into the rivers (Obasohan *et al.*, 2010). Unlike inorganic pollutants and pathogens monitoring in Nigeria water systems, organic pollutants monitoring had suffered major neglects in terms of qualitative and quantitative monitoring.

Due to poor institutional funding by the Nigeria governments, studies on the levels of polynuclear aromatic hydrocarbons (PAHs) and other organic contaminants in the country are very scanty. Until recently, most studies on organic compounds dates back to the 1970s and 1980s when there were some equipment and little funding to conduct research. The poor funding had resulted in poor human resources base coupled with lack of instrumentation to monitor the level and distribution of these organic pollutants in the environment (Taiwo *et al.*, 2012). Despite these challenges, few studies have recently reported some levels of Poly aromatic hydrocarbons in Nigeria water systems. Poly aromatic hydrocarbons have been listed as priority pollutant that needs to be monitored in both industrial and domestic effluents and freshwater systems (Emoyan, 2009). The health impacts of poly aromatic hydrocarbons include carcinogenic, cardiovascular, bone marrow and liver toxicity. (Emoyan, 2009) reported the concentration range of 0.2309 – 1.0468 mg/L for poly aromatic hydrocarbons in surface water due to contamination from kokori oil field in the Niger Delta. Fluoren was the dominant of the sixteen poly aromatic hydrocarbons priority pollutants investigated. The source of water contamination was identified to be mainly petrogenic.

In a more recent study on Lagos lagoon, (Adeyemi *et al*., 2011) reported the levels of nine organochlorine pesticides residue in water using solid phase extraction followed by Gas chromatography quantification. The concentration range for the nine organochlorine pesticides are 0.006-0.950 µg/L, ND-0.067 µg/L, ND-0.123 µg/L, O.015-0.774 µg/L, 0.015-0.996 µg/L, 0.012-0.910 µg/L, 0.005-0.477 µg/L, 0.015-0.9096 µg/L and 0.080-0.790 µg/L for chlordane, heptachlor, methoxychlor, hexachlorobenzene, endosulfan, dichloro phenyltrichloroethane, dichloro phenyldichloroethylene, dieldrin and aldrin respectively.

In another study on the Lagos lagoon, (Adeboyejo *et al*., 2011) found the following range of organochlorine pesticides in water samples: aldrin (ND-658 ng/L), chlordane (218.0-702.0 ng/L), endrin (ND – 2551 ng/L), DDD (20.3-268 ng/L), pp-DDE (0-176 ng/L), α-HCH (ND-2300 ng/L), γ-HCH (ND-783ng/L), β-HCH (28.9 – 518 ng/L), δ-HCH (0-498 ng/L), endosulfan (ND-3726 ng/L) and heptachlor (ND-1405 ng/L).

Adeniyi *et al*., (2011) reported Poly Aromatic Esters concentrations in the river and tap water of south western Nigeria. Water samples from Lagos, Oyo, Osun, Ondo and Delta States of Nigeria and the city's water treatment plants were analysed for the presence of phthalate esters. Extraction with dichloromethane $CHCl_2$ and liquid chromatography was used for compound separation. Several phthalate esters, dimethyl (DMP), diethyl (DEP) and di-n-butyl (DBP) were found present at levels of 10 – 1472 mg/L in river water and 91-1219 mg/L in tap water from the city's water treatment plants.

Yuyun *et al*., (2007) reported the spatial and temporal distribution of polycyclic aromatic hydrocarbons Qiantang River, China which is an important resource for drinking water. 218 samples including 180 water and 38 sediment samples were collected in January, April, July and October 2005. The concentration of total fifteen poly aromatic hydrocarbons in sediment ranges from 91.3-614.4 ng/g dry weight with the mean value of 313.1 ng/g dry weight, and three and four ring poly aromatic hydrocarbons were dominant species. The ratio of AN/ (AN+Phen) and Flur/ (Flur +Pye) were calculated to evaluate the possible sources of poly aromatic hydrocarbons. These ratios reflected a pattern of petrogenic input of poly aromatic hydrocarbons in Qiantang River. (Sadao and Shigeki, 2005) described a method for the simultaneous determination of twenty-two volatile organic compounds in water by headspace solid phase micro extraction gas chromatography mass spectrometry. Three types of Solid phase micro extraction fibers (carboxy polydimethyl siloxane [CAR-PDMS], divinyl benzene polydimethyl siloxane [DVB-PDMS] and 100 µm poly dimethyl siloxane) were evaluated to achieve the method detection limits and linear range required in Japanese water regulation. (Juan *et al*., 2010) reported a multi-residual method based on stir bar sorptive extraction coupled with thermal desorption gas chromatography- mass spectrometry developed to measure forty-nine organic pollutants (Organochlorine pesticides, poly aromatic hydrocarbons, poly chlorinated biphenyls, poly brominated diphenyl ethers and nonyl phenol) in sea water. Using 100 mL of water, the method exhibited good linearity, with recoveries between 86% and 118% with relative standard deviation between 2% and 24% for almost all compounds. (Saida *et al*., 2008) revealed physicochemical analysis carried out on Tangiers bay, located in the extreme west of the Mediterranean sea, and in the North West of Morocco, receives various pollutants through the mghogha canal from urban and industrial rejections of Tangiers city temperature (21-23^{o}C), pH (6-7.5), suspended matters (70-300 mg/l), dissolved oxygen (1.15-4.5 mg/l), chemical and biochemical demands of oxygen (345 -975 mg/l and 55 -245 mg/l respectively) showed an important pollutant load in samples taken from Mghogha canal.

2.2 Chemistry of some inorganic pollutants in water

Anions are radicals, which include nitrate ion, nitrite ion, phosphate ion, sulphate ion, hydroxyl ion etc. Excessive levels of some essential anions however can be detrimental to the organism in water or human beings using the water (Msangi and Cline, 2016). Anions in water that are of interest to us in this research work are nitrate, phosphate, sulphate, chloride and these will be discussed in relation to their chemistry in water. Nitrogen occurs in water as nitrate or nitrite anions, as ammonium cations and in a variety of organic compounds (Manaham, 2011).

2.2.1 Nitrates

Nitrates in water occur by the leaching of fertilizers from soil during surface runoff and also nitrification of organic matter. The presence of high concentration of nitrates is an indication of pollution (Lee and Kim, 2016). In discussing the chemistry of nitrate in water, nitrate cycle is used. High concentrations of nitrate ion in drinking water may cause the disease methemoglobinemia in small children (Srivastava and Ramanathan, 2008). Because of this and other diseases linked to nitrate, its concentration in public water supplies is monitored and regulated by United States federal law at an acceptable level of 0.1mg/L.

Nitrate occurs naturally from mineral sources and animal wastes, and anthropogenically as a by-product of agriculture and from human wastes. Nitrate is the most oxidised form of nitrogen cycle, which includes activities in the atmosphere, hydrosphere, and biosphere (Seitzinger *et al*., 2006). Figure 2.1 shows the major transformations from the nitrogen cycle. This includes assimilation of inorganic forms of nitrogen (ammonia and nitrate) by plants and microorganisms (Brandes *et al*., 2007), heterotrophic conversion of organic nitrogen from one organism to another, ammonification of organic nitrogen to produce ammonia during the decomposition of organic matter (Brandes *et al.*, 2007) and nitrification of ammonia to nitrate and nitrite by the chemical process of oxidation.

$$NH^{+}_{4} + 2O_{2} \; \underrightarrow{NO^{-}_{3}} + H_{2}O + 2H^{+}$$

$$NH^{+}_{4} \xrightarrow[\text{Oxidation}]{\text{bacteria}} 2O_{2} \xrightarrow[\text{Oxidation}]{\text{bacteria}} NO^{-}_{3}$$

Other transformations include denitrification (bacteria reduction) of nitrate to nitrous and (N_2O) and molecular nitrogen (N_2) under anoxic conditions, and fixation of nitrogen (reduction of nitrogen gas to ammonia and organic nitrogen) by microorganisms (Killops and Killops, 2013).

2.2.2 Sulphates

Sulphates occur naturally in numerous minerals, including barite ($BaSO_4$), epsomite ($MgSO_4.7H_2O$) and gypsum ($CaSO_4.2H_2O$). These dissolved minerals contribute to the mineral content of many waters (Rudolf *et al.*, 2014).

Sulphates products are used in the production of fertilizers, chemicals, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents and emetics. They are also used in mining, wood pulp, metal and plating industries, in sewage treatment and in leather processing (Rudolf et al., 2014). Aluminum Sulphate (alum) is used as a sedimentation agent in the treatment of water. Copper sulphate has been used for the control of algae in raw and public water supplies (Somdec *et al.*, 2013).

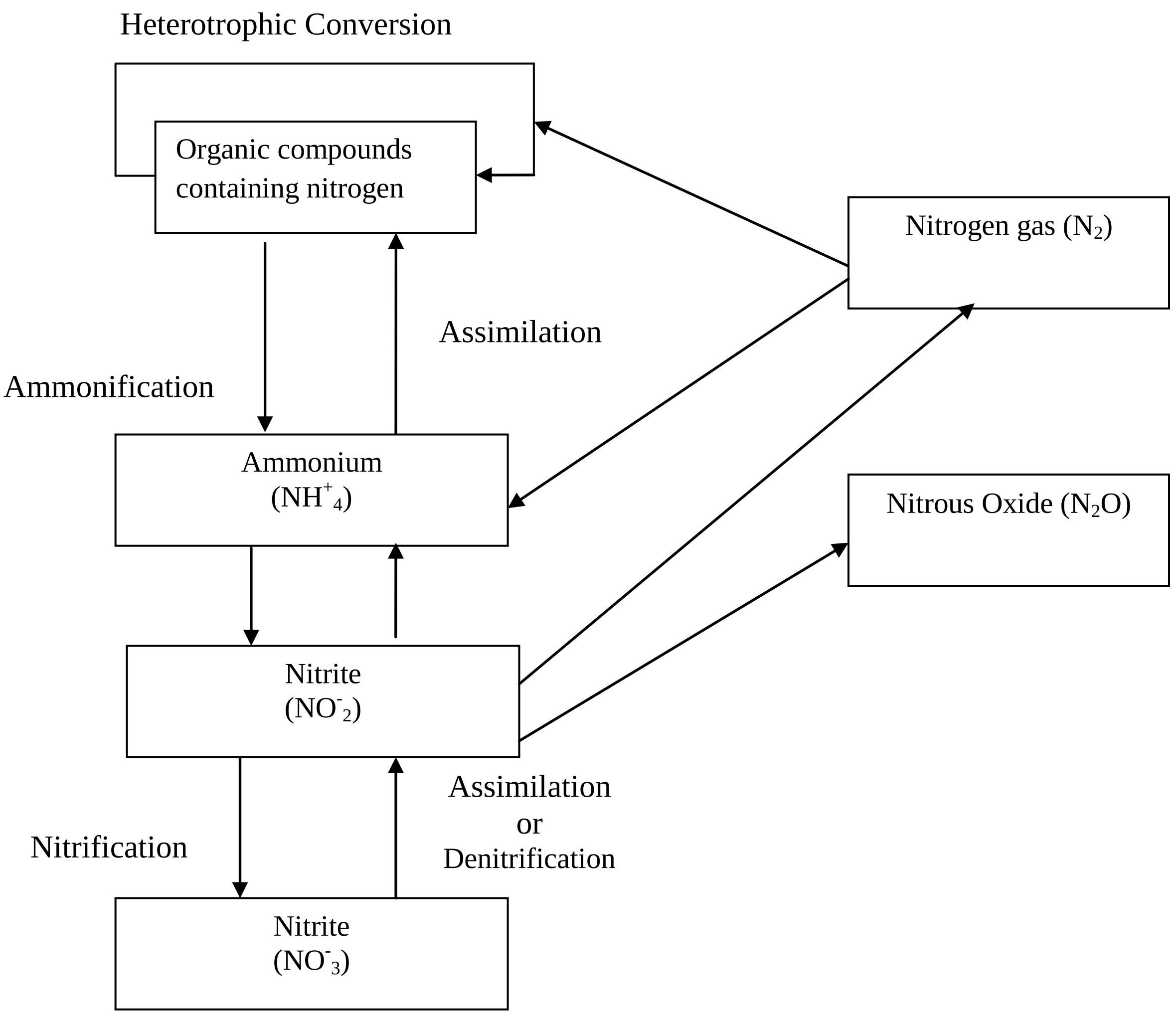


Figure 2.1: Simplified Biological Nitrogen cycle (Galloway *et al*., 2004)

Sulphates are discharged into water from mines, smelters, Kraft pulp, paper mills, textile mills and tanneries. Sodium, potassium and magnesium sulphates are all highly soluble in water, where as calcium, barium sulphates and many heavy metal sulphates are less soluble. Atmospheric sulphur dioxide, formed by the combustion of fossil fuels and in metallurgical roasting processes, may contribute to the sulphate content of surface waters. Sulphur trioxide produced by the photolytic or catalytic oxidation of sulphur dioxide, combines with water vapor to form dilute sulphuric acid, which falls as “acid rain” (Deepa *et al*., 2016).

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2\,(g) + O_2\,(g) \longrightarrow 2SO_3\,(g)$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The sulphur cycle as shown in figure 2.2 are often termed as follows:

(a) Assimilative sulphate reduction (sulphur assimilation) in which sulphate ($SO^{2-}{}_4$) is reduced to organic sulphydryl groups (R-SH) by plants, fungi and prokaryotes.

(b) Desulphuration and dissimilative sulphur reduction in which organic molecules can be desulphurated, producing H_2S. (Parkes and Sass, 2007).

(c) Oxidation of hydrogen sulphide produces elemental sulphur (S), oxidation state = 0. The photosynthetic green and purple sulphur bacteria and some chemolithotrophs do this reaction. Further oxidation of elemental sulphur produces sulphate (Rickard and Luther, 2007).

2.3 Chemistry of some heavy metals in water

Heavy metals are elements having atomic weights between 63.546 and 200.590 and a specific gravity greater than 4.0 living organisms require trace amounts of some heavy metals, including cobalt, copper, iron, manganese, chromium, molybdenum, vanadium, strontium and zinc. Excessive levels of essential metals, however, can be detrimental to the organism (Akgun *et al*., 2015).

All heavy metals exist in surface waters in colloid, particulate, and dissolved phase, although dissolved concentrations are generally low. The solubility of trace metals in surface water is predominantly controlled by the water pH, the type and concentration of ligands on which the metal could adsorb, and the oxidation state of the mineral components and the redox environment of the system (Aslam *et al*., 2011).

The behavior of metals in natural waters is a function of the substrate sediment compositions, the suspended sediment composition and the water chemistry. Metals also have a high affinity for humic acids, organo-clays, and oxides coated with organic matter (Aslam *et al*., 2011).

The water chemistry of the system controls the rate of adsorption and desorption of metals to and from sediments. Adsorption removes the metal from the water column and stores the metal in the substrate. Desorption returns the metal to the water column, where recirculation and bioassimilation, may take place (Akgun *et al*., 2015) metals may be desorbed from the sediment if the water experiences an increase in salinity, a decrease in redox potential or a decrease in pH (Burrow *et al*., 2009).

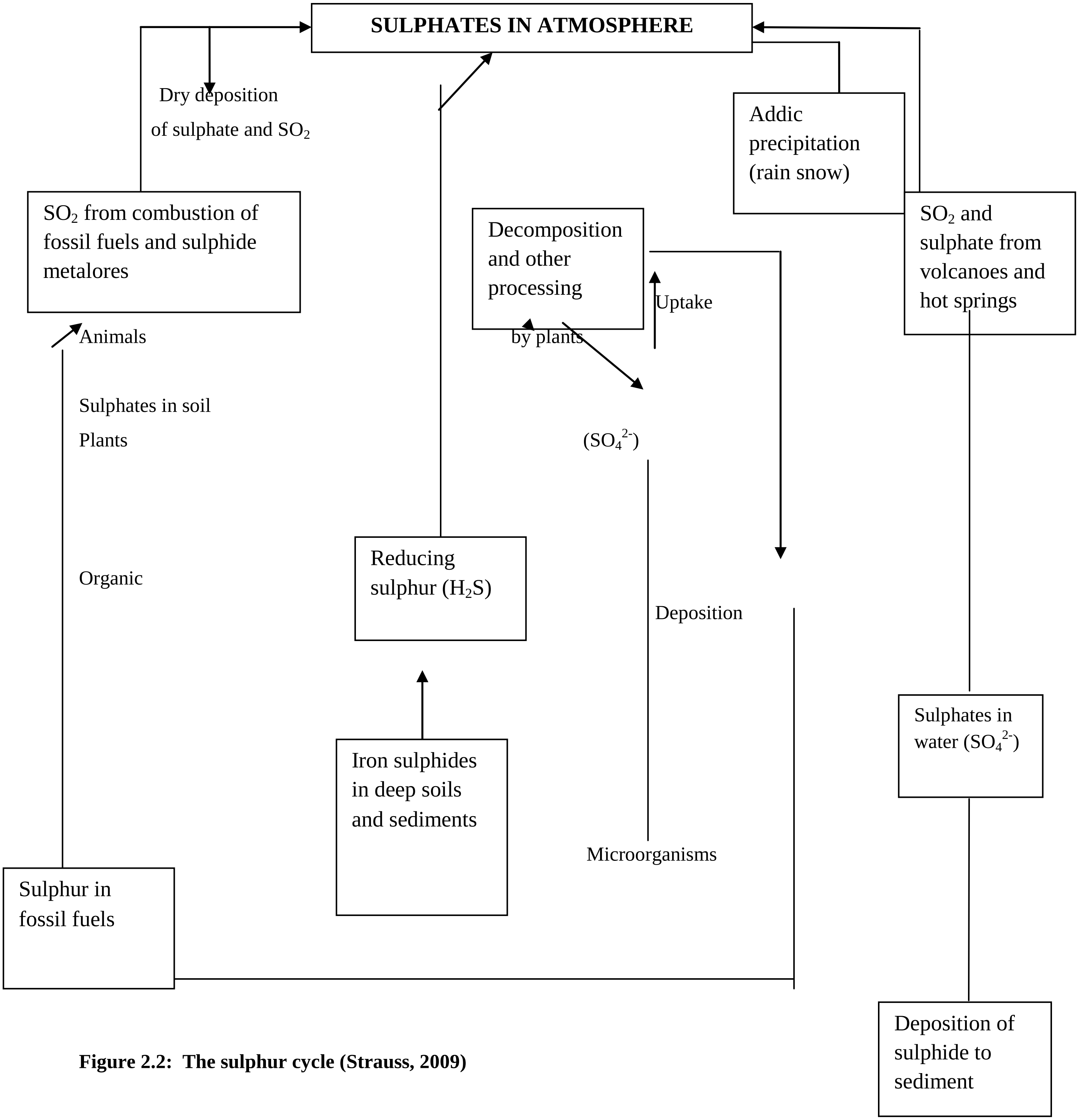


Figure 2.2: The sulphur cycle (Strauss, 2009)

Heavy metals in surface water systems can be from natural or anthropogenic sources. Currently, anthropogenic inputs of metals exceed natural inputs. Excess metal levels in surface water may pose a health risk to humans and the environment (Burrow *et al.*, 2009).

2.3.1 Copper (II) ion

Metals in the soil solution are subject to mass transfer out of the system by leading to water, plant uptake, or volatilization. Fish can excrete essential metals such as copper, zinc and iron that are present in excess (Richard, 2007).

The chemistry of copper in water can be summarised as follows: copper metal dissolves in nitric acid (HNO_3). Actually, the nitrate ion oxidizes the copper metal to copper (II) ion while itself being transformed to NO_2 gas in the process, the copper (II) ion then binds to six water molecules. The physical changes observed include the formulation of a blue color due to the hexa aqua copper ion $(Cu\ (H_2O)_6)^{2+}$, and a brown gas (NO_2) is evolved (Richard, 2007).

$$Cu(s) + 4H_3O^+ (aq) + 2NO^-_3 \longrightarrow [Cu\ (H_2O)_6]^{2+}{}_{(aq)} + 2NO_2\ (g)$$

Hydroxide ion binds to the copper (II) ion even more strongly than water. As a result, hydroxide ion can displace water from the copper (II) ion, yielding copper hydroxide, a blue precipitate (Burrow et al., 2009).

$$[Cu\ (H_2O)_6]^{2+}{}_{(aq)} + 2OH^- \longrightarrow Cu(OH)_2\ (s) + 6H_2O(s)$$

Heating copper hydroxide produces copper oxide, a black solid

$$Cu\ (OH)_{2(s)} \longrightarrow CuO(s) + H_2O(s)$$

Copper oxide dissolves in acid, regenerating the copper (II) ion, which once again binds to water.

$$CuO_{(s)} + 2H_3O^+ + 3H_2O \longrightarrow [Cu(H_2O)_6]^{2+}{}_{(aq)}$$

2.3.2 Lead (II) ion

The chemistry of lead (II) in water is as follows: lead metal dissolves in nitric acid to give lead nitrate, which is a white powder (Robert, 2004).

$$3Pb_{(s)} + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

The nitrate ion oxidizes the lead metal to lead (II) ion while itself being transformed to NO_2 gas in the process. The lead (II) ion then binds to six water molecules to give a ligand, which is hexa aqua, lead ion (Burow et al., 2009).

$$Pb_{(s)} + 4H_3O^+ + 2NO_3^- \longrightarrow [Pb(H_2O)_6]^{2+} + 2NO_2$$

2.4 Chemistry of some organic pollutants

Organic pollutants are organic compound, which resist photolytic, biological, and chemical degradation. They are characterised by low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues. They are also semi-volatile, enabling them to move long distances in the atmosphere before desorption occurs (El-Shahawi *et al*., 2010).

Organic pollutants are also either noted for the semi-volatility, that property of their physico chemical characteristics that permit these compounds to occur in the vapor phase or adsorbed on atmosphere particles, there by facilitating their long range transport through the atmosphere.

The group of organic pollutants includes polycyclic aromatic hydrocarbons, hydrogenated hydrocarbons (organic chlorine and volatile organic compounds) (Kelly *et al*., 2007).

Laboratory investigations and environment impact studies in wildlife have provided evidence that organic pollutants may be involved with endocrine disruption, reproductive and immune dysfunction, neurobehavioral, development disorders and cancer (El-Nemr *et al*., 2013).

Organic pollutants are often hydrogenated and most often chlorinated. The carbon-chlorine bond is very stable towards hydrolysis and the greater the number of chlorine substitutions and functional groups, the greater the resistance to biological and photolytic degradation (El-Shahawi *et al*., 2010). Chlorine attached to an aromatic (benzene) ring is more stable to hydrolysis than chlorine in aliphatic structures. As a result, chlorinated persistent organic pollutants are typically ring structures with a chain or branch chain frame work. (El- Nemr *et al*., 2013).

2.4.1 Volatile organic compounds

Volatile organic compounds (VOCs) are class of chemical compounds that share two main properties.

(i) They evaporate easily from water into the air and
(ii) They contain carbon: they are components that have high vapour pressure and low water solubility (Kwon and Finneran, 2008).

Many volatile organic compounds are human-made chemicals that are used and produced in the manufacture of paints, pharmaceuticals and refrigerants. They are typically industrial solvents such as trichloroethylene; fuel oxygenated such as methyl tetra-butyl ether (MTBE) or by-products produced by chlorination in water treatment, such as chloroform (Kwon and Finneran, 2008).

They are often components of petroleum fuels, hydraulics fluids, and paint thinner and dry cleaning agent. They are associated with product such as gasoline, plastics, adhesives, dry-cleaning fluids and biological source, which include trees, cows, termite (methanol) and cultivation (Ninemets *et al*., 2004).

Crude oil tanking can also release volatile organic compounds in to the atmosphere. Manufacture of volatile compounds has increased dramatically during the past 40-50 years. It is not a surprise that they found their ways into our water supply.

The United States Environmental Protection Agency (USEPA) estimates that VOCs are present in one fifth of the nation's water supplies more than seven hundred (700) synthetic organic compounds have been identified in various drinking water supplies. This contamination originates from a variety of sources, including household products and leakage or improper disposal of chemical wastes from commercial and industrial establishments. Volatile organic compounds can enter groundwater from a variety of sources. Benzene for instance, may enter groundwater from gasoline or oil spills on the ground surface or from leaking underground fuel tanks spilled or improperly disposed of VOCs may be released into the environment. Any portion that does not evaporate may soak into the soil and can be carried into groundwater by rain, water and Snow Belt (Miranda and Kenneth, 2011).

Factor that influence the likelihood of contamination include among others, proximity of the water to the source of contamination, the amount of VOCs that are spilled or discarded, depth of the well (shallow wells are affected by surface spills more quickly and severely than deep wells); local geology (groundwater that is protected by thick, dense soil is less vulnerable to contamination); and time (groundwater moves slowly, so it can take months or years after a spill before contamination releases well).(Benotti and Snyder, 2009).

The harmful effects of VOCs vary considerably. At high levels, some VOCs may damage the central nervous systems, the kidney or the liver. They may cause irritation to mucous membranes if inhaled. Some VOCs are known or suspected carcinogens. The United States Environmental Protection Agency has established maximum contaminant levels (MCLs) for the following VOCs as shown in table 2.3 (Clair, 2007). The chemistry of some volatile organic compounds would be discussed in this section based on their physical properties and chemical reactions they exhibit. The various VOCs include: chloroform, saturated carboxylic acids, phenols and benzofuran.

2.4.1.1 Chloroform

Chloroform is an organic compound with formula $CHCl_3$. It is a colourless, sweet-smelling, dense liquid with a density of 1.483g/cm^3, a melting point of -63.5^{o}C and boiling point of 61.2^{o}C. It is a trihalomethane, and is considered hazardous. Its solubility in water is 0.8g/100mL (20^{o}C). Several million tons are produced annually as a precursor to Teflon and refrigerants, but its use for refrigerants is being phased out (Sung *et al*., 2006).

In industry, chloroform is produced by heating a mixture of chlorine and either chloromethane or methane. At 400-500^{o}C, a free radical halogenation occurs, converting these precursors to progressively more chlorinated compounds.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

Chloroform undergoes further chlorination to give CCl_4.

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

The output of this process is a mixture of the four chloromethane; chloromethane, dichloromethane, chloroform and carbon tetrachloride, which are then separated by distillation (Sung *et al*., 2006).

Table 2.3 The Environmental Protection Agency (EPA) Maximum Contaminant Level (MCL) of Volatile Organic Compounds (VOCs) [Clair, 2007].

VOLATILE COMPOUNDS	MAXIMUM CONTAMINANT LEVEL (μg/L)
Benzene	5
Carbon tetrachloride	5
Para-dichlorobenzene (p-DCB)	75
1, 2-Dichloroethane (1, 2-DCA)	5
1, 1-Dichloroethylene (1, 1-DCE)	7
Dichloromethane (DCM)	5
Tetrachloroethylene (PCE)	5
Trichloroethylene (TCE)	5
Vinyl chloride	2
1, 1, 2-Trichloroethane (1, 2-TCE)	5

The major use of chloroform today is in the production of the chlordifluoromethane, a major precursor to tetrafluoroethylene.

$$CHCl_3 + 2HF \rightarrow CHClF_2 + 2HCl$$

The reaction is conducted in the presence of a catalytic amount of antimony pentfluoride. Chlordifluoromethane is then converted into tetrafluoroethylene, the main precursor to Teflon (Samuel, 2009).

Chloroform is a common solvent in the laboratory because it is relatively underactive, miscible with most organic liquids, and conveniently volatile. Chloroform is used as a solvent in the pharmaceutical industry and for producing dyes and pesticides (Kwak *et al*., 2008).

2.4.1.2 Saturated Carboxylic Acids

Carboxylic acids are organic acids characterised by the presence of it one carboxyl group, which has the formula – C(=O)OH, usually written as – COOH or –CO_2H carboxylic acids are Bronsted – Lowry acids that is proton donors. Salts and unions of carboxylic acids are called carboxylates (Kwak *et al*., 2008). The general formula of a carboxylic acid is therefore R-COOH, where R can be monovalent functional group. Among the simplest examples are the formic acid H-COOH, which occurs in ants, and acetic acid H_3C-COOH group, that gives vinegar its sour taste. Acids with two or more carboxyl groups are called dicarboxylic, tricarboxylic etc. The simplest dicarboxylic example is ethanedioic acid $(COOH)_2$, which is just two connected carboxyls. Mellitic acid ($C_{12}H_6O_{12}$) is an example of a hexa carboxylic acid. Other important natural examples are citric acids (in lemons) and tartaric acid (in tamariads). Carboxylic acids are the most common type of organic acid. When its carboxyl group is deprotonated, the conjugate base is resonance stabilised increasing is stability. This causes carboxylic acids to be more acidic than alcohols (Kwak *et al*., 2008). Carboxylic acids are polar, because they are both hydrogen bond acceptors (the carbonyl) and hydrogen-bond donors (the hydroxyl); they also participate in hydrogen bonding. The hydroxyl and carbonyl group forms the functional group carboxyl.

Carboxylic acids has tendency to self associate therefore usually exist as dimeric pairs in non-polar media. Carboxylic acids (Carbon 1-5) are soluble with water; whereas higher carboxylic acids are less soluble due to the increasing hydrophobic nature of the alkyl chain (Haynes, 2011). Carboxylic acids tend to have higher boiling points than water because of their increased surface area and tendency to form stabilised dimers. They are typically weak acids, which are partially dissociated into H^+ cations and $RCOO^-$ anions in neutral aqueous solution (Hosea *et al*., 2005).

$$RCOOH\ (aq) \longleftrightarrow RCOO^-(aq) + H^+\ (aq)$$

Carboxylic acids often have strong odour, especially the volatile derivation. Most common are acetic acid (vinegar) and butyric acid (rancid butter). Carboxylic acids react with bases to form carboxylate salts, in which the hydrogen of the hydroxyl (-OH) group is replaced with a metal cation. Thus, ethanoic acid found in vinegar reacts with sodium hydrogen trioxocarbonate (IV) (baking soda) to form sodium ethanoate, carbondioxide and water.

$$CH_3COOH + NaHCO_3 \longrightarrow CH_3COO^- Na^+ + CO_2 + H_2O$$

In addition, carboxylic acids react with alcohols to give esters. This process is used in production of polyesters (Hosea *et al*., 2005).

$$CH_3COOH\ (aq) + C_2H_5OH \longleftrightarrow CH_3COOC_2H_5 + H_2O$$

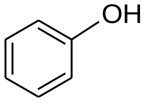
The hydroxyl group on carboxylic acids may be replaced with a chlorine atom using thionyl chloride ($SOCl_2$) to give acyl chloride (Hosea *et al*., 2005).

$$CH_3COOH + SOCl_2 \longrightarrow CH_3COCl + SO_2 + HCl$$

[Ethanoyl chloride]

2.4.1.3 Phenols

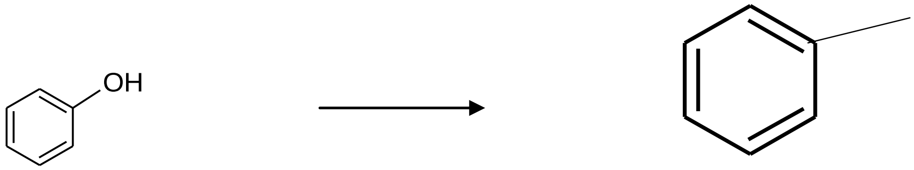
Phenols are class of chemical compounds consisting of a hydroxyl (-OH) bonded directly to an aromatic hydrocarbon group. The simplest of the class is phenol (C_6H_5OH). It is also known as phenolics.



Phenol structure

Phenols have unique properties and are classified as alcohols because the hydroxyl group is not bonded to a saturated carbon atom. They have higher acidities due to the aromatic rings tight coupling with the oxygen and a relatively loose bond between the oxygen and hydrogen. The acidity of the hydroxyl group in phenols is the intermediate between that of aliphatic alcohols and carboxylic acids (their pKa is usually between 10 and 12) (Ribeiro *et al.*, 2007).

Loss of a positive hydrogen ion (H^+) from the hydroxyl group of a phenol forms a corresponding negative phenolate ion or phenoxide ion, and the corresponding sets are called phenolates (e.g. sodium phenolates) or phenoxides.



Phenolate ion

In addition, phenols can be synthesised by the addition of benzene and propene in H_3PO_4 to form cumene then oxygen is added with H_2SO_4 to form the phenol. This is known as Hock process. (Weber *et al*., 2004).

$$\underset{\text{(Benzene)}}{C_6H_6} + \underset{\text{(propene)}}{C_3H_6} \xrightarrow[250^oC\ (H_3Po_4)]{} \underset{\text{(cumene)}}{C_9H_{12}}$$

When cumene reacts with oxygen it forms cumene hydro peroxide

$$\underset{\text{(Cumene)}}{C_9H_{12}} + O_2 \xrightarrow[95 – 135^oC]{} \underset{\text{(Cumene hydro peroxide)}}{C_9H_{12}O_2}$$

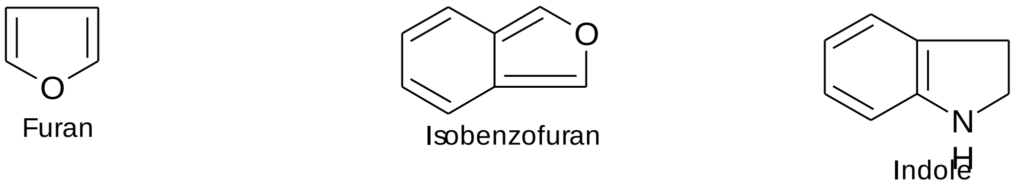
$$\underset{\text{(Cumene hydro peroxide)}}{C_9H_{12}O_2} \xrightarrow[50\text{-}90^oC\ (H_3O^+)]{} \underset{\text{(phenol)}}{C_6H_5OH} + \underset{\text{(acetone)}}{C_3H_6O}$$

2.4.1.4 Benzofuran

Benzofuran is a heterocyclic compound consisting of fused benzene and furan rings. This colorless solid is a component of coal tar (Solomon *et al*., 2004). Benzofuran is extracted from coal tar. It is also obtained by dehydrogenation of 2-ethylphenol [Collin and Hooke, 2007].

$$\underset{\text{(2-ethylphenol)}}{C_8H_{10}O} \xrightarrow[-H_2O]{} \underset{\text{(benzofuran)}}{C_8H_6O}$$

Benzofuran has a molecular formula of C_8H_6O with a melting point of -180^oC and boiling point of 173^oC. Related compounds of benzofuran include Furan, Indole and Isobenzofuran. The structures are given below [Collin and Hooke, 2007).



Furan Isobenzofuran Indole

Structures of Benzofuran related compounds

2.5 Background review of pollution status from some industrial companies

Studies carried out in most cities in Nigeria had shown that industrial effluent is one of the main sources of surface water pollution in Nigeria (Ekiye and Zejiao, 2010). Individual effluents when discharged directly into the rivers without prior treatment have capacity of increasing water quality parameters.

2.5.1 Pharmaceutical Industry

Pharmaceutical and personal care products (PPCPs) industries suffer from inadequate effluent treatment due to the presence of recalcitrant substances and insufficient carbon sources and nutrients. A large number of pretreatment systems are employed to remove these pollutants to prevent a host of problems that may otherwise arise in the biological process, and reduce the efficiency of the treatment plant (Kanu and Achi, 2011).

Problem caused by excessive PPCPs in the environment include possible inhibition on microorganisms, a reduction in the cell aqueous phase transfer rates, a sedimentation hindrance due to the development of filamentous microorganisms, development and flotation of sludge with poor activity, clogging and the emergence of unpleasant odors. Therefore, it is not surprising that research efforts have been directed towards the development of efficient treatment technologies including various physicochemical and biological processes. Some of the most representative and personal care products found in receiving waters include antibiotics, lipid regulators, anti inflammatory, antiepileptic, tranquilizers and cosmetic ingredients containing oil and grease with very different chemical structures (Lateef, 2004).

Conventional biological processes (activated sludge, trickling filters) can effectively accomplish carbon and nitrogen removal, as well as microbial pollution control. Their removal efficiencies are influenced apart, the chemical properties of specific compounds, by microbial activity and environmental conditions. The application of a pretreatment to hydrolyze the effluents and bioaugmentation, may improve the biological degradation (Phiri *et al*., 2005).

Kavitha *et al*., (2012) revealed an intensive analytical programme for four months of monitoring pharmaceutical waste water. The characteristic of the waste water for the inlet to outlet of septic tanks variation were TSS ranged between 4300-4394 mg/L, TDS ranging between 2846-1308 mg/L, COD ranging between 7280-9.9mg/L, BOD ranging between 4132-6.6 mg/L, chlorides ranging between 1000-300 mg/L, sulphates between 500-300mg/L and pH ranging between 7.43-7.14 mg/L. Evaluation of data presented revealed that the order of reduction efficiency was COD <TDS<BOD<TSS.

2.5.2 Soap and Detergent Industry

Alkyl sulphates (AS) are anionic surfactants widely used in household and personal cleansing applications. Aquatic toxicity of AS under laboratory conditions indicated effects at relatively low concentrations (50-230 µg/L) for some sensitive species.

Belanger *et al*., (2004) conducted a comprehensive study of an AS mixture composed of tetra-C_{14} and pentadecyl (C_{15}) chain lengths to better understand effects on microbial and macro invertebrate populations and communities.

Industrial effluents from soap manufacturing industries are known to contain complex chemicals most of which are very toxic and capable of destroying the microbial habitats in a serious adverse way. For example, characterization of the composite waste water from bath soap and food processing plants indicated that the waste was highly contaminated with organic compounds as indicated by COD and BOD values (Iheukwumere and Achi, 2014).

The seasonal variation in bacterial heavy metal biosorption in a receiving river as affected by industrial effluents has been assessed in a study. Kanu *et al*., (2006) observed an overall seasonal variation of heavy metals such as lead, zinc and manganese in the rainy season as compared to other metals for dry season. The concentrations of heavy metals were also, generally low in some samples and no similar trends were observed in the control samples. Except for iron and zinc, the concentrations of the other heavy metals were relatively low. Moreover, effluent from the soap manufacturing plant contained significant concentrations of oil and grease amounting to 563 mg/L. Soap manufacturing effluent and the combined wastes discharged from an industrial complex were subjected to different treatment processes, namely dissolved air flotation, chemical coagulation-sedimentation, and biological treatment via a completely mixed activated sludge process. Although coagulation using alum followed by sedimentation removed 52% of COD, residual values did not comply with the regulatory standards. Biological treatment of the composite combined waste water significantly removed the organic contaminants in wastewater. Average residual BOD, COD, oil and grease values were 30, 92 and 8.3 mg/L respectively (Yusuf and Sonibare, 2004).

2.6 Health impacts of some pollutants

Different analytical water quality parameters used for testing the quality of water and their source of occurrence with potential health effects are reviewed in table 2.4.

Table 2.4 Different analytical water quality parameters used for testing the quality of water and their source of occurrence and potential health effects with United States Environmental protection Agency guidelines (Patil et al, 2012).

Parameter	Source of Occurrence	Potential Health Effect
Turbidity	Soil runoff	higher level of turbidity is associated with disease causing bacteria
Colour	Due to presence of dissolve salts	
Odour	Due to biological degradation	Bad odour unpleasant
Electrical Conductivity	Due to different dissolved solids	Conductivity due to ionisable ions. High conductively increases corrosive
pH	pH is changed due to different gases and solids	Affects mucous membrane, bitter taste, corrosion
Dissolved oxygen	Presence due to dissolved oxygen	Dissolved oxygen corrode waterlines, boilers and heat exchangers, at low level marine animals cannot survive.
Total hardness	Presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in water supply. Hardness minerals exist to some degree in every water supply	poor lathering with soap; deterioration of the quality of clothes scale forming.
Total .alkalinity	Embritlement of boiler steel	Due to dissolve gases (CO_2), boiled rice turns yellowish.
TDS	Presence of all dissolved salt	Undesirable taste; gastro-intestinal irritation; corrosion or incrustation

Table 2.4 (cont'd). Different analytical water quality parameters used for testing the quality of water and their source of occurrence and potential health effects with United States Environmental protection Agency guidelines (Patil et al, 2012)

Parameter	Source of Occurrence	Potential Health Effect
Calcium	Precipitate soaps, anionic	Interference in dyeing, textile and paper industry.
Magnesium	Surfactants, anionic and sifters	Same as above
Ammonia	Corrosion of copper and degradation of organics	Due to dissolved gases; zinc alloys by formation of complex ions
Barium	Discharge of drilling wastes; discharge from metal refineries; erosion of natural deposits.	Increase in blood pressure
BOD	Organic material contamination in water	High BOD decreases level of dissolved oxygen
Carbonate	Due to dissolution of carbon (IV) oxide	Produce imbalance, unsatisfactory production, and short product life.
Chloride	Water additive used to control microbes disinfect.	Eye/nose irritation, stomach discomfort, and increase corrosive character of water.
Nitrate	Runoff from fertilizer use; leaking from septic tanks, Sewage; erosion of natural deposits	Effect on infants below the age of six months. symptoms include shortness of breath and blue baby syndrome (Akiwumi et al., 2012)

Volatile Organic Compounds may have a variety of harmful health effects. At high levels of exposure, many volatile organic compounds can cause central nervous system depression (drowsiness, stupor). All can be irritating upon contact with the skin, or to the mucous membrane (Clair, 2007).

2.7 Principle of liquid-liquid extraction

Liquid-liquid extraction also known as solvent extraction and partitioning is a method use to separate compounds based on their relative solubility in two different immiscible liquids, usually water and an organic solvent. It is an extraction of a substance from one liquid phase into another and a basic technique in chemical laboratories, where it is performed using a separating funnel. The choice of pH and solvent are important aspects of this technique because it allows sequential separation of several components of mixture by this processing, the production of fine organic compound, the processing of perfumes and other industries, it is early acquired with a little practice, the procedure is fast and simple (Selvi *et al*., 2012).

In liquid-liquid extraction there is a feed phase, which contain a components to be removed and the addition of a second phase (solvent phase) which is immiscible with feed phase. Some of the component (solute) is transferred from the feed phase to the solvent phase. After extraction, the feed and solvent phases are called the raffinate (R) and extract (E) phases respectively. (Nikolaos *et al*., 2005).

One of the two phases is an organic phase while the other is an aqueous phase, under equilibrium conditions, the distribution of solute is over the phases which is determined by the distribution law. After the extraction, the two phases can be separated because of their immiscibility.

Component is then separated from the extract phase by a technique such as distillation and the solvent is regenerated. Further extractions can be carried out to remove more components. Liquid-liquid extraction efficiency can be enhanced by adding one or more extractant to the solvent phase. The extractant interacts with component increasing the capacity of the solvent. To recover the solute from the extract phase the extractant-solute complex has to be degraded. For immiscible liquids, distribution coefficient goes thus: (Ristichevic *et al*., 2009).

$$\text{Distribution Coefficient, K} = \frac{mass\ fraction\ solute\ in\ E\ phase}{mass\ fraction\ in\ R\ phase}$$

2.8 Principle of various instrumental techniques relevant to this study

Three instruments were used majorly in this research work which include

(a) Flame Atomic Absorption Spectrophotometry (FAAS)

(b) HACH DR/EL 5 spectrophotometer

(c) Gas chromatography- Mass spectrometry (GC-MS). The principle of each one will be explained below.

2.8.1 Flame Atomic Absorption Spectrophotometry (FAAS)

A spectrophotometer is a device for producing colored light of a selected wavelength. A photometer is a device for measuring the intensity of the light and when incorporated in spectrophotometer, it is used to measure the intensity of the monochromatic beam produced (Nabil, 2011).

Flame photometer, is used for the determination of lithium, sodium and potassium. It is also useful for the determination of calcium and strontium (Pourreza and Ghanemi, 2009).

Atomic absorption spectrophotometer is used for the determination of a large number of metals in drinking water without extensive sample pretreatment. It is used for surface water and effluents successfully only the samples may have to be pretreated to avoid interferences. The use of organic solvents with oxyacetylene, oxyhydrogen or nitrogen (II) oxide acetylene flames enables the determination of metals, which form refractory oxides (Jiri *et al.*, 2011).

Atomic absorption spectroscopy resembles flame photometry. In both methods, a sample is aspirated into a flame where it becomes atomised. The only difference is that flame photometry measures the intensity of light emitted but in the case of AAS, a light beam is directed through the flame into a monochromator and then onto a detector that measures the intensity of light absorbed. AAS is more sensitive in that it depends upon the presence of free unexcited atoms. However, in flame photometry, the ratio of unexcited to excited atoms at any moment is very high. Each metallic element has its own. Characteristic absorption wavelength, a source lamp made up of that element is employed and which makes the method relatively free of spectral or radiation interferences. The amount of light intensity absorbed in the flame is proportional to the concentration of the element in the sample (Sneddon *et al.*, 2006).

2.8.2 HACH DR/EL Spectrophotometer

(a) Digital titrator

The expected sample concentration is estimated from the table given in each procedure and a sample volume is selected and titration cartridge accordingly. The cartridge is slide into the titrator receptacle and lock in position with a slight turn has shown below. The polyethylene cap is removed from the end of the cartridge and a clean delivery tube is inserted. A delivery tube with a straight barrel is used for hand-held titrations while a delivery tube with a 90^o bend is used for stationary setups. (HACH Company, 2014).

The digital titrator will be mounted on a support for stationary titrations, use a Titrastir® or a clamp holder and clamp to attach the titrator to a laboratory stand. The titra stir also stirs the sample at a constant speed, leaving the analyst free to detect the endpoint. A cartridge is first attached to the digital titration, the piston must be engaged and the delivery tube must be flushed by holding the titrator with the tip of the cartridge point up, then advance the plunger release button to engage the piston with the cartridge after which the delivery knob is turned until all the air is expelled and several drops of solution flow from the tip and the counter reset knob is used to turn the digital counter back to zero. The tip is wiped or rinse with deionised water. The sample volume is measured in the smallest graduated cylinder or pipette, and then the sample is transferred into 125 mL or 250 mL Erlenmeyer flask and diluted with deionised water if necessary. The necessary reagents are added to the sample and swirl to mix. The delivery tube tip is immersed in the solution and swirl the flask while titrating. Accurate results will occur if the delivery tube tip is held above the solution. By turning the delivery knob, titration starts. The knob will continue to be turned and swirled the sample until the end point is reached. The number of digits that appeared in the digital counter window is recorded. The concentration of the sample is calculated thus:

$$sample\ concentration\ =\ digit\ required\ x\ digit\ multiplier$$

Where:

Digit required= the number that appeared in the digital counter window.

Digit multiplier= the number from the table given in the procedure. This takes into account the sample dilution and titrant strength.

(b) HACH Spectrophotometer (DR/EL5)

The correct sample cell adapter is installed in the sample cell module, the soft key under HACH program is pressed, the appropriate stored program numbers with the numeric key is entered and press enter. The sample and blank solution is prepared for measurement as described for each specific method of parameter. A clean sample cell is filled with the required amount of sample for the test (the sample) the appropriate reagents are added and mixed. Another clean sample cell is filled with the required amount of reagent blank (the blank) and the appropriate reagent is added and mixed. The blank from the sample cell is removed and replaced with the sample and the lid closed. The results will be displayed (HACH Company, 2014).

2.8.3 Gas Chromatography– Mass Spectrophotometry

Gas chromatography analyses were performed with a Hewlett-Packard 7890 series gas chromatography equipped with 5975C mass spectrometer detector and splitters injection mode with a pulse pressure of 5.9818 psi. Chromatographic separation was carried out using a polar column (30 m length, 0.32 mm i.d and 0.25 nm film thickness). The oven temperature was $250^{o}C$ for 31 minutes followed by temperature programmed to $200^{o}C$ at $17^{o}C/min$. Helium was used as carrier gas.

2.9 Surface water modelling

Regression model

Ho: Null hypothesis H1: Alternative hypothesis

Fitted model of regression of surface water loads on Distance (DT)

$$Y = \alpha + \beta Xi$$

Application of surface water model on channelization of Asa River from discharge points, upstream to downstream.

$$Y = b1x3 + b2x2 + b3x + C$$

Where Y = Dependent variables, α = Intercept, β = Regression coefficient

Xi = Independent variable, i = Number of variables, C = Constant

Hypothesis: $Ho = \beta = 0 \, vs \, H1: \beta \neq 0$

Ho: $\beta = 0$ this implies that the regression coefficient is not significantly different from zero.

2.10 Assessment of metal contamination in sediments and water

The degree of contamination in sediments was evaluated using four parameters: Enrichment Factor (EF), Contamination Factor (CF), Geo-accumulation Index (I_{geo}), modified Hazard Quotient (mHQ) and Ecological Contamination Index (ECI).

Enrichment Factor (EF).

The Enrichment Factor (EF) of metals presented in table 2.5 is a useful indicator reflecting the status and degree of environmental contamination (Feng *et al*., 2004). The EF calculations, compare each value with a given background level, either from the local site, using older deposits formed under level similar conditions, but without anthropogenic impact, or from a regional or global average composition (Choi *et al*., 2012).

The EF was calculated using the method proposed which is

$$EF = (Me/Fe)sample/(Me/Fe)background$$

Where: $(Me/Fe)_{sample}$ is the metal to Fe ratio in the sample of interest

$(Me/Fe)_{background}$ is the natural value of metal to Fe ratio

Fe used as the element of normalization (1.5%)

Mean Shale concentration (mg/kg): Pb = 20, Cu = 11.2, Co = 29, Cr = 90, Ni = 68, Zn = 95, Al = 15.53, Fe = 46700 and Mn = 850.

Contamination Factor (CF)

The level of contamination of sediment in table 2.6 by metal is expressed in terms of a contamination factor (CF) calculated as:

$$CF = Cm\,Sample/Cm\,Background$$

Where: Cm_{Sample} = Sample concentration of a given metal in river sediment

$Cm_{Background}$ = Background value concentration of the metal which is equal to the World surface rock average.

World surface rock average (mg/kg): Pb = 16, Cu = 32, Co = 13, Cr = 71, Ni = 49, Zn = 20, Al = 15.6, Fe = 35900 and Mn = 750.

Geo-accumulation index (I_{geo})

The geo-accumulation index was used to determine the pollution level of sediments and presented in table 2.7. The calculated I_{geo} values were based on world surface rock average.

$$Igeo = Log2\ [Cn\,Sample/1.5 * Bn]$$

C_n = Concentration of the heavy metal in the sample.

B_n= Geochemical background value (world surface rock average given by Muller quoted by Salah et al., 2012).

Factor 1.5 = minimize the effect of possible variation in the background values which may be attributed to lithogenic variations in the sample.

World surface rock average (mg/kg): Pb = 16, Cu = 32, Co = 13, Cr = 71, Ni = 49, Zn = 20, Al = 15.6, Fe = 35900 and Mn = 750.

Modified hazard quotient (mHQ)

The modified hazard quotient classification is presented in table 2.8

$$mHQ = [Ci\,(1/TELi + 1/PELi + 1/SELi]1/2$$

C_i = concentration of heavy metal in the sediment sample

TEL_i = threshold effect level

PEL_i = probable effect level

SEL_i = severe effect level

$$HQ = Cmetal/SQG$$

C_{metal} = concentration of heavy metal in the sediment sample

SQG = sediment quality guidelines

Ecological contamination index (ECI)

The ecological contamination index is an aggregative empirical approach that estimates the risks associated with an ecosystem using a source-specific factor derived primarily from factor analysis. The proposed ranking of risks posed by heavy metals to ecological systems computed based on the proposed formulation is presented in table 2.9

$$ECI = Bn\sum mHQi$$

Where: Bn = reciprocal of derived eigen value of heavy metal concentration only

Overall Pollution Index (OPI) for water

Overall Pollution Index (OPI) for water is reviewed in table 2.10

$$OPI = \sum iPi/n$$

Pi = pollution index of ith parameter

N = number of parameters

Table 2.5. Enrichment Factor (EF) classifications (Mmolawa *et al*., 2011).

Enrichment Factor	Enrichment Factor (EF) classifications
EF<2	Deficiency to minimal enrichment
2≤EF<5	Moderate enrichment
5≤EF<20	Significant enrichment
20≤EF<40	Very high enrichment
EF≤40	Extremely high enrichment

Table 2.6. Contamination Factor (CF) and their levels (Salah *et al*., 2012).

Contamination Factor	Contamination level
CF<1	Low contamination
1≤CF<3	Moderate contamination
3≤CF<6	Considerable contamination
CF>6	Very high contamination

Table 2.7. Muller's classification for geo-accumulation index (I_{geo}) [Salah *et al*., 2012].

I_{geo} value	Class	Sediment Quality
≤0	0	Unpolluted
0-1	1	from unpolluted to moderately polluted
1-2	2	moderately polluted
2-3	3	from moderately polluted to strongly polluted
3-4	4	strongly polluted
4-5	5	from strongly polluted to extremely polluted
>6	6	extremely polluted

Table 2.8. Classification of modified Hazard Quotient (mHQ) [Benson et al., 2018]

mHQ	Degree of risk
mHQ > 3.5	Extremely severity of contamination
3.0 < mHQ < 3.5	Very high severity of contamination
2.5 < mHQ <3.0	High severity of contamination
2.0 < mHQ <2.5	Considerable severity of contamination
1.5 < mHQ < 2.0	Moderate severity of contamination
1.0 < mHQ <1.5	Low severity of contamination
0.5 < mHQ < 1.0	Very low severity of contamination
mHQ < 0.5	Nil to very low severity of contamination

Table 2.9. Classification of Ecological Contamination Index (ECI) [Benson et al., 2018]

ECI	Degree of contamination
ECI > 7	Extremely contaminated
6 < ECI < 7	Highly contaminated
5 < ECI < 6	Considerably to highly contaminated
4 < ECI < 5	Moderately to considerably contaminated
3 < ECI < 4	Slightly to moderately contaminated
2 < ECI < 3	Uncontaminated to slightly contaminated
ECI < 2	Uncontaminated

Table 2.10. Overall Pollution index (OPI) for water (Shuguang *et al.*, 2011)

Overall Pollution Index	Class	Water quality
0-1	I	Acceptable excellent
1-2	II	Slightly polluted
2-4	III	Polluted
>4	IV	Heavily polluted

CHAPTER THREE

MATERIALS AND METHODS

3.1 Introduction

In this study, the American Public Health Association (2005) standard protocol for physical, chemical, organic pollutants of water and sediments sampling, transport, storage and analysis was used.

3.1.1 Sampling protocol

Equipment: Sampling equipment used for water was stainless steel sampler and Eckman grab sampler with stainless steel trowel was used for sediments. Materials used in packaging the sediment sample was treated aluminum foil.

Glassware: All glassware were washed with metal free detergent and rinsed with tap water. They were then soaked in 1% nitric acid for 24 hours.

Personal Protection equipment (PPE): Hand gloves, goggles, boots and nose mask were used as protection wares.

Control sampling: Control samples were taken from site at least approximately 5-6 km far away from the sites under study. This was to allow assessment of potential contamination.

Sampling coding: All samples were given a key code to reflect the environmental matrix and specific location of matrix; for example EW/GS/KC/SW/SD/GW (EW – Effluent; GS

– detergent company; KC – pharmaceutical company B; SW – surface water; SD – sediment; GW – groundwater).

“Insitu” monitoring equipment: Horibar U10 portable water quality checker alongside a portable spectrophotometer was used to measure the Insitu parameters of the water samples and the readings properly registered in a note book.

Geo-referencing and photographic registers: A Global Positioning System (GPS) device was used to locate sampling sites with precision and the aim is to ensure future location of sites. Some digital photographs were also taken for reference purpose.

Labeling: Clear labeling was used for all samples during analysis and a code was given to each sample. A key list of the code was generated for proper interpretation.

Data analysis: Correlation analysis was used to determine the degree of association between water quality parameters (pH, total solids, temperature, Biochemical Oxygen Demand, Chemical Oxygen Demand etc). This was employed to guide assumptions made about the possible source of pollutants (natural or anthropogenic). Also, the mean and standard deviation, a measure of how widely values are dispersed from the average value (the mean) was used on recovery studies obtained from the concentration of Organic Compounds. SPSS 16.0 was used on surface water modelling.

3.1.2 Transportation and storage protocol

3.1.2.1 Preservation

Water: Samples for Biochemical Oxygen Demand were collected in 25 mL Winkler bottles and fixed immediately with Winkler’s reagent (2 mL of Manganous II sulphate and 2 mL of alkaline iodide solution); Samples for physicochemical parameters were collected in plastic bottles and stored in ice-chest box at 4^{o}C while OCs determination were collected in pre-sterilised glass bottles and aluminum foil was used to air tight the bottles to avoid temperature changes and preserved with 2 mL conc. tetraoxosulphate (VI) acid per litre at 4^{o}C to prevent the loss of volatile compounds until chemical analysis.

Sediments: Sediment samples were wrapped in pretreated aluminum foil paper and maintained at about 4^{o}C using ice padded coolers. They were transported to the laboratory and stored in the refrigerator until chemical analysis.

3.1.2.2 Transportation

Transportation was ensured to minimize the possibility of contamination of the samples (and even cross contamination); maintaining their integrity and preservation until they reached the laboratory for storage and subsequent analysis.

3.1.2.3 Storage

The samples were kept for a maximum of seven days before extraction. This was to avoid accumulation of samples and possible chemical degradation. Before storage, sediment samples were sieved to remove pebbles and other unwanted materials; properly homogenised and appropriate desiccant added.

3.1.3 Sampling protocol for socio economic assessment

Socio economic impact assessment was used in this study to review the effects of Asa River on people living in Ilorin Kwara State using questionnaire method. The evaluation of the assessment was based on (a) domestic factor (b) health impact factor (c) environment impact assessment factor. The socio economic impact assessment factors include location, occupation and types of water. Statistical analysis result, which includes frequency counts, T-test and ANOVA, was used for the justification of the study.

Sampling technique for questionnaire: Nine zones were selected around the Asa Dam zones in Ilorin metropolis of Kwara State.

Instrumentation: The researcher uses the non-postal questionnaire instrument for the purpose of this study, which was administered directly by the researcher and with the help of research assistants that are trained. An appropriate instrument has therefore been developed for the particular group of subjects under study taking into consideration the research questions and hypothesis already postulated. The researcher chooses to use the non-postal questionnaire method because it is cheaper, less time consuming and easier to administer than the interview method. The questionnaire used for this study is made up of two sections: A and B. Information concerning the demographic characteristics of the respondents are contained in section A while section B contains twenty-five items which are grouped under four-point rating scale.

Phase validity: The questionnaire was brief, straight forward and could be answered within a reasonable time.

3.2 Study area and sampling sites

Asa River is one of the most important rivers in Ilorin, Kwara State, Nigeria. It is used for household and irrigation purposes. It receives wastes from both municipal and industrial sources. Four industrial companies were randomly selected within the Asa River vicinity for the present study namely detergent company, pharmaceutical company A, pharmaceutical company B and battery company respectively. Surface water, sediments and groundwater available in these sites were also sampled. The study sites and control with coding are presented in table 3.1, these tables also highlights brief description of the sampling points in each study area and the control site.

3.2.1 GIS sampling map of the study sites

Throughout the study, a Global Positioning System was used to get the location coordinates of the study sites. This also enabled the generation of a sampling map showing the study area in Ilorin, Kwara State, Nigeria (figure 3.1) and the one showing each company with direction of flow into Asa River (figure 3.2).

3.3 Standards and solvents

Standards: The powder pillow standards were sourced from HACH Company, USA while, organic compounds standard were sourced from New Haven, CT, USA.

Solvents: All solvents used in this research work were of analytical grade (mostly BDH products).

Table 3.1 Sampling Location and site description

S/No	Sample Location	Longitude	Latitude	Site description
1	EW-GS-1	4^{o} 32’14.55” E	8^{o} 27’50.94”N	Effluent collected from a detergent company located at Asa-dam Road, Ilorin, Kwara State at the back close to the fence, which overflows passes into a gutter through an outlet. The effluent was soapy in nature.
2	EW-TP-2	4^{o} 33’ 0.39” E	8^{o} 28’ 24.52” N	Effluent collected from a pharmaceutical company **A** situated at New Yidi Road, Ilorin, Kwara State. It is white – brownish in colour.
3	EW-KC-3	4 ^{o} 32’ 35.55” E	8^{o} 28’ 50.47” N	Effluent collected from pharmaceutical company **B** situated at Oko-erin road, Ilorin, Kwara State. Dirty white colour effluent water was obtained.
4	EW-FB-4	4^{o}33’ 58.63” E	8^{o} 28’ 11.64”N	Effluent collected from detergent company situated at Gaa-imam road close to Stella Obasanjo multipurpose hall, Ilorin, Kwara State. A light colour water effluent was collected.
5	GS/SW1/SD1	4^{o}32’ 20.57” E	8 ^{o}27’ 27.84”N	A soapy surface water /sediment was collected (553 m) away from the detergent industry.
6	GS/SW2/SD2	4 ^{o}32’28.96’’E	8^{o}27’58.83’’ N	A soapy surface water/sediment was collected (1240 m) away from the industry.
7	GS/SW3/SD3	4^{o}32’38.32’’ E	8^{o}28’17.54’’ N	A soapy surface water/sediment was collected (1856 m) away from the industry.
8	KC/SW1/SD1	4^{o}32’26.62’’ E	8^{o}28’25.14’’N	A stream located within Kwara State Stadium Complex, Taiwo Road, Ilorin was sampled (889 m) away from the industry B.
9	KC/SW2/SD2	4^{o}32’31.33’’E	8^{o}28’26.42’’N	A stream located within Kwara State Stadium Complex, Taiwo Road, Ilorin was sampled (1039 m) away from the industry B.
10	KC/SW3/SD3	4^{o}32’35.68’’ E	8^{o}28’27.51’’ N	A stream located within Kwara State Stadium Complex, Taiwo Road, Ilorin was sampled (1188 m) away from the industry B.
11	KC-GS/SW1/SD1	4^{o}32’40.95’’ E	8^{o}28’29.15’’N	Meeting point one of pharmaceutical site B and detergent site inside stadium complex (3701 m) from the industries.
12	KC-GS/SW2/SD2	4^{o}32’47.86’’E	8^{o}28’31.76’’N	Meeting point two of pharmaceutical site B and detergent site inside stadium complex (3976 m) from the industries.
13	KC-GS/SW3/SD3	4^{o}32’56.31’’E	8^{o}28’35.12’’N	Meeting point three of pharmaceutical site B and detergent site inside stadium complex (4358 m) from the industries.
14	KC-GS/SW4/SD4	4^{o}33’9.61’’E	8^{o}28’35.59’’ N	Meeting point four of pharmaceutical site B and detergent site inside stadium complex (4595 m) from the industries.
15	KC-GS-TP/SW1/SD1	4^{o}33’16.91’’ E	8^{o}28’36.21’’ N	Meeting point one of pharmaceutical site B/detergent/pharmaceutical site A at New Yidi stream (4846 m) from the industries.

Table 3.1[cont’d]: Sampling location and site description

S/No	Sample Location	Longitude	Latitude	Site description
16	KC-GS-TP/SW2/SD2	4^{o}33’25.55’’E	8^{o}28’37.41’’N	Meeting point two of pharmaceutical site detergent/pharmaceutical site A at New Yidi stream (5042 m) from the industries.
17	KC-GS-TP/SW3/SD3	4^{o}33’31.67’’E	8^{o}28’38.72’’N	Meeting point three of pharmaceutical site B/detergent site/ pharmaceutical site A at New Yidi stream (5255 m) from the industries.
18	KC-GS-TP-AS/SW/SD	4^{o}33’38.44’’E	8^{o}28’39.93’’N	Meeting point of pharmaceutical site B/detergent/pharmaceutical site A as it enters Asa River.
19	FB/SW1/SD1	4^{o}34’1.36’’E	8^{o}28’7.97’’N	An adjoining stream before the industry at Gaa – imam, Ilorin was sampled (1380 m).
20	FB/SW2/SD2	4^{o}33’57.46’’E	8^{o}28’12.73’’N	An adjoining stream after an industry at Gaa – imam, Ilorin was sampled (1380 m).
21	FB/SW3/SD3	4^{o}33’42.89’’E	8^{o}28’25.23’’N	A stream mixing point off Coca cola Road from an industry was collected (1380 m).
22	FB-AS/SW/SD	4^{o}33’38.81’’E	8^{o}28’41.98’’N	Battery industry site surface water as it enters Asa River (1436 m).
23	AS1/SW1/SD1	4^{o}33’39.25’’E	8^{o}27’1.29’’N	Asa river surface water/sediment point one - after the dam (668 m) towards AS2
24	AS2/SW2/SD2	4^{o}33’41.86’’E	8^{o}27’22.63’’N	Asa river surface water/sediment point two –Dangote area (1162 m) towards AS3
25	AS3/SW3/SD3	4^{o}33’32.30’’E	8^{o}28’1.28’’N	Asa River surface water/sediment point three - Along 7up Bridge (1192 m) towards the industries joining.
26	AS4/SW4/SD4	4^{o}33’43.58’’E	8^{o}28’57.88’’N	Asa River surface water/sediment point four - Unity bridge (7181 m) after the four industries joining.
27	AS5/SW5/SD5	4^{o}33’43.80’’E	8^{o}29’12.56’’N	Asa River surface water/sediment point five – Emir bridge (7652 m) After the four industries joining.
28	AS6/SW6/SD6	4^{o}33’55.07’’E	8^{o}29’40.90’’N	Asa River surface water/sediment point six – Amilegbe bridge (8628 m) after the four industries joining.
29	CONTROL 1/SW/SD	4^{o}33’21.02’’E	8^{o}26’30.76’’N	Control 1 at Asa dam water corporation (1217 m) towards AS1
30	CONTROL 2/SW/SD	4^{o}33’20.05’’E	8^{o}26’16.08’’N	Control 2 at Egbejila before the dam site

Table 3.1[cont'd]: Sampling location and site description

S/No	Sample Location	Longitude	Latitude	Site description
31	GS/GW	4^{o}32'28.55''E	8^{o}27'28.78'' N	Borehole situated not far away from the detergent industry.
32	TP/GW	4^{o}33'7.16''E	8^{o}28'24.85'' N	Borehole situated in front of pharmaceutical industry A.
33	KC/GW	4^{o}32'18.89''E	8^{o}28'37.87''N	Bore hole not far away from pharmaceutical industry B.
34	FB/GW	4^{o}33'46.40''E	8^{o}28'11.09''N	Borehole not far from a battery industry.
35	AS5/GW	4^{o}33'46.80''E	8^{o}29'9.58''N	A well situated at Emir Road not far away from the bridge
36	AS6/GW	4^{o}33'50.35''E	8^{o}29'37.93''N	A well situated not far away before Amilegbe bridge.

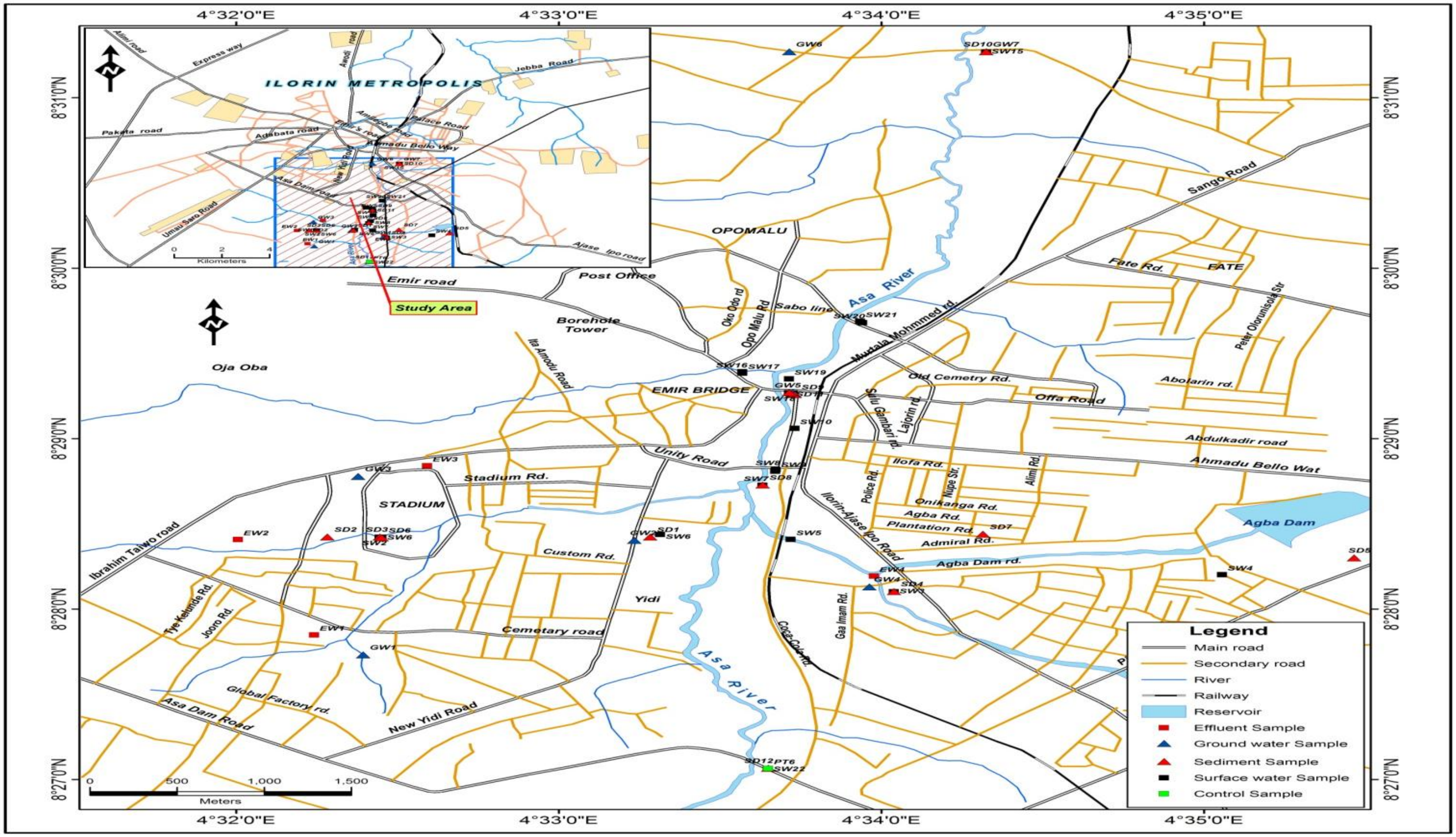


Figure 3.1: Map of Ilorin Showing Sampling Points in Asa River.

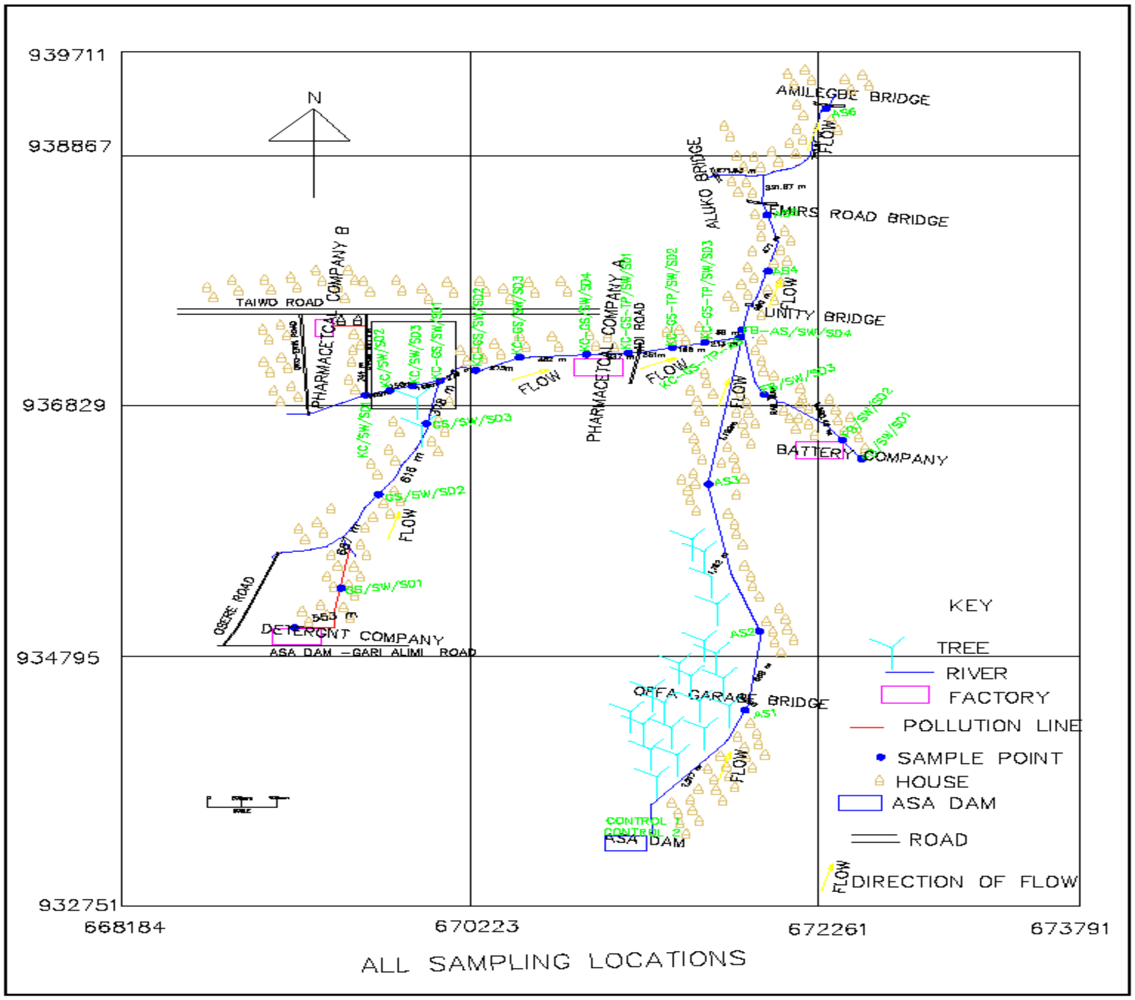


Figure 3.2: Study Sites and sampling locations

3.4 Study of surface water quality and bottom sediments parameters

In the present research work, sampling of water and sediments were done in four sampling periods spanning the two seasons: dry and rainy. The periods were as follows: dry season 1 [February, 2013 – April, 2013]; rainy season 1 [May, 2013- October, 2013]); dry season 2 [November, 2014 – April, 2015] and rainy season 2 [June 2014 – October, 2014]. The frequency and number of samples collected are presented in table 3.2 while, table 3.3 reveal the parameters determined in water and sediment samples.

3.5 Effluents and surface water analysis

The American Public Health Association (2005) and HACH Company (2014) standard methods were used for the physicochemical parameters determination.

3.5.1 Determination of pH

pH measurement is by using an electrochemical method with a combination of glass electrode and a reference potential provided by a standard calomel electrode.

Reagent preparation: i) Potassium Hydrogen tartrate $KHC_4H_4O_6$ (saturated at 25^oC) pH 3.6 at 25^oC. An excess of 8-10 g fine crystalline $KHC_4H_4O_6$ in 100 mL distilled water in glass stopper bottle. (ii) Potassium Hydrogen phthalate $KHC_8H_4O_4$, 0.05 M pH 4.0 at 25^oC. 10.21g of $KHC_8H_4O_4$ in distilled water and dilute to 1 litre.

Buffer: The pH meter was standardised with two buffer solutions of different pH valves of 4 and 9 to serve as check for proper instrument response.

3.5.2 Determination of temperature

The temperature of the effluent and surface water was determined using thermometer.

Table 3.2: Frequency and number of samples collected for water and sediments analyses

Type of samples	sampling points	frequency	Number of samples
Effluent water	8	4	32
Surface water	26	4	104
Groundwater	6	4	24
Sediments	26	4	104

Table 3.3: Parameters determined in water and sediments samples

Sample	Parameters
Water samples (effluent, surface and groundwater)	pH, temperature, Electrical conductivity, alkalinity, Total solids, Total Dissolved Solids, Total Suspended Solids, Chloride, Nitrate, Phosphate, Sulphate, Ammonia, Copper, Cadmium, Lead, Zinc, Iron, Magnesium, Calcium, Sodium, Chromium, organic pollutants (alkanes, alkenes, aromatics and carboxylic acids).
Sediment	Lead, Copper , Cobalt, Chromium, Nickel, Zinc, Aluminium, Manganese, Iron

3.5.3 Determination of turbidity

Turbidity is measured by simple comparison of the interference of light rays passing through a sample with that in standard samples and the procedure applied in this research is nephelometric method which is based on the comparison of the intensity of light scattered by a given sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same condition. Turbid meter calibration: The manufacture is operating instruments and the pre-calibration scale was used.

Turbidities 0-40 units: The sample was shaken to disperse the solid contents thoroughly, and then the air bubbles that may occur were allowed to disappear. The sample was measured into the turbid meter cell and the turbidity was read directly from the instrument scale.

Turbidities exceeding 40 units: Suitable volume of 5 mL, 10 mL or 20 mL etc. were pipette into 50 mL or 100 mL volumetric flask and diluted with one value of turbidity free water until it falls to values between 30 and 40 units. The dilution factor was noted and used to compute the turbidity of the original sample.

Calculation: $Turbidity\ unit\ (NTU)\ =\ A * (B + C)/C$

Where A = Turbidity readily for diluted sample

B = Volume (mL) of dilution water used

C = Volume (mL) of sample taken for dilution

3.5.4 Determination of colour

Pure water is generally colourless. The presence of organic matter modifies this colour to green, straw, yellow or brown. It is the presence of this colour that was measured in water. For analytical purposes, water colour may be defined as color due to dissolved organic content.

The standards in Nessler cell were put to 50 mL mark and the water sample into a nessler also at 50 mL mark. The cells were placed on a white surface and the colours of the sample were matched against the standards and compared the colours by looking vertically downwards through the tubes towards the white surface. The colour of the standard closest to the sample was selected and the corresponding values were recorded for the sample in Hazen (Hu).

3.5.5 Determination of conductivity

Conductivity is a measure of mobile ions in the sample. The cell was standardised and a cell factor was established by measuring the conductivity of a standard potassium chloride solution, after which the cell was rinsed by repeated immersion in distilled water and later immersed the cell in the sample several times before obtaining a reading by approaching the end point from a low reading upward and once from a high reading downward because the cell constants were subject to slow change even under ideal conditions and sometimes to more rapid change under adverse conditions.

Calculation: The cell constant was calculated K (cm^{-1})

$$K = R\,(kcl) * Ct\,cm$$

Where: R (KCl) is the measured resistance of standard potassium chloride solution

C_t = Conductivity ($_N Scm^{-1}$) of the standard KCl at 25^oC

Then the conductivity Cs (μScm^{-1}) of the sample is given by $Cs = K/Rs$

Where Rs = measured resistance of the sample

3.5.6. Determination of total hardness

Total hardness was determined by adding 2 mL of ammonia solution to 50 mL of each sample and two drops of Eriochrome blue-black indictor added. This was then titrated with 0.01M EDTA in the burette.

$$Total\ hardness\ (mg/L) = Titre\ Value\ x\ 20$$

3.5.7 Determination of Calcium hardness

In calcium hardness determination, solo chrome dark-blue indicator was added to duplicate 50mL of each water sample. A few drops of ammonia solution were added to suppress other ions except Ca^{2+} and mg^{2+} before titrating. Potassium cyanide solution was also added to filter suppress metal ions.

$$Calcium\ hardness\ (mg/L) = Titre\ value\ x\ 20$$

3.5.8 Determination of Magnesium hardness

Magnesium hardness was obtained by subtracting calcium hardness from total hardness given by the equation below:

$$Magnesium\ hardness\ (mg/L) = Total\ hardness - calcium\ hardness$$

3.5.9 Determination of Total Solids

Total solid is the amount of solid particles in the water samples. A clean evaporating dish was heated at 103-105^oC for one hour, then cooled, desiccates and weighed. A measured aliquot of sample was transferred to the pre weighed dish and evaporated to dryness after which the evaporated sample was dried at least one hour at 103-105^oC and then cooled in the desiccators and weighed until a constant weight was obtained.

Calculation: Total residue (solids) mg/L $= \frac{(A-B)*1000}{c}$

Where A = weight of sample + dish in mg
B = weight of dish in mg
C = Volume of sample in mL

3.5.10 Determination of Dissolved Solids

Dissolved solids is defined as those solids capable of passing through a glass tube filter and dried to constant weight at 180°C. The sample is filtered through the glass tube filter, rinsed with three 10mL portions of distilled water and continues to apply vacuum for about 3 minutes after filtration is complete to remove as much water as possible. 100mL of the filtrate is transfer to a weighed evaporating dish and evaporate to dryness. The evaporated sample is dried for at least one hour at 180°C and cooled in a desiccator and weighed. The drying cycle is repeated until a constant weight is obtained.

$Dissolved\ solid\ (mg/L) = (A - B)\ x\ 1000/\mathrm{C}$

Where A = weight of dried residue + dish in mg
B = weight of dish in mg
C = Volume of sample used in mL

3.5.11 Determination of Suspended Solids

A suspended solid was determined by first taking the weight of a filter paper 100 mL of each water sample was filtered using the filter paper. The used filtered paper was put in an oven at 50°C for 10 minutes. It was taken out and weighed.

$$Ymg \ = Final\,weight \ - initial\,weight$$

$$mg/L \ = Y * 1000 \ / \ Volume\,of\,water\,sample\,used$$

3.5.12 Determination of alkalinity

Alkalinity determination was done by measuring 50 mL of each sample into a conical flask and two drops of Sodium trioxosulphate (IV) added to remove traces of chlorine. Three drops of methyl orange indicator was then added and titrated with 0.01 M tetraoxosulphate (VI) acid in the burette.

$$Alkalinity\,(mg/L) \ = Titre\,value\,x \ 20$$

3.5.13 Determination of dissolved oxygen/biochemical oxygen demand

Biochemical oxygen demand is defined as the amount of oxygen required by bacterial to break down the decomposable organic matter present in any water, waste water or treated effluent. It is a measure of the concentration of organic matter present in the kind of water. Biochemical oxygen demand is determined by measuring the amount of dissolved oxygen present in any given samples before and after incubation in the dark at 20^{o}C for five days.

Reagent preparation:

i) Manganous sulphate: 480 g of sulphate was dissolved in distilled water and diluted to 1litre.

ii. Alkaline potassium iodide: 500 g of Sodium hydroxide, 20 g of Sodium azide and 130 g of Potassium iodide were dissolved in distilled water to make 1 litre.

iii. Concentrated H_2SO_4

iv. Sodium thiosulphate (0.025M): 6.205 g $Na_2S_2O_3$. $5H_2O$ was dissolved in boiled and cooled distilled water to 1litre and preserved by adding 5 mL chloroform

v. Starch indicator: An emulsion of 10 g was prepared in a beaker with a small quantity of distilled water and then transferred into 1litre of boiling water and allowed to boil for a few minutes and settle overnight. 5 mL of chloroform was added and stored in a 10^{o}C refrigerator.

Procedure: Water sample was collected in a glass stopper bottle brim full and the contact of the sample with air was avoided. Immediately after collection, 1 mL of Manganous sulphate by means of pipette was added by dipping the end of the pipette just below the surface of the water sample and 1 mL of alkaline potassium iodide solution was added and the stopper was inserted for adequate mixing by inverting the bottle several times and the precipitate formed was allowed to settle half way and mix again, then 1 mL of conc. tetraoxo sulphate (VI) acid was added and the solution was allowed to stand for about five minutes and 100 mL of the solution was poured into an Erlenmeyer flask and immediately 0.025 M sodium thiosulphate was added drop by drop from a burette until the yellow color almost disappeared, after which 1 mL of starch solution was added which gave a blue color and the addition of the sodium thiosulphate was added again until the blue color just disappeared and the volume of thiosulphate was recorded.

Calculations: $mL\ of\ 0.025\ M\ sodium\ thiosulphatex\ 2$

= ppm Dissolved Oxygen

$BOD5\ (mg/L)\ =\ DOinitial - DOfinal$

3.5.14. Determination of chemical oxygen demand

Chemical Oxygen Demand is a measure of the amount of oxygen required for complete oxidation of organic matter to carbon (IV) oxide and water. The determination was achieved by using strong oxidizing agents under acidic conditions.

Reagent preparation: i) 4.8 M H_2SO_4: 250 mL H_2SO_4 was measured and 750 mL of distilled water was added to it (ii) Ammonium oxalate (0.0125 M): 0.888l g of pure ammonium oxalate was dissolved in 200 mL of distilled water and made up to 1 litre (iii) Potassium permanganate (0.0125 M): 0.4 g of Potassium permanganate ($KMNO_4$) was dissolved in 1 litre of distilled water.

Procedure: Sample of 100 mL was transferred into a flask. 10 mL of 4.8 M H_2SO_4 was added with 10 mL of 0.0125 M Potassium permanganate added and boiled in a water bath for about 30 minutes after which 10 mL of ammonium oxalate was added and titrated hot with Potassium permanganate to its pink colouration and the volume of potassium permanganate used was recorded.

Calculation:

$$\frac{mL\ \ of potassium\ permanganate\ solution\ used\ x\ 100}{mL\ of\ sample}$$

3.5.15 Determination of sulphate

Sulphate content in water sample was measured by adding sulfa ver 4 pillow in 25 mL of water sample followed by vigorous shaking to obtain a uniform mixture which was allowed five minutes for reaction to take place. A spectrophotometer was set and run at a wavelength of 450 nm and blanks were used for calibration and quality check.

3.5.16. Determination of nitrate

The program for the nitrate determination was entered and the wavelength set at 500 nm. A 25 mL sample cell was filled with the sample; bromine water was added in drops with the development of yellow colour, followed by a drop of phenol solution to produce a colorless solution. A nitra ver 5 nitrate powder pillow was added and the cell stopper put in place. The cell was shaken vigorously for one minute and then allowed to stand for five minutes to complete the reaction. Another cell was filled with 25-mL sample but without addition of the nitra ver 5 nitrate reagent, placed in the cell compartment and used to zero the instrument (nitrate in the untreated sample was not detected). The prepared sample was then placed in the cell compartment and the concentration of the nitrate read in mg/L NO_3-N.

3.5.17 Determination of Ammonia

It was measured spectroscopically at 425 nm by using a color complex Nessler's reagent. The conditions of reaction are alkaline and cause severe interference hardness in water.

3.5.18 Determination of phosphate

Phosphate content in water samples was measured by adding phos ver 3 phosphate reagent pillow in 25 mL of water sample followed by vigorous shaking to obtain a uniform mixture which was allow five minutes for reaction to take place. A spectrophotometer was set and run at a wavelength of 880 nm and blanks were used for calibration and quality check.

3.5.19 Determination of heavy metals

5 mL of 1 M concentrated Hydrochloric acid was added to the water sample per litre. The sample was agitated with the acid so that it can mix thoroughly. 100 mL of the acidified sample was measured into a 250 mL conical flask. 5 mL concentrated HCl was added and heated on a hot plate at 60^oC for 15 minutes. It was removed from heating, cooled to about $45\text{-}50^oC$ and filter crucible into a clean filter flask. The filter was rinsed with minimum amount of distilled water. The filtrate was transferred to a 100 mL volumetric

flask, and 5 mL distilled water was used to rinse the remaining substance which was added to the filtrate in the volumetric flask. The filtrate was diluted to 100 mL mark and agitated to mix very well. Stock and standard metal solutions were prepared. An aliquot of the filtrate was taken. The appropriate hollow cathode lamp was obtained. The Flame Atomic Absorption Spectrophotometer was set to the appropriate wavelength and then determines the concentration of the metal of interest on the instrument.

3.5.20 Determination of organic compounds in water samples

Organic Compounds was determined using extraction by hexane and separation via gas chromatography. The industrial and surface water samples were filtered through a membrane filter with 0.45 nm pore size before extraction procedures. Water sample of 100 mL was transferred into a separating funnel and 100 mL of organic solvent (50 mL: 50 mL - hexane: dichloromethane) added and the mixture separated for 45minutes by thorough shaking, afterwards the extract was poured into beaker and left for few minutes to evaporate then the remaining extract filtered using cotton wool as a separating medium in a pasture pipette and anhydrous Sodium tetraoxosulphate (VI) Na_2SO_4 in excess was added to absorb the remaining water in the sample and this was totaled into a vial bottle up to 2 mL ready for Gas Chromatography analysis.

3.6 Sediment analysis for heavy metals

Air-dried sediment (0.15-0.20 mm) was weighed at 0.5-1.0 g into a clean 100 mL Teflon beaker and wet with 5 mL distilled water. Conc. $HClO_4$ acid of 2 mL was added with 12 mL conc. HF acid and heated to near dryness, 8 mL conc. HF acid was added and heated to near dryness followed by 2 mL conc. $HClO_4$ acid added and 5 mL of distilled water and heated to near dryness. The remaining residue was dissolved in 8 mL conc. HCl acid and 20 mL distilled water was added, also make up to 100 mL volume and store in polyethylene bottles. Heavy metals were determined with the spectrophotometer at various different wavelengths.

3.6.1 Sediment analysis for organic compounds

Organic Compound was determined using Hexane and Dichloromethane with separation via Gas chromatography. 10 g of the sediment sample was weighed into the separating funnel and 25 mL of dichloromethane was added and the mixture separate for 20 minutes by thorough shaking, afterwards the extract was transferred into another separating funnel and 75 mL of dichloromethane added for 20 minutes at three consecutive times until an aliquot of the sample, was obtained, afterwards the extract was poured into a beaker and left for few minutes to evaporate in a water bath to dryness and hexane was used to reconstitute the sample. Then the remaining extract was filtered using cotton wool as a separating medium in a pasture pipette and anhydrous Na_2SO_4 in excess was added to absorb any unwanted substance in the sample and concentrated to 2 mL vial glass bottles ready for Gas Chromatography analysis.

3.7 QUALITY ASSURANCE MEASURES

This is a set of operating principles undertaken during sample collection, analysis and calculation to ensure that accurate reproducible and reliable results were obtained.

Analysis

1. All refrigerated samples were allowed to attain laboratory temperatures before analysis was carried out.
2. All apparatus was properly washed with acid water rinsed with deionised water and dried after use.
3. Beakers used for solid determination were weighed to constant weight.
4. Replicate analysis was carried out to ensure reliable and reproducible results.

Calculations

1. Readings for analysis were carefully checked before recording
2. Appropriate significant figures were used for calculation.

CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Characteristics of the industrial effluent

The pollution load in the industrial effluents on other environmental matrix (surface water, sediment and groundwater) of Ilorin environs were evaluated, the samples were analysed for various physicochemical parameters and the results were compared with values of National Environmental Standards and Regulations Enforcement Agency (NESREA). The results obtained on characteristics of effluents are presented in table 4.1a to 4.1c and discussed.

4.1.1 pH

The Hydrogen ion concentration (pH) of the effluent samples from all the four sampling sites was in the range of 8.2-8.4 with mean of 8.3±0.08 for EW-GS-1, EW-TP-2 recorded a range of 6.5-6.8 and mean of 6.7±0.18 while,EW-KC-3 and EW-FB-4 recorded 6.3-6.8(6.60±0.18) and 4.80-6.20 (5.5±0.75) respectively (table 4.1a). Mean values of 7.0±0.14 and 6.5±0.28 were recorded in the dry and rainy seasons respectively. The effluents of EW-FB-4 had lowest pH, while EW-GS-1 had highest pH. Comparing with NESREA standard the pH value in the effluent of EW-FB-4 was below the permissible limit and may adversely affect the aquatic life due to its high acidic nature. These results are in line with the findings of (Chowdhury *et al*., 2013) and (Butterworth *et al*., 2010).

4.1.2 Temperature

Temperature is an important indicator of water quality with regards to survival of aquatic organisms. The effluents temperature depends on the process of production in the industry. The temperature values of various industrial effluents ranged from 23-29^{o}C for EW-GS-1 with mean of 25.6±2.87 (Table 4.1). EW-TP-2 ranged from 24-28.5^{o}C with a mean value of 26.3±2.33 (Table4.1a). EW-KC-3 ranged from 25-27^{o}C with a mean value of 25.9±0.85 (table4.1a) while EW-FB-4 ranged from 23.5-27.5^{o}C with a mean value of 25.5±2.04 (table4.1a). The highest value was found in the effluent of EW-GS-1. The mean temperatures for dry and rainy seasons were between 27.5±0.71 and 24.1±0.71 respectively (figure 4.1). The temperature values in all the effluents sampled were within the permissible limits of NESREA Standard which is <40. These results are supported by the recent work of (Chowdhury *et al*., 2013). EW-TP-2reveals high temperature in the effluents causing thermal pollution (Roberts *et al*., 2007) due to the usage of water for steam production and cooling processes.

4.1.3 Turbidity

Turbidity had between the value of 10.5-13.5 NTU with mean of 12.1±1.38 for EW-GS-1; 8.0-10.5 NTU with mean of 9.3±1.04 for EW-TP-2; 13.0-17.5 NTU with mean value of 15.3±2.10 for EW-KC-3 while EW-FB-4 had 6.0-8.6 NTU with mean of 7.5±1.25; dry season recorded 11.1±1.41 and 10.95±1.13 for rainy season. The highest mean value was recorded at EW-KC-3, which is far above the recommended NESREA standard of 5 NTU for effluent in industrial companies. The lowest mean was recorded at EW-FB-4 and it is above the recommended standard.

4.1.4 Colour

Colour had between the value of 13.0-15.0 Hu with a mean value of 14.0±0.81 for EW-GS-1; 13.0-25.0 Hu with mean of 19.5±6.40 for EW-TP-2; 10.0-15.0 Hu with mean of 12.5±2.45 for EW-KC-3 while EW-FB-4 had 9.0 – 14.0 Hu with mean of 11.5±2.38 (table 4.1a). Dry season recorded 13.0±4.24 and 15.5±1.41 for rainy season (figure 4.1). The highest mean value was recorded by site EW-TP-2 which was above the recommended value of NESREA standard of 15 Hu and the lowest mean value was at EW-FB-4, which does not exceed the permissible level.

4.1.5 Conductivity

Electrical conductivity had between 100.67 – 103.26 µs/cm with mean of 102.21±1.27 for EW-GS-1; 89.04 – 97.17 µs/cm with mean of 93.32±4.94 for EW-TP-2; 98.75 – 106.43 µs/cm with mean of 102.35±4.17 for EW-KC-3 and 101.76 – 107.65 µs/cm with mean of 104.95±3.13 for site EW-FB-4 (table 4.1a); dry season had mean of 101.74±2.70 and rainy season had 97.68±0.01. The highest mean value was recorded at sampling site EW-FB-4 and the lowest mean at EW-TP-2.

4.1.6 Total hardness, Magnesium hardness and Calcium hardness.

Total hardness had between 52.0-56.0 mg/L (54.25±1.71) for sampling EW-GS-1; EW-TP-2 had 48.0 -54.0 mg/L (50.25±2.75); 40.0-50.0 mg/l (44.75±4.99) for site EW-KC-3 and EW-FB-4 ranged between 48.0-52.0 mg/L (50.25±1.71) while dry season had 49.0±0.0 and rainy season 51.0±5.66. The highest mean value was recorded at site EW-GS-1(table 4.1b) with the lowest mean at EW-KC-3 but all were below the WHO standard value of 200 mg/L.

Magnesium hardness had between 20.0-24.0 mg/L (21.0±2.0) for sampling site EW-GS-1; EW-TP-2 had a range of 24.0 mg/L (24.0±0.0); 16.0 – 24.0 mg/L (18.5±4.12) for EW-KC-3 while EW-FB-4 ranged between 16.0-20.0 mg/L (18.0±2.31). Dry season recorded mean of 19.25±1.41 and rainy season 22.5±2.83.

Calcium hardness had between 30.0-36.0 mg/L (33.25±2.75) for EW-GS-1; EW-TP-2 had a range of 24.0-30.0 mg/L (26.75±2.75); 23.0-26.0 mg/L (24.25±1.26) for EW-KC-3 and EW-FB-4 ranged between 28.0-36.0 mg/L (32.25±3.86). Dry season had 29.75±1.41 and rainy season 28.5±2.83 values respectively.

4.1.7 Total Solid, Total Dissolved Solid and Suspended Solid

Total Solid (TS) which recorded values between the range of 386.0-402.0 mg/L (394±8.16) for EW-GS-1; 294.0 – 306.0 mg/L (299.75±6.13) for EW-TP-2; 326.0 – 366.0 mg/L (345.75±22.2) for EW-KC-3 and EW-FB-4 ranged between 308.0 – 326.0 mg/L (316.75±9.57) (table 4.1b); Dry season recorded mean value of 349.0±5.66 while rainy season recorded 329.13±3.54. The results for TS are below the NESREA permissible limit of 500 mg/L.

Total Dissolved Solid (TDS) recorded values between the ranges of 337.0 – 344.0 mg/L (340.25±3.3) for EW-GS-1; 234.0 – 237.0 mg/L (235.5±1.29) for EW-TP-2; 256.0 – 282.0 mg/L (269±14.4) for EW-KC-3 while EW-FB-4 recorded range of 261.0±4.76 (table 4.1b); The values were within the NESREA standard of 500 mg/L. Dry season recorded a mean of 281.5±0.00 and rainy season mean of 271.4±2.12 was recorded.

Table 4.1a: Concentrations (mean±SD) of physicochemical parameters for industrial effluents (February 2013-April 2015).

Sample Code	pH	Temp. (^oC)	Turbd.(NTU)	Colour (Hu)	Cond. (µS/cm)
EW-GS-1	8.30±0.08	25.60±2.87	12.10±1.38	14.00±0.81	102.21±1.21
EW-TP-2	6.70±0.18	26.30±2.33	9.30±1.04	19.50±6.40	93.32±4.94
EW-KC-3	6.60±0.18	25.90±0.85	15.30±2.10	12.00±2.45	102.35±4.17
EW-FB-4	5.50±0.75	25.50±2.04	7.50±1.25	11.50±2.38	104.95±3.13
NESREA	6.5-9.5	<40	5	15	NS
RANGE	5.50-8.30	25.50-26.30	9.30-15.30	11.50-19.50	93.32-104.95

Temp. = Temperature; Turbd. = Turbidity; Cond. = Conductivity; NS = Not Stated

Suspended solid had between 48.0 – 60.0 mg/L (53.75±5.32) for EW-GS-1; EW-TP-2 ranged from 60.0 – 69.0 mg/L (64.25±4.92); 70.0 – 85.0 mg/L (76.75±7.89) for EW-KC-3 and 51.0 – 60.0 mg/L (55.75±4.92) was recorded for EW-FB-4 (table 4.1b); Dry season recorded mean of 67.5±5.66 while rainy season mean of 57.75±1.41.

4.1.8 Alkalinity

Alkalinity had between 130.0-140.0 mg/L with mean of 135.25±4.27 for EW-GS-1; 50.0-60.0 mg/L with mean of 55.0±4.08 for EW-TP-2; 50.0-55.0 mg/L with mean of 52.5±2.89 for EW-KC-3 and 40.0-55.0 mg/L with mean of 46.75±5.35 for EW-FB-4 (table 4.1c); dry season had mean of 74.88±6.36 while rainy season had mean of 69.88±6.36. The highest alkalinity value was recorded at site EW-GS-1 and the lowest value recorded at site EW-FB-4 but the values do not exceed the NESREA standard (150 mg/L) for effluent discharge in to surface water samples.

4.1.9 Dissolved Oxygen, Biochemical Oxygen Demand and Chemical Oxygen Demand

Dissolved Oxygen (DO) had between the value of 4.8 – 5.0 mg/L (4.9±0.11) for EW-GS-1; 3.8 – 5.6 mg/L (4.34±0.83) for EW-TP-2; 3.4 – 3.6 mg/L (3.45±0.1) for EW-KC-3 while EW-FB-4 had a range of 7.2 – 7.2 mg/L (7.2±0.00) (figure 4.1c); Dry season recorded 4.88±0.14 and 5.08±0.99 for rainy season. The DO values are above the NESREA standard (4.0 mg/L) for all sites except EW-TP-2. Biochemical Oxygen Demand (BOD) had between the value of 3.6 – 3.8 mg/L (3.7±0.11) for EW-GS-1; 2.8 - 3.8 mg/L (3.25±0.41) for EW-TP-2; 2.8 - 3.0 mg/L (2.85±0.1) for EW-KC-3 while EW-FB-4 had a range of 3.6 – 3.8 mg/L (3.65±0.1) (figure 4.1c); dry season recorded 3.35±0.00 and 3.38±0.42 for rainy season. Chemical Oxygen Demand (COD) had between the value of 5.8 – 6.5 mg/L (6.15±0.35) for EW-GS-1; 6.2 7.4 mg/L (6.8±0.64) for EW-TP-2; 5.6 – 6.5 mg/l (6.05±0.47) for EW-KC-3 and EW-FB-4 recorded a range of 4.6 – 6.9 mg/l (5.75±1.27) (table 4.1c); Dry season recorded 6.03±0.14 and 6.35±0.28 for rainy season. The BOD and COD results for the sampling sites are within the NESREA standards of 30 and 60 mg/L respectively.

4.1.10 Nutrient loading in effluent samples

Sulphate ranged from 23.5 - 25.0 mg/L (24.13±0.63) for EW-GS-1; 15.0 – 23.5 mg/L (19.13±4.50) for EW-TP-2; 18.5 – 21.5 mg/L (20.0±1.47) for EW-KC-3; 38.0 – 42.0 mg/L (39.88±1.93) for EW-FB-4 (table 4.2) while 25.63±10.43 and 25.94±7.88 were recorded for arid and wet periods respectively (figure 4.2). Nitrate values for EW-GS-1 ranged from 2.6 – 3.3 mg/L (2.95±0.35); EW-TP-2 had between 2.7 – 3.7 mg/L (3.2±0.52); EW—KC-3 had between 3.5 – 8.5 mg/L (5.78±2.6); EW-FB-4 had between 2.4 – 2.8 mg/L (2.6±0.18) as presented in table 4.2 while mean of 3.15±0.49 and 4.11±2.38 was obtained for dry and rainy seasons respectively (figure 4.2). Ammonia value of between 0.004 – 0.008 mg/L (0.006±0.002) for EW-GS-1; EW-TP-2 had between 0.003 – 0.008 mg/L (0.005±0.002); EW-KC-3 had between 0.012 – 0.016 mg/L (0.014±0.002) and EW-FB-4 had between 0.00 – 0.00 mg/L (0.00±0.00); while both dry and rainy season had 0.007±0.005 and 0.006±0.004 respectively. Phosphate ranged between the value of 0.5 – 0.7 mg/L (0.6±0.08) for EW-GS-1; 0.9 – 1.2 mg/L (1.05±0.13) for EW-TP-2; 0.25 – 0.5 mg/L (0.36±0.11) for EW-KC-3; 0.5 – 0.7 mg/L (0.6±0.008) for EW-FB-4; while dry and rainy season had 0.68±0.30 and 0.63±0.26 respectively. All the values for sulphate, nitrate, ammonia and phosphate are within NESREA permissible limits of 250, 10, 0.3 and 3.5 mg/L respectively.

Table 4.1b: Concentrations (mean±SD) in mg/L of physicochemical parameters loadings of Asa River water quality (February 2013-April 2015).

Sample Code	TH	CaH	TS	TDS	SS
EW-GS-1	54.25±1.71	33.25±2.75	394.00±8.16	340.25±3.3	53.75±5.32
EW-TP-2	50.75±2.75	26.75±2.73	299.75±6.13	235.50±1.29	64.25±4.92
EW-KC-3	44.75±4.99	24.25±1.26	345.75±22.2	269.00±14.4	76.75±7.89
EW-FB-4	50.25±1.71	32.25±3.86	316.75±9.57	261.00±4.76	55.75±4.92
NESREA	NS	NS	500	500	25
RANGE	44.75-54.25	24.25-33.25	299.75-394.00	235.50-340.25	53.75-76.75

TH = Total Hardness; CaH = Calcium Hardness; TS = Total Solids; TDS = Total Dissolved Solids; SS = Suspended Solids; NS = Not Stated

Table 4.1c: Concentrations (mean±SD) in mg/L of physicochemical parameters loadings of Asa River water quality (February 2013-April 2015).

Sample Code	ALK	DO	BOD	COD	BOD/COD ratio
EW-GS-1	135.25±4.27	4.90±0.11	3.70±0.11	6.15±0.35	0.60
EW-TP-2	55.00±4.08	4.34±0.83	3.25±0.41	6.80±0.74	0.48
EW-KC-3	52.50±2.89	3.45±0.10	2.85±0.41	6.05±0.47	0.47
EW-FB-4	46.75±5.35	7.20±0.00	3.65±0.10	5.75±1.27	0.63
NESREA	150	4	50	90	
RANGE	46.75-135.25	3.45-7.20	2.85-3.70	5.75-6.80	

ALK = Alkalinity; DO = Dissolved Oxygen; BOD = Biochemical Oxygen Demand; COD = Chemical Oxygen Demand; NS = Not Stated

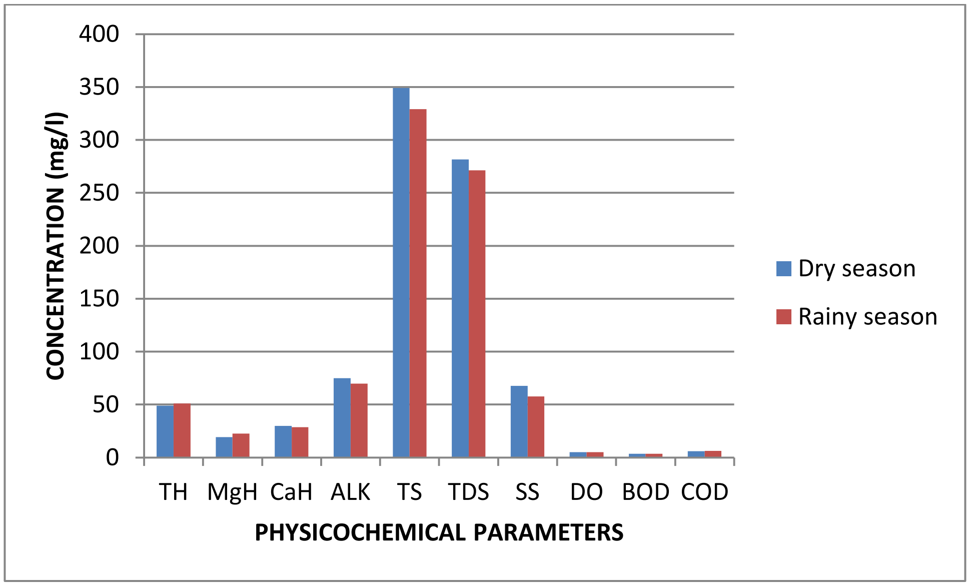


Figure 4.1: Seasonal variation in the concentrations of physicochemical parameters of effluent water samples.

4.1.11 Chloride

Chloride value of between 27.5 – 31.5 mg/L (29.5±1.83) was obtained for EW-GS-1; EW-TP-2 had between 28.0 – 36.0 mg/L (32.25±9.83); EW-KC-3 had between 13.0 – 19.0 mg/L (15.88±3.07) and EW-FB-4 had between 9.0 – 11.0 mg/L (10.3±1.01) as presented in table 4.2; while both rainy and dry season had 21.65±7.88 and 22.31±11.9 respectively (figure 4.2). These values are within NESREA standard of 250 mg/L.

4.1.12 Metals and heavy metals

Metals and heavy metals at the four sampling stations showed varied degree of concentrations; Calcium had between the values of 12.6 – 14.4 mg/L (13.5±0.93) for EW-GS-1; 9.5 – 11.4 mg/L (10.43±1.01) for EW-TP-2; 9.5 – 9.8 mg/L (9.63±0.13) for EW-KC-3; 11.2 – 14.4 mg/L (12.8±1.79) for EW-FB-4 (table 4.3); while dry and wet season had 11.93±2.53 and 11.23±1.14 respectively (figure 4.3).

Magnesium had between the values of 7.5 – 7.8 mg/L (7.63±0.13) for EW-GS-1; 6.8 – 7.0 mg/L (6.88±0.09) for EW-TP-2; 5.1-8.6 mg/L (6.83±1.94) for EW-KC-3; 6.7 – 7.5 mg/L (7.1±0.41) for EW-FB-4; while dry and wet season had 6.58±0.94 and 7.64±0.62 respectively.

Sodium had between 2.3 and 2.4 mg/L (2.45±0.13) for EW-GS-1; 2.0-2.3 mg/L (2.18±0.14) for EW-TP-2; 1.8-2.3 mg/L (2.05±0.24) for EW-KC-3; 2.1-2.6 mg/L (2.35±0.24) for EW-FB-4; while arid and wet periods had 2.25±0.1 and 2.26±0.33 respectively.

Table 4.2: Concentrations (mean±SD) in mg/L of nutrient loadings in industrial effluents

Sample Code	SO_4^{2-}	NO_3^-	NH_3	PO_4^{3-}	Cl^-
EW-GS-1	24.13±0.63	2.95±0.35	0.01±0.00	0.60±0.08	29.50±1.83
EW-TP-2	19.13±4.50	3.20±0.52	0.01±0.00	1.05±0.13	32.25±9.83
EW-KC-3	20.00±1.47	5.78±2.60	0.014±0.002	0.36±0.11	15.88±3.07
EW-FB-4	39.88±1.93	2.60±0.18	0.00±0.00	0.60±0.008	10.30±1.01
NESREA	250	10	0.3	3.5	250
RANGE	20.00-39.88	2.60-5.78	0.00-0.01	0.36-1.05	10.30-32.25

SO_4^{2-} = Sulphate ion; NO_3^-= Nitrate ion; NH_3 = Ammonia; PO_4^{3-} = Phosphate ion; Cl^- = Chloride ion

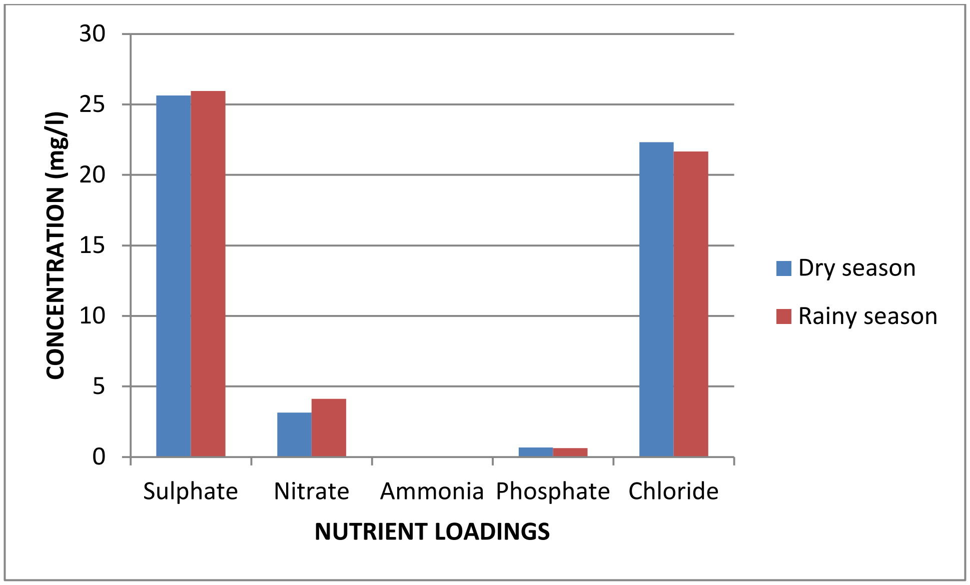


Figure 4.2: Seasonal variation in the concentrations of nutrient loading parameters of effluent water samples.

Iron had 2.3-2.7 mg/L (2.5±0.18) for EW-GS-10.7-1.3 mg/L (1.0±0.29) for EW-TP-2; 0.5-0.85 mg/L (0.68±0.27) for EW-KC-3; 2.4-2.7 mg/L (2.55±0.13) for EW-EB-4 (table 4.3); while dry and rainy season had 1.65±1.07 and 1.71±0.76 respectively (figure 4.3).

Copper had between 0.3-0.6 mg/L (0.45±0.13) for EW-GS-1; 0.25-0.35 mg/L (0.28±0.06) for EW-TP-2; 0.2-0.55 mg/L (0.38±18) for EW-KC-3; 0.3-0.7 mg/L (0.5±0.18) for EW-FB-4; while arid and wet period had 0.29±0.08 and 0.51±0.15 respectively.

Zinc had between 3.7-5.0 mg/L (4.13±0.60) for EW-GS-1; 2.3-2.9 mg/l (2.6±0.29) for EW-TP-2; 1.8-2.5 mg/L (2.15±0.35) for EW-KC-3, 2.7-.4.0 mg/L (3.13±0.60) for EW-FB-4; while both dry and wet period had 3.33±0.9 and 2.68±0.75 respectively.

Cadmium had between the values of 0.002-0.004 mg/L (0.003±0.01) for EW-GS-1, 0.004-0.006 mg/L (0.005±0.001) for EW-TP-2; 0.005-0.006 mg/L (0.006±0.001) for EW-KC-3 and 0.00-0.00 mg/L (0.00±0.00) for EW-FB-4; while both arid and wet period recorded 0.004±0.001 and 0.003±0.002 respectively.

Lead had 0.6-0.8 mg/L (0.7±0.08 mg/L) for EW-GS-1; 0.3-0.6 mg/L (0.45±0.13) for EW-TP-2; 0.01-0.02 mg/L (0.016±0.005) for EW-KC-3 and 1.1-1.8 mg/L (1.45±0.35) for EW-FB-4; while arid and wet periods have values of 0.57±0.46 and 0.74±0.68 respectively.
Chromium had 0.32-0.6 mg/L (0.44±0.13) for EW-GS-1; 0.15-0.25 mg/L (0.19±0.44) for EW-TP-2; 0.15-0.20 mg/L (0.18±0.02) for EW-KC-3 and 0.22-0.40 mg/L (0.31±0.08) for EW-FB-4 (table 4.3); while arid and wet periods recorded 0.33±0.17 (figure 4.3).

The physicochemical parameters, nutrient loading with metals and heavy metals results of the effluent discharge was not dependent on season but on what was produced at the time of sampling which may vary at one particular period to the other. For instance, pharmaceutical company may produce paracetamol drug and syrup produced today while another time B-complex might be produced. Also series of deviation in values from the National Environmental Standards and Regulations Enforcement Agency’s standard (NESREA) was observed; temperature, pH, turbidity, electrical conductivity, total hardness, biochemical oxygen demand, sulphate, nitrate, sodium, calcium, magnesium, iron and cadmium were found within the permissible limit for effluent discharge into all categories of water while total solids, dissolved oxygen, chloride, lead, copper, zinc and chromium were found to exceed the permissible limits (Imam *et al*., 2008).

4.2 Asa River water quality in relation to industrial effluent discharge

In this study, the effect of the discharge of effluent into river Asa on the quality of surface water within the immediate catchment of the river was investigated. Water samples from immediate stream of point of discharge from the industry downstream were investigated. Water samples from surface streams were subjected to physicochemical investigations to ascertain the effect of the effluent on the quality of surface water downstream.

Table 4.3: Concentrations (mean±SD) in mg/L of metals and heavy metals loadings in industrial effluents

Sample Code	Ca	Mg	Na	Fe	Cu	Zn	Cd	Pb	Cr
EW-GS-1	13.50±0.93	7.63±0.13	2.45±0.13	2.50±0.18	0.45±0.13	4.13±0.60	0.00±0.00	0.70±0.08	0.44±0.13
EW-TP-2	10.43±1.01	6.88±0.09	2.18±0.14	1.00±0.29	0.28±0.06	2.60±0.25	0.01±0.00	0.45±0.13	0.19±0.04
EW-KC-3	9.63±0.13	6.83±1.94	2.05±0.24	0.68±0.27	0.38±0.18	2.15±0.35	0.01±0.00	0.02±0.01	0.18±0.02
EW-FB-4	12.80±1.79	7.10±0.41	2.35±0.24	2.55±0.13	0.50±0.18	3.13±0.60	0.00±0.00	1.45±0.35	0.31±0.08
NESREA	------	-----	200	0.5	1.0	2.0	0.1	0.1	0.1
RANGE	9.63-13.50	6.83-7.63	2.05-2.45	0.68-2.55	0.28-0.50	2.15-4.13	0.00-0.01	0.02-1.45	0.18-0.44

Ca = Calcium; Mg = Magnesium; Na = Sodium; Fe = Iron; Cu= Copper; NS = Not Stated

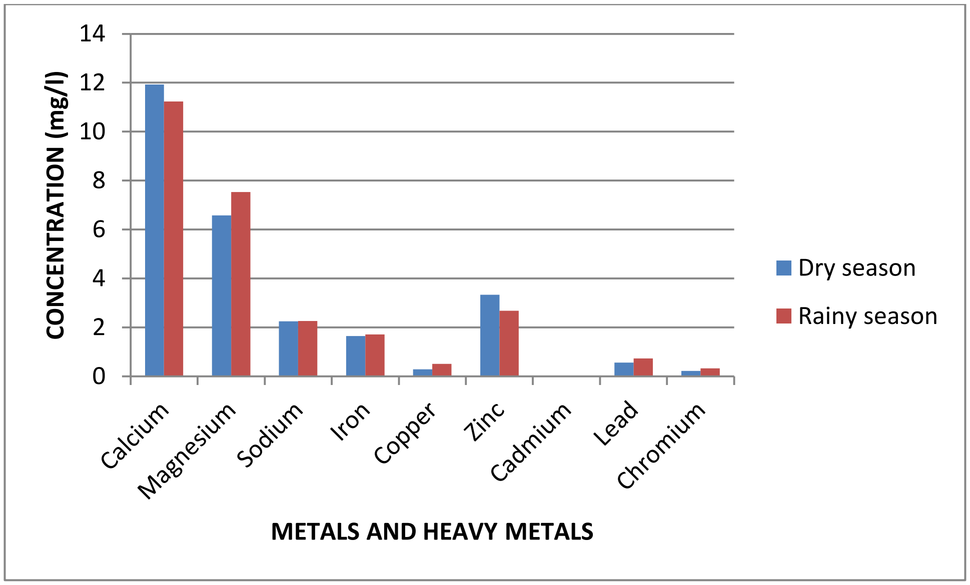


Figure 4.3: Seasonal variation in the concentrations of metals and heavy metals parameters of effluent water samples.

4.2.1 Surface water quality assessment

Surface water quality assessment provides the base line information on water safety. Since water quality in any source of water and at the point of use, can change with time and other factors, continuous monitoring of water is essential. The physicochemical parameters results obtained from this study is discussed below: Surface water samples from twenty-six sampling sites were analysed and the results of the mean values for two years are presented in tables and figures for physical, chemical, metals and heavy metals.

4.2.2 pH

The Hydrogen ion concentration (pH) of the surface water samples from all the twenty-six sampling sites are described in table 4.4a as follows: The surface water of site FB/SW2 recorded the lowest pH which was in conformity with was found in the effluent sample while site KC-GS-TP/SW had the highest pH. The pH values are expressed as the negative logarithm of Hydrogen ion concentration. For acidic water, pH varies from 0 to 7 and alkaline water pH varies from 7 to 14. It determines the solubility of chemical nature of most substances. Medium values are favourable for biological production. The pH values recorded in this work are indicative of good water quality which was within the acceptable limits (NIS 2007; WHO 2011). The high values of pH (8.25±0.13 and 8.05±0.24) recorded at sites KC-GS-TP/SW and KC-GS-TP-AS/SW respectively reveal in the appendix could have been due to the influx of industrial effluent and the synergist effects of these effluents on the water bodies. A slight alkaline pH value recorded may be due to the alkaline treatment given to the effluents before discharging into the river. (Eletta *et al*., 2005), stated that influx of effluent in alkaline form into water could affect the pH. The fluctuations observed in the surface pH indicated the buffering capacity of total alkalinity, high water volume and greater water retentions may have been the reason why pH was in neutral or moderate alkaline medium during the rainy season and for most part of this study. Using the pH as a water quality index, Asa River has good water quality with the mean pH of 7.0, 7.53 for sites AS3/SW3, AS4/SW4 and KC-GS-TP/SW respectively; since most natural waters have pH between 6.5 and 8.5 (Tepe *et al*., 2005) and such pH values will also allow the survival of aquatic organisms and its use as drinking water.

4.2.3 Colour

The colour of water samples are revealed in table 4.4a as follows: Bhatia, (2009) stated that pure water is colourless. Thus, any water with a characteristic colour insinuates contamination. The highest value for colour was observed has 26.14 Hu during the rainy season and 19.45 Hu during dry season (Appendix table 13). The maximum permissible value for colour is 15 Hu (NIS, 2007) has been exceeded by most sites in this study. Colour of surface water has been affected in both seasons due to dissolved salts, coloured rainwater as well as other contaminants. Colour could also be due to the presence of decaying organic matter, iron compounds, leaching of organic materials into surface waters, wastewater of industrial processes, eutrophication and suspended solids. Asa River during both dry and rainy seasons respectively was 100% greater than the recommended maximum permissible value for colour. These results are in line with the findings of (Dami *et al*., 2012).

4.2.4 Turbidity

Turbidity results are described in table 4.4a for the discharge points, point of entry into Asa River, upstream and downstream. Sampling site KC-GS-TP-AS/SW has the highest value followed by AS6/SW6, AS4/SW4, AS1/SW1, KC-GS-TP/SW, FB/SW, KC/SW, GS/SW and CONTROL 1/2, while site KC-GS/SW has the minimum value. The highest value recorded by sampling site KC-GS-TP-AS/SW may be linked with the land use within these steep areas dominated by intensive small scale farming activities where majorly food crops and vegetables are grown. The area occur in the flood plains with very high human and livestock population density coupled with heavy industrial effluent discharges at sampling site KC/SW1 which flows down to other aforementioned sampling sites.

4.2.5 Conductivity

Conductivity is a numerical expression of the ability of water to carry on electric current, which in ionic strength as conductivity is a measure of total ions. The ionic strength of a sample depends on the ionization of solutes and other substances dissolved in it. The electrical conductivity of the twenty-six sampling sites in this study was found to be high at the point of discharge site KC/SW1 and KC-GS-TP/SW3 (Appendix table 7 and 9) of industrial effluents to downstream (AS4/SW4, AS5/SW5, AS6/SW6) compared to upstream (AS1/SW1, AS2/SW2 and control 2). These results are in line with the findings of (Ogundiran and Fawole, 2014).

Low electrical conductivity experienced at control 2 could be due to nature of soft water; while high conductivities may be due to high aggregation of total solids recorded in sites KC/SW1, KC-GS-TP/SW3, AS4/SW4, AS5/SW5, and AS6/SW6 (table 4.4a) and this observation conformed with the report of (Mustapha, 2008) and (Adewoye, 2007) on Oyun River and Asa River respectively. Sampling site CONTROL2/SW which is less impacted sub-catchment had lower concentrations as compared to sites located in areas with high human activities like agriculture practices and industrial activities (sites KC/SW1, KC-GS-TP/SW3 etc,).

Table 4.4a: Concentrations (mean±SD) of physicochemical parameters at industrial effluents discharge point channels, upstream to downstream of Asa River (February 2013-April 2015).

	Sample Code	pH	Colour (Hu)	Turbidity (NTU)	Cond. (µS/cm)
DP	GS/SW	7.62±0.85	24.87±3.19	15.83±1.92	96.86±6.40
	KC/SW	7.12±0.99	23.20±5.73	16.87±1.55	99.31±7.74
	KC-GS/SW	7.86±0.15	19.33±2.08	13.60±0.57	100.08±0.30
	KC-GS-TP/SW	7.53±0.00	28.53±12.77	19.43±2.21	103.42±1.07
	FB/SW	6.87±0.85	19.83±1.77	18.54±1.06	93.75±6.54
PE	KC-GS-TP-AS	7.53±0.22	30.00±1.63	23.00±8.09	104.23±0.87
	FB-AS	6.90±0.22	19.40±8.56	16.90±5.36	94.80±3.09
US	AS1/SW1	6.90±0.22	20.40±7.18	19.10±5.65	95.62±2.34
	AS2/SW2	7.18±0.10	25.80±0.96	20.40±5.94	99.74±0.23
	AS3/SW3	7.00±0.18	22.00±6.38	20.00±6.38	98.45±3.74
DS	AS4/SW4	7.00±0.18	24.80±7.27	22.80±6.09	101.62±.32
	AS5/SW5	6.98±0.15	22.80±7.27	21.00±0.38	100.67±1.20
	AS6/SW6	6.93±0.33	22.80±6.08	22.80±4.37	99.19±0.86
	CONTROL1/2	7.00±0.11	16.25±10.11	14.75±7.80	84.65±3.46
	NESREA	6.5-8.5	15	5	NS
	WHO PL	6.5-9.5	15	5	100
	RANGE	6.87-7.62	19.33-30.00	13.60-23.00	93.75-103.42

●Cond. = Conductivity; NS = Not Stated; PE = Point of Entry into Asa River; US = Upstream Points; DS = Downstream Points; WHO PL = World Health Organization Permissible Limit.

4.2.6 Total hardness, Magnesium hardness and Calcium hardness

Total hardness and Calcium hardness results are described in table 4.4b for the discharge points, point of entry into Asa River, upstream and downstream. Hardness is most commonly expressed in milligram of Calcium carbonate equivalent per litre. The high value of hardness is mostly due to high value of Calcium and Magnesium in all the sites during the period of investigation. Total hardness in water samples as shown by the analyses have concentrations all within the World Health Organization guide range for surface water both for wet and dry seasons. Total hardness in water samples have a mean and standard deviation of 54.68 mg/L and 26.87 for dry season as against a mean of 54.68 mg/L and standard deviation of 38.18 for wet seasons (figure 4.4b). From the mean and standard deviation, concentrations of total hardness in water are higher in rainy season than dry season. This is obvious due to high standard deviation during the wet season than dry season because of the solvent action of rain water coming in contact with soil and rocks is capable of dissolving Calcium and Magnesium that promote water hardness. Although, water hardness has no harmful effect on human health except that it can react with ordinary soap to form scum, plume solvent, scale formation in boilers and in hot water systems.

4.2.7 Total Solids, Total Dissolved Solid and Suspended Solid

Total Solids, Total Dissolved Solid and Suspended Solid results are described in table 4.4b for the discharge points, point of entry into Asa River, upstream and downstream.

Total suspended solids are the cause of suspended particles into the water body, it influences turbidity and transparency. The high value of total solids recorded in sampling sites AS6/SW6, AS5/SW5 and AS4/SW4 in the dry season compared to that of rainy season may be attributed to low volume of water experienced during the dry season while the dilutions of ionic substances is as a result of large volume of water in the area could be the main reasons for lower level of total solids encountered in the rainy season. In addition, high value of total solids observed in the sites mentioned above during the dry season, could also be as a result of influx of effluents from industrial premises, thereby bringing about increase in the level of conducting ions, electrical conductivities and turbidity of the affected water bodies. It could also be due to siltation, deterioration and heavy precipitation. These observations agreed with the findings of (Okoye *et al.*, 2010) on River Ogunpa and Ona; (Musungu *et al*., 2014) on River Nyando, Lake Victoria Basin in Kenya, (Ayoola and Kuton, 2009) on Lagos Lagoon in Nigeria and (Ogundiran and Fawole, 2014) on Asa River, Nigeria.

Total dissolved solid content in water is a measure for salinity. A large number of salts are found dissolved in natural waters, the common ones are carbonates, bicarbonates, chlorides, sulphates, phosphates and nitrates of Calcium, Magnesium, Sodium, Potassium, Iron and Manganese etc. a high content of dissolved solid elements affect the density of water, influences osmoregulation of freshwater in organisms, reduces solubility of gases (like Oxygen) and utility of water for drinking, irrigational and industrial purposes.

Table 4.4b: Concentrations (mean±SD) in mg/L of physicochemical parameters at industrial effluents discharge point channels, upstream and downstream of Asa River. (February 2013-April 2015).

	Sample Code	TH	CaH	TS	TDS	SS
DP	GS/SW	53.00±3.46	33.42±2.92	368.30±23.26	298.35±30.92	69.93±10.75
	KC/SW	50.17±7.29	31.33±6.43	369.20±23.54	288.60±28.38	80.60±10.35
	KC-GS/SW	56.90±0.12	31.15±0.91	396.08±4.52	317.38±2.32	78.08±1.42
	KC-GS-TP/SW	62.50±0.00	35.03±0.40	415.10±4.65	334.63±1.53	80.53±3.76
	FB/SW	44.75±1.73	24.17±0.76	324.25±52.71	264.08±45.39	60.17±8.01
PE	KC-GS-TP-AS	62.50±2.89	34.80±2.75	439.50±15.02	350.80±11.87	88.80±3.40
	FB-AS	55.00±2.58	31.00±1.15	402.80±44.18	322.8±36.67	80.00±7.62
US	AS1/SW1	55.00±2.58	31.50±1.00	423.00±48.51	333.80±43.00	89.30±5.70
	AS2/SW2	58.80±2.75	33.50±1.91	434.80±25.13	343.80±19.94	91.00±5.48
	AS3/SW3	55.30±2.50	32.00±1.63	439.50±13.02	352.80±9.57	87.00±3.83
DS	AS4/SW4	55.30±2.50	31.00±2.58	452.50±14.46	354.30±15.28	98.30±4.92
	AS5/SW5	55.30±2.50	32.50±1.00	445.00±15.60	353.80±10.72	90.80±5.50
	AS6/SW6	55.30±2.50	31.30±2.99	454.80±16.48	363.80±15.33	91.00±1.15
	CONTROL1/2	41.00±4.55	25.75±3.30	346.75±83.43	290.25±71.30	56.50±25.48
	NESREA	NS	NS	500	500	25
	WHO PL	200	NS	1000	50	>10
	RANGE	44.75-62.50	24.17-35.03	368.30-452.50	264.08-354.30	56.50-98.30

TH = Total Hardness; CaH = Calcium Hardness; TS = Total Solids; TDS = Total Dissolved Solids; SS = Suspended Solids; NS = Not Stated; DP = Discharge points; PE = Point of Entry into Asa River; US = Upstream Points; DS = Downstream Points; WHO PL = World Health Organization Permissible Limit.

4.2.8 Alkalinity

Alkalinity results are described in table 4.4c for the discharge points, point of entry into Asa River, upstream and downstream.

Wide variations were observed in the figures of alkalinity for all the sampling sites except CONTROL1/SW. Site GS/SW1 recorded the widest variation. This shows continuous and cumulative effect of high alkaline content of the waste being discharged into the river. The alkalinity of the river water is essentially due to the presence of bicarbonates. This trend of the alkalinity is reflected in the pH of the water and it is in conformity with the findings of (Adebayo and Adediran, 2005) on Asa River. The national and international water quality standard for total alkalinity is 100 mg/l for (NAFDAC, 2007; SON, 2007 and WHO, 2007). This study reveals that site GS/SW was above national and international set standards.

4.2.9 Dissolved Oxygen, Biochemical Oxygen Demand and Chemical Oxygen Demand

Dissolved Oxygen, Biochemical Oxygen Demand and Chemical Oxygen Demand results are described in table 4.4c for the discharge points, point of entry into Asa River, upstream and downstream.

The DO observed in this study most were higher than the 6.0 mg/l recommended level by (NESREA 2007; NIS 2007). (James *et al*., 2011), also reported that the desired range for the culture of warm water fish is 5 mg/L and above but not more than 12 mg/L. Lower value of DO was also obtained for dry season in this work and this may be due to low level of dilution rate and water volume during dry season with little self-purification process of the pollutants (Ogundiran and Fawole, 2014).

The DO level obtained for sites KC/SW, KC-GS/SW, FB/SW, AS2/SW2 and AS3/SW3 fall below the 10 mg O_2L^{-1} recommended for unpolluted waters (Kirschner *et al*., 2009), but far greater than 6.0 recommended value documented by (NIS, 2007 and WHO, 2011). The continuous influx of industrial discharge into the water might likely support the growth of aquatic weeds and formation of flocks on the surface of the water, hence a reduction in the dissolution of oxygen into water. (Igbinusa and Okoh, 2009) however stressed that the depletion of dissolved oxygen in a water body could be due to common practice of dumping of wastes into such water body which was observed in major sampling sites like Unity and Emir respectively.

The high biochemical oxygen demand recorded in sites KC-GS-TP-AS/SW, AS5/SW5 and AS6/SW6 in the dry season could be as results of accumulation pattern of organic materials due to continuous influx of industrial effluents into the water bodies which may eventually results in reduction of Oxygen content, this observation conformed with the reports of (Olayinka, 2013, Musungu *et al*., 2014, Ayoola and Kuton 2009), and that when organic matter is abnormally high in an aquatic phase, the BOD level reduces and this may eventually disrupt the behavioural responses of the organisms and reduces the fitness of a natural population of fish.

The BOD pattern observed in this work indicate considerable level of nutrients and this conforms with the report of (Wipfli and Baxter, 2010) that rivers with high BOD have high nutrient levels in the water where organisms consumes most of the Oxygen. High amount of BOD recorded during the rainy season at site AS6/SW6can be attributed to increase effect of surface runoff, soil erosion and effluents discharges into these receiving water bodies and this conforms considerably to the submission of (James *et al*., 2011).

All organic compounds with few exceptions can be oxidised by the action of strong oxidizing agents under acidic conditions. The COD determination is a measure of the Oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. During COD determination, Oxygen demand value is useful in specifying toxic condition and presence of biologically resistant substances. It is an important, rapidly measured parameter for industrial wastewater studies and control of waste treatments. COD test is used to measure the load of organic pollutants in the industrial wastewater.

The COD and BOD values both are a measure of the relative oxygen – depletion effect of a waste contaminant. The BOD/COD ratio reveals that effluent discharge into the water bodies are untreated because the ratio values (0.69-0.99) are between (0.3-0.8) for untreated effluents. Both have been widely adopted as a measure of pollution effect. In the present investigation, the average COD values lie between 5.2 from site KC-GS-TP/SW2 to 6.85 of site KC/SW1 (table 4.4c). It was noted that in all the surface water collected from the sampling sites, the COD values are very much higher than 4.0 mg/L, which is the maximum permissible limit according to United States Public Health (USPH) standard. High COD has indirect relation with decrease of DO which together decline life quality of aquatics.

4.2.10 Correlation matrix of physicochemical parameters between effluent and surface water

The table 4.5 reveals the correlation matrix of physicochemical parameter from effluent water obtained at different industrial companies to surface water. 8 is the degree of freedom at 5% significant level with critical table value = 0.632. Total solid (TS) and biochemical oxygen demand (BOD) data (0.51 and 0.59) reveal $r_{cal} < r_{table,}$ therefore null hypothesis Ho is accepted and conclude that these parameters in effluent do not have influence on the surface water while, pH, Colour (Col), Turbidity (Turbd), Conductivity (Cond.), Total Hardness (TH), Alkalinity (ALK) and Chemical Oxygen Demand (COD) (0.78, 1.00[3], 0.90, 0.99 and 0.78) have $r_{cal} > r_{table}$, therefore null hypothesis is rejected and concluded that these parameters in effluent water have significant influence on surface water.

Table 4.4c: Concentrations (mean±SD) in mg/L of physicochemical parameters at industrial effluents discharge points channels, upstream to downstream of Asa River (February 2013-April 2015).

	Sample Code	ALK	DO	BOD	COD	BOD/COD ratio
DP	GS/SW	109.33±44.88	6.38±0.64	4.05±0.85	5.72±0.58	0.71
	KC/SW	82.25±48.30	6.86±0.25	4.29±0.72	6.13±0.85	0.69
	KC-GS/SW	92.48±5.65	6.18±0.89	4.61±0.41	5.80±0.37	0.79
	KC-GS-TP/SW	60.87±0.75	5.57±0.98	4.57±0.68	5.78±0.16	0.79
	FB/SW	70.42±45.76	6.67±0.18	4.22±0.45	5.68±0.21	0.74
PE	KC-GS-TP-AS	65.00±4.08	4.85±0.10	4.00±0.23	6.38±0.33	0.63
	FB-AS	55.00±4.08	5.03±0.22	4.23±0.44	6.10±0.75	0.69
US	AS1/SW1	53.80±4.79	5.33±0.47	4.58±0.39	6.23±0.61	0.73
	AS2/SW2	62.50±3.07	6.10±0.18	5.15±0.13	5.93±0.44	0.87
	AS3/SW3	62.50±3.07	6.35±1.55	5.30±1.29	5.35±0.58	0.99
DS	AS4/SW4	62.50±3.07	4.80±0.63	4.10±0.68	6.20±1.21	0.66
	AS5/SW5	62.50±3.07	4.55±0.30	3.75±0.34	6.65±0.70	0.56
	AS6/SW6	62.50±3.07	4.40±0.28	3.60±0.43	6.15±0.35	0.59
	CONTROL1/2	57.50±6.45	5.90±0.62	4.85±0.38	6.93±0.64	0.69
	WHO PL	100	NS	6	10	
	NESREA	NS	4	50	90	
	RANGE	53.80-109.33	4.40-6.86	3.60-4.61	5.68-6.65	

ALK = Alkalinity; DO = Dissolved Oxygen; BOD = Biochemical Oxygen Demand; COD = Chemical Oxygen Demand; NS = Not Stated;
DP = Discharge Points; PE = Point of Entry into Asa River; US = Upstream Points; DS = Downstream Points; WHO PL = World Health Organization Permissible Limit.

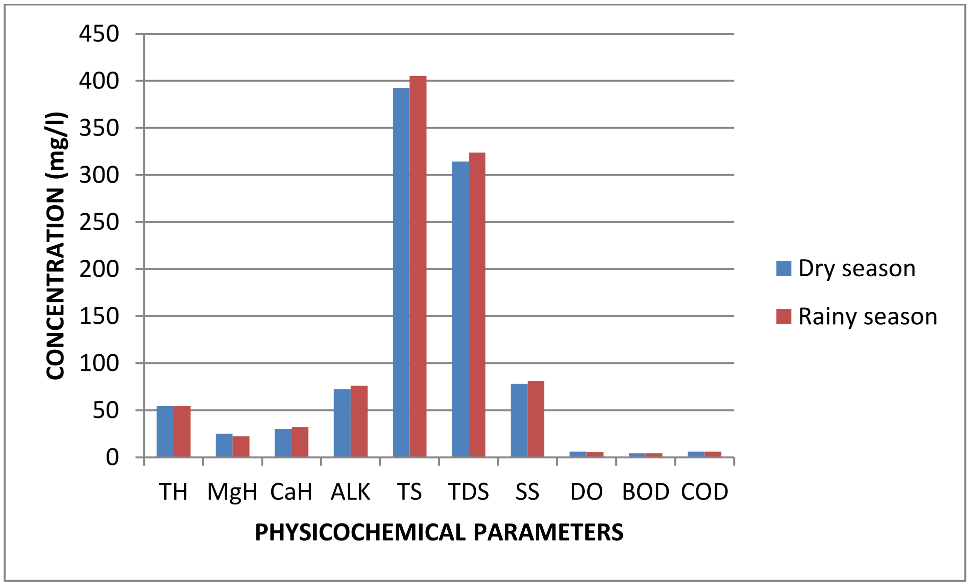


Figure 4.4: Seasonal variation in the concentrations of physicochemical parameters for surface water samples.

Table 4.5: Correlation matrix of physicochemical parameters between effluent and surface water

Parameters	pH	Col.	Turbd.	Cond.	TH	ALK	TS	BOD	COD	
pH	1									
Col.	0.78	1								
Turbd.	1.00	0.78	1							
Cond.	1.00	1.00	0.78	1						
TH	0.90	1.00	1.00	1.00	0.78	1				
ALK	0.99	0.90	1.00	1.00	1.00	0.78	1			
TS	0.51	0.99	0.90	1.00	1.00	1.00	0.78	1		
BOD	0.59	0.51	0.99	0.90	1.00	1.00	1.00	0.78	1	
COD	0.78	0.59	0.51	0.99	0.90	1.00	1.00	1.00	0.78	1

Col. = colour; turbd. = turbidity; cond. = conductivity; TH = total hardness; ALK = Alkalinity; TS = Total Solid; BOD = Biochemical Oxygen Demand; COD = Chemical Oxygen Demand.

4.2.11 Nutrient loading of surface water

Nutrient loading results are described in table 4.6 for the discharge points, point of entry into Asa River, upstream and downstream.

Sulphate is ecologically important for growth of plants and its short supply may inhibit the development of plankton. Sulphur is also very important in protein metabolism. Nitrogen is less soluble in water than Oxygen, but as it's constitutes 78% of the atmosphere, it still account for 65% of the dissolved gases at equilibrium.

Nitrogen is important, as it is a necessary element in the structure of protein, chlorophyll, RNA and DNA. It is essentially required by all living organisms, being a necessary element of biochemical substances.

There was a marked seasonal variation on the nutrients level of the sampling sites with the lowest value at sampling site CONTROL1/SW while sites KC-GS-TP-AS/SW, AS5/SW5, AS6/SW6 etc had higher values. Dry and rainy seasons recorded lower and higher values (figure 4.5) respectively as confirmed by (Ogundiran and Fawole, 2014).

The high concentrations of sulphate, nitrate and chloride could have resulted from leaching and runoff of sulphate fertilizers from nearby farmlands and sulphate rich effluents from nearby industrial premises.

The concentrations of these ions were higher during the rainy season, because the period is usually the peak of agricultural activities around the river area. Probably, this could also have resulted from washing of pens, cow dung, bathing, washing of cars and home appliances with phosphate based detergents and soaps into the water, which could have also caused the high level concentrations of these ions.

These events can lead to eutrophication of the water bodies with subsequent bloom in algae and changes to water quality. (Duncan *et al*., 2012 and Smith *et al*., 2011) reported that non-point source of nutrients inputs from water shed are leading cause of eutrophication and water quality problems while (Becker *et al.*, 2010) implicated sulphate in the eutrophication of water bodies.

Eutrophication was more pronounced in sites GS/SW, FB/SW, AS5/SW5 and AS6/SW6 probably due to its shallowness. (Koiv *et al*., 2011) noted that this could affect water quality by giving rise to unpleasant taste, odor and colour, which affects the dissolution of other gases, most especially dissolved Oxygen as a result of algae blooms. It could also pose a threat to fish population in rivers, because it may destroy food web, decrease biodiversity at higher trophic level (Scheffer *et al*., 2006) leads to disappearance of population and induces changes in yield and species composition (Miranda, 2008).

4.2.12 Correlation matrix of nutrient loading between effluent and surface water

The table 4.7 reveals the correlation matrix of nutrient loading parameter from effluent water obtained at different industrial companies to surface water. 4 is degree of freedom at 5% significant level with critical table value = 0.811. Ammonia and Chloride data (-1.00 and 0.32) reveal $r_{cal} < r_{table,}$ therefore null hypothesis Ho is accepted and conclude that these parameters in effluent do not have influence on the surface water while, sulphate, nitrate and phosphate (1.00[2] and 0.93) have $r_{cal} > r_{table}$, therefore null hypothesis is rejected and concluded that these parameters in effluent water have significant influence on surface water. It was also noted that relationship exists between nitrate and chloride concentrations (appendix graph).

Table 4.6: Concentrations (mean±SD) in mg/L of nutrient loadings in industrial effluents discharge point's channels, upstream to downstream of Asa River(February 2013-April 2015).

	Sample Code	SO_4^{2-}	NO_3^-	NH_3	PO_4^{3-}	Cl^-
DP	GS/SW	24.44±1.63	3.87±0.53	0.04±0.01	0.99±.13	31.87±8.81
	KC/SW	24.57±1.43	4.87±1.26	0.03±0.01	0.90±0.28	29.28±12.28
	KC-GS/SW	22.05±1.32	4.24±0.31	0.03±0.00	0.87±0.04	37.70±1.21
	KC-GS-TP/SW	29.47±1.94	4.93±0.06	0.05±0.01	0.99±0.07	53.77±3.28
	FB/SW	25.00±3.03	2.93±0.19	0.03±0.01	0.65±0.15	28.88±5.45
PE	KC-GS-TP-AS	32.30±6.36	5.40±1.10	0.05±0.00	1.09±0.25	57.30±3.23
	FB-AS	18.10±5.65	3.85±0.81	0.03±0.01	1.10±0.29	18.30±3.75
US	AS1/SW1	19.90±5.36	4.15±0.84	0.04±0.01	1.25±0.35	20.20±4.44
	AS2/SW2	26.10±2.21	4.65±0.58	0.05±0.00	1.25±0.35	22.70±5.20
	AS3/SW3	23.60±8.56	4.40±1.10	0.04±0.00	1.20±0.41	21.80±8.39
DS	AS4/SW4	25.10±10.26	4.65±1.10	0.05±0.01	1.30±0.29	24.30±11.27
	AS5/SW5	24.50±8.95	4.55±0.93	0.05±0.01	1.38±0.49	23.30±9.54
	AS6/SW6	27.30±9.54	5.00±0.87	0.06±0.01	1.58±0.67	24.80±11.27
	CONTROL1/2	18.00±4.08	4.05±0.24	0.05±0.01	0.50±2.54	21.75±3.86
	WHO PL	250	50	0.3	5	250
	NESREA	100	20	0.3	3.5	100
	RANGE	18.10-32.30	2.93-5.40	0.03-0.05	0.50-1.58	18.30-57.30

SO_4^{2-} = Sulphate ion; NO_3^-= Nitrate ion; NH_3 = Ammonia; PO_4^{3-} = Phosphate ion; Cl^- = Chloride ion; DP = Discharge Points; PE = Point of Entry into Asa River; US = Upstream Points; DS = Downstream Points.

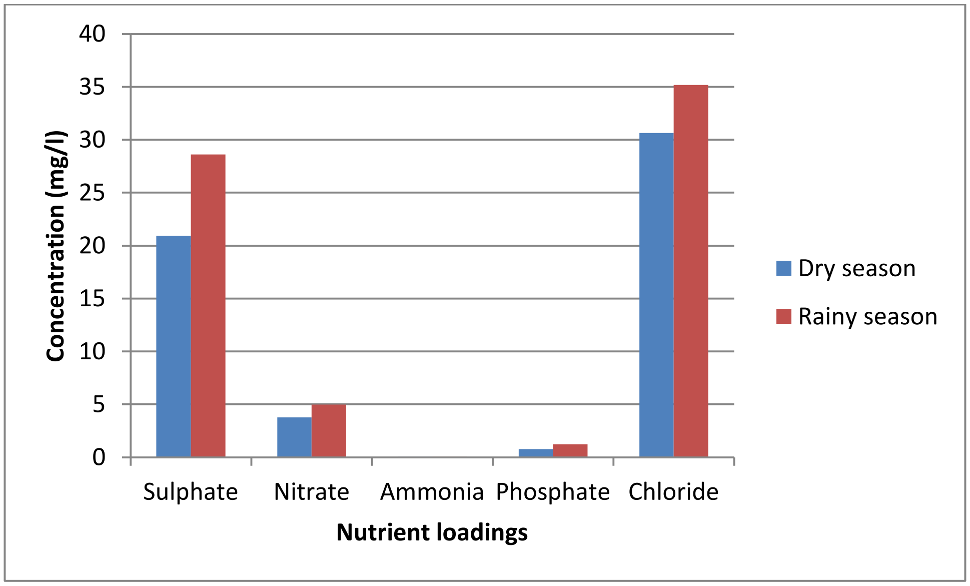


Figure 4.5: Seasonal variation in the concentrations of nutrient loading parameters for surface water samples.

Table 4.7: Correlation matrix of nutrient loadings between effluent and surface water

Parameters	Sulphate	Nitrate	Ammonia	Phosphate	Chloride
Sulphate	1				
Nitrate	1.00	1			
Ammonia	-1.00	1.00	1		
Phosphate	0.93	-1.00	1.00	1	
Chloride	0.32	0.93	-1.00	1.00	1

4.2.13 Metals and heavy metals

Metals and heavy metals at the twenty-six sampling sites showed varied degree of concentrations as presented in table 4.8a to 4.8b.

In any fresh water where Calcium is the dominating cation (Spears *et al*., 2012), the ionic composition of such water usually exhibit variations in the values obtained for Sodium and Calcium, and this may be attributed to chemical denudation due to dilution from heavy rain coupled with the rivers circulation and weathering from rock, and runoffs from surrounding water shed. An irregular pattern of Sodium and Calcium recorded in this work might be traced to heavy downpour of rain resulting in flood, which might have contained a high concentration of Magnesium and this could be the reason for the significant difference in the concentration of ion between the two seasons.

Asa River was exposed to heavy metals containing contaminating materials, capable of initiating the impairment of the water quality. This present investigations has revealed the concentrations of certain heavy metals such as Iron, Copper, Zinc, Cadmium, Lead and Chromium which were generally high in sampling sites GS/SW1, KC-GS-TP-AS/SW, AS5/SW5, AS6/SW6 respectively. The values obtained in table 4.8a and 4.8b for surface water heavy metal concentrations could be adduced to anthropogenic activities going on around the sampling sites and because of its exposure to domestic, agricultural and industrial influences. All the heavy metals concentrations obtained in this work were found to be higher except for Cadmium which was lower than what was reported by (Ogundiran and Fawole, 2014).

Iron level of samples as shown in table 4.8a are above the maximum acceptable limits of 0.3 mg/L, however the site CONTROL1/SW was below the maximum allowable concentrations of 1.0 mg/L. the mean value of 2.38±1.03 and 2.46±6.97 (figure 4.6) in the dry and rainy season for iron is higher than the maximum allowable and acceptable concentration recommended by WHO (Appendix) for portable water. It should be noted that concentration of iron above 1.0 mg/L could cause ill health such as gastrointestinal irritation (Ukpong *et al*., 2013).

All the values for Copper are below the maximum allowable concentration of 1.5 mg/L recommended by WHO. The mean values for dry and rainy seasons of 0.56±0.49 and 0.65±1.45 is clearly below the maximum allowable limit and the acceptable limit of 1.0 mg/L (Appendix).

Zinc concentration in all the samples are below the NESREA and WHO permissible limit of 5.0 mg/L except for sites GS/SW2 and KC/SW3, which are higher. The mean values of 3.58±0.42 and 3.88±2.05 recorded during dry and rainy seasons for all the samples were also below these limits (Appendix).

Cadmium concentration in most of the samples were above the maximum allowable limit of 0.003 mg/L except for sites FB/SW, FB-AS/SW3 and CONTROL1&2/SW which were below the recommended concentration by WHO. The mean values of both dry and rainy season 0.0048±0.01 and 0.0049±0.01 (figure 4.6) were also above the recommended limit of 0.003 mg/L. it should be noted that concentration of Cadmium above 0.003 mg/L can cause bones to become weaker, stomach irritation, vomiting and diarrhea may result. Small amounts of Cadmium taken over many years may cause kidney damage and fragile bones. The principal industries that use Cadmium are metal smelting, electronics, nuclear power, paint pigment production and other metal working and refining companies. Some of the above mentioned which are closed to Asa River contributed to the high level of Cadmium in the water.

Lead concentrations in all the samples were clearly above the maximum allowable limit of 0.05 mg/L recommended by WHO except site CONTROL1/SW. The mean concentration for both dry and rainy season 0.53±0.06 and 0.81±1.56 (figure 4.6) for all the samples were above these allowable limits. These trace elements are shown to bio-accumulate sometimes and even undergo bio-magnification in organisms such as fishes and even plants with serious health implications to the aquatic ecosystem. The case of Mina mata

(organic mercury poisoning) and Ita-Ita (Cadmium poisoning) in human beings is enough to drive home the serious health hazards due to these metals (Chowdhury *et al*., 2016).
From table 4.8b, it may be observed that the values for Chromium are far above the WHO permissible limit of 0.05 mg/Land NESREA of 0.1 mg/L, the mean value of 0.36±0.18 and 0.51±1.67 (Appendix) for dry and rainy seasons indicated that the water is polluted.

Chromium in excess is toxic thus leading to liver and kidney damages, internal hemorrhage and respiratory disorders, as well as causing cancer in humans and animals through inhalation exposure, but it has not been shown to be carcinogenic through ingestion exposure (Pandey *et al*., 2014).

The result indicates pollution due to high concentration of heavy metals along the Asa River course. The values of heavy metals obtained along the main river show higher difference than the WHO recommended standards. Moreover, considering the fact that irrigated agriculture and fishing were practiced along the downstream of the river, these heavy metals bioaccumulate in fishes, and irrigated plants especially vegetables, tomatoes, maize plant, lettuce and cabbage which when consumed by humans, cause serious health implication.

Generally, water samples from sites GS/SW1, KC-GS-TP-AS/SW, AS5/SW5, AS6/SW6, KC-GS-TP/SW3 and KC-GS-TP/SW2 (Appendix table 21 to 27) recorded higher metal values than that of CONTROL1/SW and the cumulative metal contamination is in order of site AS6/SW6>AS5/SW5>KC-GS-TP/SW2>KC-GS-TP/SW3>CONTROL1/SW with the metal pollution index of Cd>Cr>Cu>Pb>Fe>Zn with respect to sampling site AS5/SW5.

Table 4.8a: Concentrations (mean±SD) in mg/L of metals and heavy metals loadings in industrial effluents discharge points channels, upstream to downstream of Asa River (February 2013-April 2015).

	Sample Code	Ca	Mg	Na	Fe	Cu
DP	GS/SW	13.28±1.15	6.89±0.74	2.26±0.09	2.31±0.74	0.55±0.14
	KC/SW	12.48±2.50	6.60±0.42	2.33±0.14	1.77±1.17	0.53±0.16
	KC-GS/SW	12.13±0.45	7.27±0.10	2.17±0.24	1.36±0.14	0.42±0.03
	KC-GS-TP/SW	13.60±0.00	7.43±0.00	2.98±0.13	2.01±0.07	0.62±0.03
	FB/SW	9.92±0.88	7.27±0.23	2.09±0.35	2.27±0.24	0.55±0.05
PE	KC-GS-TP-AS	13.60±1.05	7.43±0.33	3.20±0.41	2.10±0.41	0.68±0.10
	FB-AS	12.70±0.12	7.93±0.28	1.98±0.39	2.90±0.29	0.52±0.13
US	AS1/SW1	12.7±0.12	7.93±0.28	2.13±0.33	3.23±0.17	0.68±0.16
	AS2/SW2	13.50±0.89	8.50±0.93	2.55±0.06	3.23±0.17	0.86±0.11
	AS3/SW3	12.80±0.16	8.03±0.21	2.60±0.78	2.70±0.18	0.74±0.25
DS	AS4/SW4	11.95±0.98	8.60±0.82	2.75±0.87	3.65±0.24	0.79±0.19
	AS5/SW5	12.70±0.20	8.00±0.16	2.81±0.71	3.58±0.08	0.79±0.19
	AS6/SW6	11.9±0.82	8.20±0.16	2.95±0.58	3.88±0.22	0.91±0.03
	CONTROL1/2	10.43±1.01	7.23±2.78	1.20±0.41	1.03±0.33	0.26±0.05
	WHO PL	200	150	200	2.0	<1
	NESREA	NS	NS	200	2.0	1.0
	RANGE	9.92-13.60	6.60-8.60	1.98-3.20	1.03-3.88	0.26-0.91

Ca = Calcium; Mg = Magnesium; Na = Sodium; Fe = Iron; Cu= Copper; NS = Not Stated, DP = Discharge Points; PE = Point of Entry into Asa River; US = Upstream Points; DS = Downstream Points.

Table 4.8b: Concentrations (mean±SD) in mg/L of metals and heavy metals loadings in industrial effluents discharge point's channels, upstream to downstream of Asa River (February 2013-April 2015).

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	Sample Code	Zn	Pb	Cr	Cd
DP	GS/SW	4.63±1.44	0.52±0.06	0.36±0.04	0.01±0.00
	KC/SW	3.91±1.78	0.38±0.30	0.29±0.07	0.01±0.00
	KC-GS/SW	4.90±0.16	0.55±0.04	0.36±0.05	0.01±0.00
	KC-GS-TP/SW	4.56±0.13	0.67±0.02	0.47±0.02	0.01±0.00
	FB/SW	3.03±0.20	0.92±0.29	0.28±0.03	0.00±0.00
PE	KC-GS-TP-AS	4.80±0.64	0.71±0.11	0.54±0.14	0.01±0.00
	FB-AS	2.55±0.24	0.55±0.24	0.50±0.09	0.00±0.00
US	AS1/SW1	2.75±0.13	0.69±0.31	0.55±0.04	0.01±0.00
	AS2/SW2	3.75±0.13	0.89±0.31	0.64±0.06	0.01±0.00
	AS3/SW3	3.40±0.29	0.80±0.42	0.59±0.11	0.01±0.00
DS	AS4/SW4	3.60±0.08	0.83±0.46	0.60±0.09	0.01±0.00
	AS5/SW5	3.40±0.28	0.80±0.36	0.60±0.07	0.01±0.00
	AS6/SW6	3.78±0.17	0.90±0.32	0.65±0.04	0.01±0.00
	CONTROL1/2	1.10±0.52	0.20±0.07	0.75±0.13	0.00±0.00
	NESREA	5	0.1	0.1	0.1
	WHO PL	5	0.01	0.05	0.01
	RANGE	3.03-4.90	0.38-0.92	0.28-0.47	0.00-0.01

Zn = Zinc; Pb = Lead; Cr = Chromium; Cd = Cadmium;NS = Not Stated, DP = Discharge Points; PE = Point of Entry into Asa River; US = Upstream Points; DS = Downstream Points.

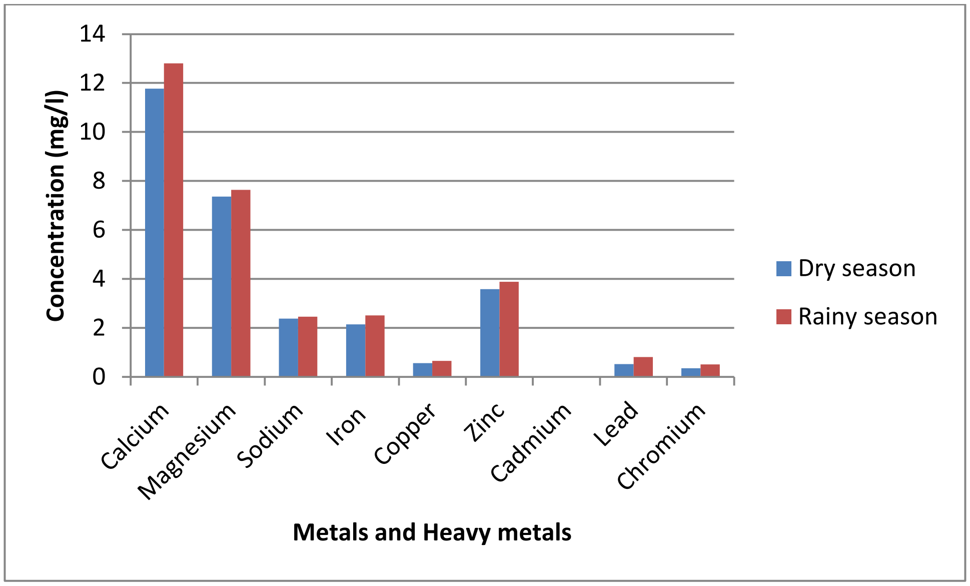

Figure 4.6: Seasonal variation in the concentrations of metals and heavy metals for surface water samples

4.2.14 Correlation matrix of metals and heavy metals parameters between effluent and surface water

The table 4.9a reveals the correlation analysis of metals and heavy metals parameter from effluent water obtained at different industrial companies to surface water. 8 is degree of freedom at 5% significance level with critical table value = 0.632. Magnesium (Mg), Calcium (Ca), Zinc (Zn) and Cadmium (Cd) data (-0.95, -0.99 and -1.00 respectively) reveal $r_{cal} < r_{table,}$ therefore null hypothesis Ho is accepted and conclude that these parameters in effluent do not have influence on the surface water while, Calcium (Ca), Copper (Cu), Iron (Fe), Sodium (Na), Lead (Pb) and Chromium (Cr) ranged from 0.96-1.00[2] have $r_{cal} > r_{table}$, therefore null hypothesis is rejected and concluded that these parameters in effluent water have significant influence on surface water.

4.2.15 Assessment of trace organics and metal contamination on Asa River surface water

The data set pertaining to Asa River surface water on overall pollution index (OPI) provides simple comparative means for assessing a site quality whether it is polluted or not as presented in table 4.9b and 4.9c respectively. The OPI values of the analysed samples were ranged from 5.0-5.1 and 3.0- 3.3 at point of industrial effluent to the main river for trace organics and metals that is KC-GS-TP-AS/SW to FB-AS/SW which indicates heavy pollution.

Table 4.9a: Correlation matrix of metals and heavy metals between effluent and surface water

Parameters	Ca	Mg	Na	Fe	Cu	Zn	Cd	Pb	Cr
Ca	1.00								
Mg	-0.95	1.00							
Na	1.00	-0.95	1.00						
Fe	0.96	1.00	-0.95	1.00					
Cu	0.98	0.96	1.00	-0.95	1.00				
Zn	-0.99	0.98	0.96	1.00	-0.95	1.00			
Cd	-1.00	-0.99	0.98	0.96	1.00	-0.95	1.00		
Pb	0.97	-1.00	-0.99	0.98	0.96	1.00	-0.95	1.00	
Cr	0.99	0.97	-1.00	-0.99	0.98	0.96	1.00	-0.95	1.00

Table 4.9b. Overall Pollution Index (OPI) values for trace organics in Asa River Surface water

Sampling sites	OPI (Trace organics)
GS/SW	5.07
KC/SW	5.12
KC-GS/SW	5.53
KC-GS-TP-AS/SW	5.07
FB/SW	5.52
FB-AS/SW	5.12
AS1/SW	5.38
AS2/SW	5.73
AS3/SW	5.67
AS4/SW	5.03
AS5/SW	4.98
AS6/SW	4.72
CONTROL	5.89
Mean	5.29

Table 4.9c. Overall Pollution Index (OPI) values for metals in Asa River Surface water

Sampling sites	OPI (metals)
GS/SW	3.42
KC/SW	3.14
KC-GS/SW	3.24
KC-GS-TP-AS/SW	3.00
FB/SW	2.92
FB-AS/SW	3.29
AS1/SW	3.40
AS2/SW	3.77
AS3/SW	3.52
AS4/SW	3.64
AS5/SW	3.63
AS6/SW	3.69
CONTROL	2.47
Mean	3.32

4.3 The Asa River sediment

Bottom sediment has been described as a long term sink for contaminants and it has also been taken to be their shelter for various life forms including both micro and macro benthic organisms. Contaminants in the sediment pose threats to human health, aquatic life and the environment. Pollutants release to surface water from industrial and municipal discharges, atmospheric deposition and polluted runoff from agricultural, urban mining areas can accumulates to environmentally harmful level in sediment. Heavy metals are intrinsic natural constituents of our environment. They are generally present in small amounts in natural aquatic environments. Apart from the natural sources, several anthropogenic ones also contributed to metal concentrations in the environment. In recent times, industrial activities have raised natural concentration causing environmental problems.

The study of the toxic effects and heavy metals in Asa River is more important in comparison with other pollutants due to their non-biodegradability nature, accumulative properties and long biological half-lives. With the increase use of wide varieties of metals and petrochemicals in industries coupled with African lifestyle of dumping wastes around indiscriminately, there is now a greater awareness of toxic metal pollution of the environment. Many of these metals tend to remain in the ecosystem and eventually move from one component of the food chain to another (Aderinola *et al*., 2009). In Nigeria, public environmental issues top the agenda at both international and national levels. This has occurred as a result of environmental degradation, environmental deterioration and under development. The rapid industrialization is also having a direct and indirect adverse effect on our environment. Industrial development manifested due to setting up of new industries or expansion of the pre-existing ones resulting into the generation of industrial effluents, spatially small scale cottage industries which discharge untreated effluents that causes water, sediment and soil pollution. Industrial growth and its associated environmental problems such as water and sediment contamination is fast increasing (Oyetibo *et al*., 2010; Fakayode, 2005). Therefore, the purpose of this research was to evaluate the sediment quality at twenty-six sampling sites along the course of Asa River, in order to identify areas where sediment contamination could be responsible for ecosystem degradation.

Sediment samples from the twenty-six sampling sites were analysed for heavy metals and the values were subjected to statistical analysis to ascertain variation that exist between the sampling sites. The values were compared with the permissible limits of the Federal Environmental Protection Agency (NESREA, 2007 and NIS, 2007) for all categories of water bodies that receives effluents. The values presented in table 4.10a to 4.11a with figure 4.7. The results of the selected nine heavy metals from the superficial sediment of the twenty-six sampling sites of Asa River revealed that Cu, Cr and Ni were present at level that exceeded the permissible levels. Low concentration of metals were recorded at CONTROL1/SD and CONTROL2/SD while they were found to be high at some sampling sites which are GS/SD1, KC-GS-TP/SD1, KC/SD1, KC-GS-TP/SD3, AS4/SD4, AS5/SD5 and AS6/SD6 respectively and this could be attributed to heavy discharge of industrial effluents into those sites. The level of all heavy metals analysed were relatively higher than the permissible levels as recommended by (WHO, 2011 and NIS, 2007). Of all the metals examined Copper, Cobalt and Chromium were found to be the most abundant in Asa River. This is in conformity to the submission of (Adefemi and Awokunmi, 2010; Ogundiran and Fawole, 2014).

Variation observed in the metals distribution from Asa River sediment could be attributed to environmental contents of the different areas in the vicinity of the river such as activities around the studied area, population density, domestic and municipal disposal, atmospheric fallout, sewage effluents, traffic volume, substantial contribution from industrial premises and natural origin. The concentrations of these metals were found to be higher in the dry season when compared to rainy season for Chromium and Copper and this may be attributed to high pollution load usually experienced during the dry season of the year. This study has confirmed that sediment is an important host for toxic metals. It has been shown that sediment permit the detection of heavy metals that may be either absent or present in low concentration in the water column.

4.3.1 Assessment of metal contamination on Asa River Sediments

The data set pertaining to Asa River sediments, geochemical background concentration, sediment quality guidelines and intermetallic correlation are presented in table 4.11b – 4.11c.

The enrichment factor (EF) is a convenient measure of geochemical trends and is used for making comparisons between areas. The EF values of heavy metals in the Asa River sediments were listed in table 4.11d.

The contamination factor (CF) was used to determine the contamination status of sediments of Asa River. The calculated CF for various heavy metals in sediments of Asa River is presents in table 4.11e.

The geo-accumulation index (Igeo) was used to determine the pollution level of sediments. The calculated Igeo values, based on the world surface rock average, are presented in table 4.11f.

The modified Hazard Quotient (mHQ) and Ecological Contamination Index (ECI) to predict the potential ecological risks associated with sediment contamination are presented in table 4.11g and 4.11h respectively.

Table 4.10a: Range and mean concentrations of sediment heavy metal loadings

PARAMETERS		GS/SD1	GS/SD2	GS/SD3	KC/SD1	KC/SD2	KC/SD3
Lead (mg/kg)	Range	0.30-0.60	0.00-0.80	0.15-0.70	0.40-0.60	0.25-0.90	0.15-0.80
	mean±SD	0.45±0.13	0.21±0.40	0.39±0.26	0.49±0.09	0.54±0.31	0.44±0.28
Copper (mg/kg)	Range	57.00-61.00	52.60-88.00	36.00-66.00	58.30-63.50	42.50-64.00	37.00-62.00
	mean±SD	59.00±1.83	58.30±6.73	52.30±14.20	60.70±2.69	55.40±9.34	48.50±11.90
Cobalt (mg/kg)	Range	38.50-44.00	30.00-46.00	30.00-45.00	36.00-42.00	28.00-48.00	36.00-50.00
	mean±SD	41.25±2.92	36.00±6.98	36.80±6.99	38.75±2.75	36.50±9.29	42.30±6.45
Chromium (mg/kg)	Range	75.00-78.00	60.00-81.00	67.00-76.00	47.50-51.00	54.00-80.00	52.00-65.00
	mean±SD	76.25±1.26	69.00±8.98	71.80±4.03	49.25±1.55	66.30±13.20	57.80±5.91
Nickel (mg/kg)	Range	20.00-23.50	24.50-27.50	28.50-31.50	13.00-17.50	25.50-28.50	27.50-33.50
	mean±SD	21.90±1.49	26.38±1.31	29.43±1.40	15.13±1.84	27.13±1.25	29.95±2.78
Zinc (mg/kg)	Range	31.00-38.50	27.50-32.50	30.00-38.00	30.00-36.00	32.00-38.00	28.50-37.00
	mean±SD	34.63±3.47	29.75±2.22	35.00±3.56	33.00±2.58	35.25±2.75	32.38±4.27
Aluminum (mg/kg)	Range	18.50-21.50	21.00-25.50	18.00-23.50	26.50-37.00	21.00-25.50	21.00-25.00
	mean±SD	20.00±1.29	23.13±2.02	20.88±2.39	32.13±4.77	23.13±2.02	23.38±1.80
Iron (mg/kg)	Range	13.50-16.50	10.00-13.50	15.00-19.50	9.50-14.00	12.00-14.00	10.50-13.00
	mean±SD	14.88± 1.25	11.75±1.44	17.38±1.89	11.50±2.12	12.88±0.85	11.88±1.11
Manganese (mg/kg)	Range	5.00-7.50	7.50-10.50	7.00-10.00	6.50-12.50	8.00-13.50	8.00-11.50
	mean±SD	6.25±1.04	9.00±1.29	8.75±1.71	9.50±2.58	11.13±2.43	9.88±2.51

•GS = detergent company points, KC = pharmaceutical company B points, TP = pharmaceutical company A, KC-GS = pharmaceutical company B – detergent meeting points, KC-GS-TP = pharmaceutical company B-detergent company-pharmaceutical company A meeting points, KC-GS-TP-AS = pharmaceutical company B-detergent company-pharmaceutical company A-Asa River meeting point, FB = Battery company points, FB-AS = Battery company-Asa River meeting point, AS1 = Asa River [after the dam point one], AS2 = Asa River [Dangote area point 2], AS3 = Asa River [Along 7UP bridge point three], AS4 = Asa river [Unity bridge point four], AS5 =Asa River [Emir bridge point five], AS6 = Asa River [Amilegbe bridge point 6], SD = Sediment.

Table 4.10b: Range and mean concentrations of sediment heavy metal loadings

PARAMETERS		KC-GS/SD1	KC-GS/SD2	KC-GS/SD3	KC-GS/SD4
Lead (mg/kg)	Range	0.10-0.30	0.00-0.10	0.05-0.15	0.03-0.08
	mean±SD	0.19±0.09	0.04±0.05	0.10±0.04	0.07±.0.03
Copper (mg/kg)	Range	40.00-45.00	23.00-26.00	30.00-32.00	25.00-29.00
	mean±SD	42.40±2.29	24.50±1.29	30.90±0.85	27.10±2.02
Cobalt (mg/kg)	Range	50.00-55.00	43.00-48.00	40.00-43.00	40.00-55.00
	mean±SD	52.80±2.22	45.80±2.22	41.60±1.25	48.50±6.35
Chromium (mg/kg)	Range	34.00-37.00	61.00-64.00	63.50-67.00	54.00-56.00
	mean±SD	35.50±1.29	62.60±1.38	65.00±1.47	54.90±0.85
Nickel (mg/kg)	Range	30.20-35.50	24.50-30.80	26.50-33.00	29.00-35.50
	mean±SD	32.30±2.34	27.70±2.94	29.63±2.78	31.63±3.01
Zinc (mg/kg)	Range	26.50-30.50	29.00-35.50	27.00-34.00	32.50-38.00
	mean±SD	28.25±10.45	31.88±2.95	30.25±3.30	35.25±2.33
Aluminum (mg/kg)	Range	26.00-32.00	26.50-30.50	30.00-35.50	32.50-38.00
	mean±SD	29.00±2.58	28.38±1.75	33.00±2.48	35.25±2.33
Iron (mg/kg)	Range	12.50-15.50	9.00-12.00	15.00-18.50	13.00-15.50
	mean±SD	14.00±1.29	10.50±1.29	16.75±1.55	14.38±1.11
Manganese (mg/kg)	Range	11.50-13.50	9.00-13.50	13.00-16.50	12.50-15.00
	mean±SD	12.50±0.91	11.13±1.89	14.75±1.55	13.88±1.11

•GS = detergent company points, KC = pharmaceutical company B points, TP = pharmaceutical company A, KC-GS = pharmaceutical company B – detergent meeting points, KC-GS-TP = pharmaceutical company B-detergent company-pharmaceutical company A meeting points, KC-GS-TP-AS = pharmaceutical company B-detergent company-pharmaceutical company A-Asa River meeting point, FB = Battery company points, FB-AS = Battery company-Asa River meeting point, AS1 = Asa River [after the dam point one], AS2 = Asa River [Dangote area point 2], AS3 = Asa River [Along 7UP bridge point three], AS4 = Asa river [Unity bridge point four], AS5 =Asa River [Emir bridge point five], AS6 = Asa River [Amilegbe bridge point 6], SD = Sediment.

Table 4.10c: Range and mean concentrations of sediment heavy metal loadings

PARAMETERS		KC-GS-TP/SD1	KC-GS-TP/SD2	KC-GS-TP/SD3	KC-GS-TP-AS/SD
Lead (mg/kg)	Range	0.20-0.50	0.30-0.40	0.00-0.80	0.50-0.80
	mean±SD	0.35±0.13	0.35±0.04	0.31±0.37	0.61±0.13
Copper (mg/kg)	Range	48.00-56.00	28.00-32.50	23.50-34.00	35.80-42.00
	mean±SD	52.00±4.62	30.40±2.21	28.40±5.41	38.50±3.06
Cobalt (mg/kg)	Range	37.00-42.00	23.00-28.00	44.00-53.00	26.20-32.00
	mean±SD	39.50±2.38	25.50±2.38	48.80±4.43	28.70±2.81
Chromium (mg/kg)	Range	58.50-67.00	46.00-49.00	50.00-56.00	48.50-52.00
	mean±SD	63.00±4.14	47.50±1.29	52.80±2.75	50.30±1.55
Nickel (mg/kg)	Range	16.00-24.50	25.00-32.50	22.50-28.50	24.00-28.80
	mean±SD	19.88±3.59	28.63±3.47	26.13±2.75	26.20±2.01
Zinc (mg/kg)	Range	24.00-27.00	28.00-33.00	28.50-34.50	31.00-36.50
	mean±SD	25.63±1.38	30.25±2.22	31.25±2.75	33.25±2.40
Aluminum (mg/kg)	Range	34.00-38.50	37.50-42.50	32.00-36.00	35.00-39.00
	mean±SD	36.13±2.02	39.75±2.22	34.00±1.83	37.13±1.75
Iron (mg/kg)	Range	17.50-21.00	14.00-17.50	15.50-18.00	21.00-26.00
	mean±SD	19.25±1.55	15.63±1.63	16.75±1.04	23.50±2.20
Manganese (mg/kg)	Range	7.00-11.50	7.00-10.50	9.50-12.50	13.00-17.00
	mean±SD	9.13±2.02	8.88±1.49	10.88±1.25	14.88±1.75

•GS = detergent company points, KC = pharmaceutical company B points, TP = pharmaceutical company A, KC-GS = pharmaceutical company B – detergent meeting points, KC-GS-TP = pharmaceutical company B-detergent company-pharmaceutical company A meeting points, KC-GS-TP-AS = pharmaceutical company B-detergent company-pharmaceutical company A-Asa River meeting point, FB = Battery company points, FB-AS = Battery company-Asa River meeting point, AS1 = Asa River [after the dam point one], AS2 = Asa River [Dangote area point 2], AS3 = Asa River [Along 7UP bridge point three], AS4 = Asa river [Unity bridge point four], AS5 =Asa River [Emir bridge point five], AS6 = Asa River [Amilegbe bridge point 6], SD =Sediment.

Table 4.10d: Range and mean concentrations of sediment heavy metal loadings

PARAMETERS		FB/SD1	FB/SD2	FB/SD3	FB-AS/SD
Lead (mg/kg)	Range	2.10-2.70	2.00-2.40	0.30-0.60	0.45-0.55
	mean±SD	2.45±0.26	2.20±0.18	0.43±0.15	0.15±0.04
Copper (mg/kg)	Range	62.50-72.50	68.50-72.00	30.00-48.00	27.00-32.00
	mean±SD	67.00±4.14	71.00±1.96	38.90±8.95	29.50±2.38
Cobalt (mg/kg)	Range	36.00-42.00	40.00-44.00	28.00-36.00	29.00-35.00
	mean±SD	38.25±2.63	42.50±1.73	32.30±3.86	31.80±2.75
Chromium (mg/kg)	Range	50.00-53.00	50.00-57.00	52.00-60.00	48.00-52.00
	mean±SD	52.50±2.08	54.50±3.11	56.30±3.50	50.30±1.71
Nickel (mg/kg)	Range	22.00-31.50	32.40-37.50	18.00-23.50	21.50-25.50
	mean±SD	26.75±4.13	34.85±2.10	20.63±2.29	23.50±1.68
Zinc (mg/kg)	Range	30.00-36.00	34.00-40.50	32.50-37.50	37.00-45.50
	mean±SD	33.00±2.74	37.50±3.03	35.00±2.38	41.00±3.76
Aluminum (mg/kg)	Range	23.50-28.50	25.00-30.50	25.00-32.00	27.50-33.00
	mean±SD	26.00±2.38	27.75±2.66	28.50±3.11	30.13±2.56
Iron (mg/kg)	Range	15.00-19.50	17.00-21.00	13.50-18.50	16.00-20.50
	mean±SD	17.00±2.12	19.00±2.04	16.00±2.38	18.13±2.21
Manganese (mg/kg)	Range	8.50-13.00	8.00-12.50	12.50-18.00	14.00-18.00
	mean±SD	10.63±2.21	10.13±2.21	14.88±2.59	16.00±2.04

•GS = detergent company points, KC = pharmaceutical company B points, TP = pharmaceutical company A, KC-GS = pharmaceutical company B – detergent meeting points, KC-GS-TP = pharmaceutical company B-detergent company-pharmaceutical company A meeting points, KC-GS-TP-AS = pharmaceutical company B-detergent company-pharmaceutical company A-Asa River meeting point, FB = Battery company points, FB-AS = Battery company-Asa River meeting point, AS1 = Asa River [after the dam point one], AS2 = Asa River [Dangote area point 2], AS3 = Asa River [Along 7UP bridge point three], AS4 = Asa river [Unity bridge point four], AS5 =Asa River [Emir bridge point five], AS6 = Asa River [Amilegbe bridge point 6], SD = Sediment.

Table 4.10e: Range and mean concentrations of sediment heavy metal loadings

PARAMETERS		AS1/SD1	AS2/SD2	AS3/SD3	AS4/SD4	AS5/SD5
Lead (mg/kg)	Range	0.25-0.50	0.25-0.50	0.20-0.50	0.25-0.30	0.20-0.40
	mean±SD	0.36±0.11	0.37±0.11	0.35±0.13	0.27±0.02	0.29±0.10
Copper (mg/kg)	Range	24.00-28.00	40.00-45.00	42.00-47.00	44.00-54.00	35.00-43.00
	mean±SD	26.30±1.71	42.10±2.17	44.30±2.22	48.80±4.99	38.30±3.32
Cobalt (mg/kg)	Range	30.00-38.00	40.00-55.00	32.00-38.00	24.00-30.50	25.00-32.00
	mean±SD	34.50±3.42	49.50±6.56	34.50±2.65	27.00±3.03	29.10±3.12
Chromium (mg/kg)	Range	40.00-55.00	61.00-68.00	60.00-63.00	52.00-58.00	50.00-58.00
	mean±SD	47.50±6.45	64.30±3.30	61.50±1.29	54.80±2.75	54.50±3.42
Nickel (mg/kg)	Range	18.50-24.00	18.00-24.50	12.50-18.50	24.00-33.50	23.00-28.80
	mean±SD	21.50±2.35	20.63±2.78	15.33±2.69	28.75±4.01	25.33±2.47
Zinc (mg/kg)	Range	31.00-35.50	28.00-32.00	30.00-36.00	42.00-47.50	48.50-54.00
	mean±SD	33.25±1.85	30.00±1.83	33.00±2.58	44.63±2.29	51.00±2.48
Aluminum (mg/kg)	Range	24.00-28.50	23.00-27.00	27.00-32.00	33.00-38.00	40.00-50.00
	mean±SD	26.25±2.10	25.13±1.75	29.50±2.38	35.75±2.22	45.75±4.35
Iron (mg/kg)	Range	16.50-21.50	16.00-20.50	19.00-23.00	17.50-22.50	21.00-23.50
	mean±SD	19.00±2.38	18.25±2.35	21.00±1.83	20.13±2.14	22.88±1.75
Manganese (mg/kg)	Range	8.00-11.00	11.00-14.50	9.50-15.00	11.00-16.50	16.00-22.00
	mean±SD	9.63±1.38	12.63±1.49	12.13±2.56	13.63±2.56	18.75±2.75

•GS = detergent company points, KC = pharmaceutical company B points, TP = pharmaceutical company A, KC-GS = pharmaceutical company B – detergent meeting points, KC-GS-TP = pharmaceutical company B-detergent company-pharmaceutical company A meeting points, KC-GS-TP-AS = pharmaceutical company B-detergent company-pharmaceutical company A-Asa River meeting point, FB = Battery company points, FB-AS = Battery company-Asa River meeting point, AS1 = Asa River [after the dam point one], AS2 = Asa River [Dangote area point 2], AS3 = Asa River [Along 7UP bridge point three], AS4 = Asa river [Unity bridge point four], AS5 =Asa River [Emir bridge point five], AS6 = Asa River [Amilegbe bridge point 6], SD =Sediment.

Table 4.10f: Range and mean concentrations of sediment heavy metal loadings

PARAMETERS		AS6/SD6	CONTROL 1/SD	CONTROL 2/SD
Lead (mg/kg)	Range	0.25-0.40	0.50-0.60	0.05-0.30
	mean±SD	0.31±0.06	0.56±0.05	0.16±0.38
Copper (mg/kg)	Range	28.00-30.50	40.00-45.00	29.00-32.50
	mean±SD	29.40±1.11	42.88±2.78	30.60±1.49
Cobalt (mg/kg)	Range	30.00-35.00	26.00-30.00	44.50-47.00
	mean±SD	32.50±2.08	27.88±1.93	45.60±1.11
Chromium (mg/kg)	Range	41.00-49.00	48.00-57.00	30.00-38.00
	mean±SD	45.00±4.00	52.50±4.65	35.40±3.64
Nickel (mg/kg)	Range	27.50-32.50	15.00-18.50	13.60-18.00
	mean±SD	30.13±2.06	16.88±1.49	15.28±1.91
Zinc (mg/kg)	Range	51.50-58.00	24.00-29.00	26.50-32.50
	mean±SD	54.63±2.93	26.50±2.38	29.25±2.75
Aluminum (mg/kg)	Range	46.00-53.00	18.00-23.00	19.50-24.50
	mean±SD	49.75±3.30	20.50±2.38	22.00±2.38
Iron (mg/kg)	Range	24.00-29.00	9.00-14.00	11.50-16.00
	mean±SD	26.50±2.38	11.50±2.38	13.88±2.21
Manganese (mg/kg)	Range	19.50-24.50	5.50-10.00	6.50-11.50
	mean±SD	22.00±2.38	7.88±2.21	9.00±2.38

•GS = detergent company points, KC = pharmaceutical company B points, TP = pharmaceutical company A, KC-GS = pharmaceutical company B – detergent meeting points, KC-GS-TP = pharmaceutical company B-detergent company-pharmaceutical company A meeting points, KC-GS-TP-AS = pharmaceutical company B-detergent company-pharmaceutical company A-Asa River meeting point, FB = Battery company points, FB-AS = Battery company-Asa River meeting point, AS1 = Asa River [after the dam point one], AS2 = Asa River [Dangote area point 2], AS3 = Asa River [Along 7UP bridge point three], AS4 = Asa river [Unity bridge point four], AS5 =Asa River [Emir bridge point five], AS6 = Asa River [Amilegbe bridge point 6], SD = Sediment.

Table 4.11a: Mean and standard deviation of sediment loading for heavy metals of dry and rainy season over the sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT 2014]
Lead (mg/kg)	0.74±0.14	0.76±0.83
Copper (mg/kg)	47.71±5.37	47.68±16.97
Cobalt (mg/kg)	33.20±2.69	36.55±41.01
Chromium (mg/kg)	55.64±5.66	53.05±15.56
Nickel (mg/kg)	24.15±1.23	25.97±2.60
Zinc (mg/kg)	32.29±1.03	37.11±2.11
Aluminum (mg/kg)	28.15±1.12	32.90±0.28
Iron (mg/kg)	15.33±0.78	18.14±0.69
Manganese (mg/kg)	10.32±0.75	13.36±0.86

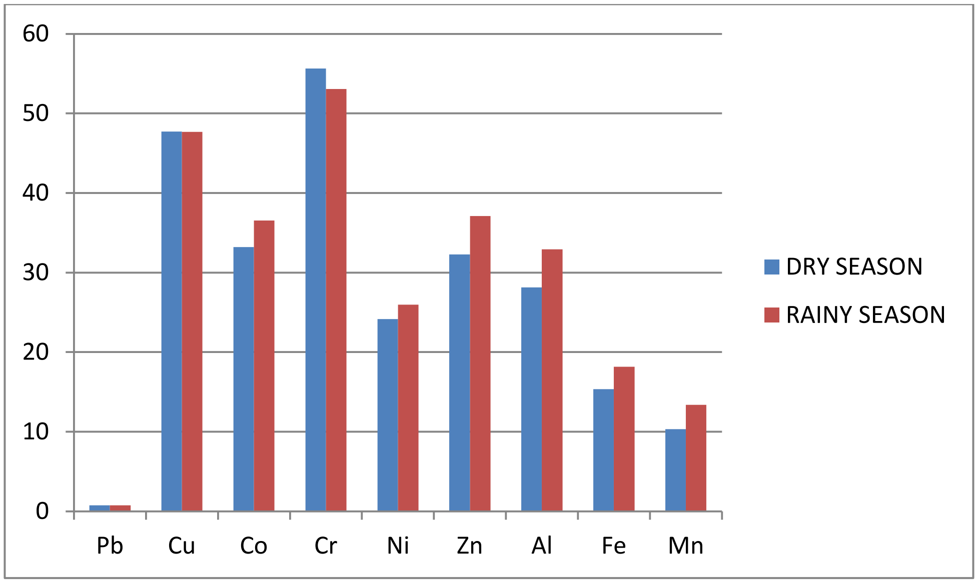

Figure 4.7: Seasonal variations in the concentrations of heavy metals parameters in sediment samples

Table 4.10a-4.10f shows the mean concentration of the heavy metals (mg/kg) in the sediment samples. FB/SD1, which is battery company sediment for point one had the highest mean concentration of Pb of all the sediment sampling points. The mean concentration of Pb obtained in this study was lower than the world surface rock average concentration as a geochemical background level. In comparison with sediment quality guideline (SQG) given in table 4.11b, the mean value did not exceed the limits, and this result shows that the Asa River sediments are not polluted by Pb. The EF values for Pb in Asa River sediments were ranged from 0.02 to 0.12. The EF values for Pb were found to be less than 20 in all sampling sites (table 4.11d), suggesting that these sites are deficiency to minimal enrichment for Pb. CF values for Pb in Asa River sediments varied from 0.00 to 0.15 with a mean of 0.03, table 4.11e. All the sampling sites have CF < 1, which denotes low contamination (table 2.6). The I_{geo} values for Pb in all sampling sites, were less than 0 (<0), table 4.11f reveal negative values which indicated that Asa River sediments in this study area are unpolluted by Pb. This result was in good agreement with the results of (Salah *et al*., 2012; Soladoye and Nwoye, 2015). The mHQ values for Pb in Asa River sediments varied from 0.04 to 0.39 with a mean of 0.15 (table 4.11g). All sampling sites have mHQ < 0.5, which suggests nil to very low severity of contamination (table 2.8). The ECI for Pb suggests uncontaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

Table 4.10a to 4.10f reveals the total mean concentration of Copper (Cu) analysed in this study. FB/SD2, which is battery company sediment point two, had the highest mean concentration of Cu of all the sampling sites. The mean concentration obtained in this study was higher than the world surface rock average concentration as a geochemical background level for seventeen sites and lower for nine sites. In comparison with sediment quality guideline (SQG), the mean value exceed the limit for WHO and USEPA guidelines and not for CCME, and this results shows that Asa River sediment is slightly polluted by Cu. The enrichment factor (EF) values for Cu in Asa River sediments vary from 2.19 at KC-GS/SD2 to 6.34 at FB/SD2. All sampling sites has EF values greater than

2 but less than 20, suggesting that Asa River sediment are classified as significant enrichment for Cu (Rabee *et al*., 2009). The CF for Cu in Asa River sediments ranged from 0.77 at KC-GS/SD2 to 2.22 at FB/SD2 with a mean value of 1.34. The CF values for Cu were $1 \leq CF < 3$ at most sampling sites. According to table 2.6, all sampling sites face moderate contamination. The I_{geo} values for Cu at the sampling sites were ranged from -0.97 to 0.57. According to Muller's classification, Asa River sediments at most sampling sites were unpolluted, except for sites FB/SD2 and FB/SD1 which had ($0 < I_{geo} < 2$) that is from unpolluted to moderately polluted. This result was in good agreement with results of (Rabee *et al*., 2009). The mHQ values for Cu in Asa River sediments varied from 1.01 to 1.73 with a mean of 1.33 (table 4.11g). All sampling sites have $1.0 < mHQ < 1.5$, which suggests low severity of contamination (table 2.8). The ECI (5.46) for Cu suggests considerably to highly contaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Co analysed in this study are presented in table 4.10a to 4.10f. KC-GS/SD1 which is meeting point of a pharmaceutical company B and detergent company at point one. The mean concentration of Co obtained in this study was higher than world surface rock average concentration as a geochemical background level for all the sampling sites. There was no recorded value for SQG of Co. The EF values for Co in Asa River sediments were from 0.88 at KC-GS-TP/SD2 to 1.82 at KC-GS/SD1, table 4.11c. Most sampling sites have EF for Co less than 2 which reveal that Asa River sediment is classified as deficient to minimal enrichment. The CF values for Co in Asa River sediments ranged from 1.96 at KC-GS-TP/SD2 to 4.06 at KC-GS/SD1, with a mean value of 2.92. At all sampling sites, the CF values for Co were more 1 and less than 3. According to (Salah *et al*., 2012) all sampling sites were moderately contaminated by Co. The I_{geo} values for Co in Asa River sediments ranged from 0.46 to 1.44. All sampling sites has I_{geo} for Co more than 0 but less than 2 ($0 < I_{geo} < 2$). According to Muller's classification table, the I_{geo} values for Co indicate that Asa River sediments are unpolluted to moderately polluted for all sampling sites (Rabee *et al*., 2009). The mHQ values for Co in Asa River sediments varied from 1.40 to 2.02 with a mean of 1.70 (table 4.11g). All sampling sites have 1.5 < mHQ < 2.0, which suggests moderate severity of contamination (table 2.8). The ECI for Co (6.38) suggests highly contaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Cr analysed in this study are presented in table 4.10a to table 4.10f respectively. GS/SD1, which is detergent company point one had the highest mean concentration of Cr of all the sampling sites. The mean concentration of Cr obtained in this study was less than the world surface rock average concentration as a geochemical background level for twenty-four sites and higher for two sites. In comparison with sediment quality guidelines (SOG), the mean value of Cr exceeded the limits for WHO, USEPA and CCME guidelines. The EF values for Cr in Asa sediments ranged from 0.39 at (KC-GS/SD1 and CONTROL 2/SD) to 0.85 at GS/SD1. All sampling sites have EF less than 2, table 4.11c. Asa sediments at all sampling sites are classified as deficient to minimal enrichment. The CF values for Cr in Asa sediments varied from 0.50 at (KC-GS/SD1 and CONTROL 2/SD) to 1.07 at GS/SD1, with a mean value of 0.79, table 4.11d. At all sampling sites, the CF value is greater than 1 but less than 3, suggestion that sediments were moderately contaminated. The I_{geo} values for Cr at all sampling sites were negative. According to Muller's classification, Asa sediments were unpolluted by Cr (Salah *et al*., 2012). The mHQ values for Cr in Asa River sediments varied from 1.32 to 1.93 with a mean of 1.65 (table 4.11g). All sampling sites have 1.5 < mHQ < 2.0, which suggests moderate severity of contamination (table 2.8). The ECI for Cr (3.98) suggests slightly to moderately contaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Ni analysed in this study is presented in table 4.10a to 4.10f. Battery company point 2 (FB/SD2) had the highest Ni mean concentration and pharmaceutical company B point 1 (KC/SD1) had the least of all the sediments. The mean value is less than world surface rock average and mean shale concentration as background level. According to WHO and USEPA guidelines, Ni concentrations mean exceeded the guidelines suggesting that Asa River sediments are polluted by Ni. The enrichment factor (EF) values for Ni in Asa River sediments range from 0.22 at control 2/SD and KC/SD1 to 0.51 at FB/SD2. All sampling sites have EF<2, these revealed deficiency to minimal enrichment. The contamination factor (CF) values for Ni in Asa River sediments ranged from 0.31 at control 2/SD, AS3/SD3 and KC/SD1 sites to 0.66 at KC-GS/SD1 with mean value of 0.51. All sampling sites have CF<1 which face low contamination by Ni. The Igeo values for Ni at all sampling sites were negative. According to Muller's classification, Asa River sediments were unpolluted at all the sites. This result was in good agreement with that of (Rabee *et al.*, 2009). The mHQ values for Ni in Asa River sediments varied from 1.24 to 1.88 with a mean of 1.53 (table 4.11g). All sampling sites have 1.5 < mHQ < 2.0, which suggests moderate severity of contamination (table 2.8). The ECI for Ni (1.70) suggests uncontaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Zn analysed in this study are presented in table 4.10a to 4.10f respectively. Asa River point 6 at Amilegbe bridge (AS6/SD6) had the highest Zn mean concentration and meeting point 1 of pharmaceutical company B-detergent company – pharmaceutical company A (KC-GS-TP/SD1) had the least of all the sediments. The mean value is higher than the world surface rock average as background level. According to WHO, USEPA and CCME guidelines, Zn concentrations mean did not exceed the guidelines suggesting that Asa River sediments are not polluted by Zn. The enrichment factor (EF) values for Zn in Asa River sediments range from 0.27 at KC-GS-TP/SD1 to 0.58 at AS6/SD6. All sampling sites have EF<2, these revealed deficiency to minimal enrichment. The contamination factor (CF) values for Zn in Asa River sediments ranged from 1.28 at KC-GS-TP/SD1 to 2.73 at AS6/SD6 with mean value of 1.72. All sampling sites have 1≤CF<3 which faces moderate contamination by Zn. The Igeo values for Zn at all sampling sites were positive except for sites GS/SD2, KC-GS/SD1, KC-GS-TP/SD1, CONTROL 1/SD and CONTROL 2/SD respectively. According to Muller's classification, most sampling sites are in class 1, which indicates, unpolluted to moderately polluted except for sites GS/SD2, KC-GS/SD1, KC-GS-TP/SD1, CONTROL1/SD and CONTROL 2/SD, which are in class 0, indicates unpolluted. This result was in agreement with that of (Salah *et al*., 2012). The mHQ values for Zn in Asa River sediments varied from 0.46 to 0.66 with a mean of 0.5 (table 4.11g). All sampling sites have mHQ < 0.5, which suggests nil to very low severity of contamination (table 2.8). The ECI for Zn (1.70) suggests uncontaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Al analysed in this study are shown in table 4.10a to 4.10f respectively. Asa River Amilegbe bridge point 6 (AS6/SD6) had the highest Al mean concentration and detergent company point 1 (GS/SD1) had the least of all the sediments. The mean value is greater than world surface rock average and mean shale concentration as background level. The enrichment factor (EF) values for Al in Asa River sediments range from 1.29 at GS/SD1 to 3.20 at AS6/SD6. Most sampling sites have EF<2, except sites KC-GS-TP/SD2, AS5/SD5 and AS6/SD6 which has 2≤EF<5 indicative of moderate enrichment. The contamination factor (CF) values for Al in Asa River sediments ranged from 1.28 at GS/SD1 to 3.19 at AS6/SD6 with mean value of 1.93. Most sampling sites face moderate contamination with 1≤CF<3 except site AS6/SD6 which face considerable contamination with 3≤CF<6. The Igeo values for Al at most sampling sites were positive. According to Muller's classification, Asa River sediments observed unpolluted to moderately polluted. The mHQ values for Al in Asa River sediments varied from 1.13 to 1.71 with a mean of 1.38 (table 4.11g). All sampling sites have 1.0 < mHQ < 1.5, which suggests low severity of contamination (table 2.8). The ECI for Al (1.50) suggests uncontaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Fe analysed in this study are shown in table 4.10a to 4.10f respectively. Amilegbe bridge Asa River point 6 (AS6/SD6) had the highest Fe mean concentration and pharmaceutical company B – detergent company meeting point 2 (KC-GS/SD2) had the least of all the sediments. The mean value less than world surface rock average and mean shale concentration as background level. According to USEPA guidelines, Fe concentrations did not exceed the guidelines suggesting that Asa River sediments are not polluted by Fe. The enrichment factor (EF) values for Fe in Asa River sediments are 0.00 for all sampling sites which reveals EF<2 and it confirms deficiency to minimal enrichment. The contamination factor (CF) values for Fe in Asa River sediments is 0.00 for all sites. All sampling sites have CF<1 which face low contamination by Fe. The Igeo values for Fe at all sampling sites were negative. According to Muller's classification, Asa River sediments were polluted at all the sites. The mHQ values for Fe in Asa River sediments varied from 0.02 to 0.03 with a mean of 0.02 (table 4.11g). All sampling sites have mHQ < 0.5, which suggests nil to very low severity of contamination (table 2.8). The ECI for Fe (0.07) suggests uncontaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The total mean concentration of Mn analysed in this study are presented in table 4.10a to 4.10f respectively. Asa River Amilegbe bridge point 6 (AS6/SD6) had the highest Mn mean concentration and detergent company point 1 had the least of all the sediments. The mean value less than world surface rock average and mean shale concentration as background level. According to USEPA guidelines, Mn concentrations did not exceed the guidelines suggesting that Asa River sediments are not polluted by Mn. The enrichment factor (EF) values for Mn in Asa River sediments range from 0.01 at most sampling sites to 0.03 at AS6/SD6. All sampling sites have EF<2, these indicated minimal enrichment. The contamination factor (CF) values for Mn in Asa River sediments ranged from 0.01 at most sampling sites to 0.03 at AS5/SD5 and AS6/SD6 respectively. All sampling sites have CF<1 which face low contamination by Mn. The Igeo values for Mn at all sampling sites reveal 0 (≤0) that is negative. According to Muller's classification, Asa River sediments were unpolluted at all the sites. This result was in good agreement with that of (Fagbote and Olaonipekun, 2010). The mHQ values for Mn in Asa River sediments varied from 0.09 to 0.17 with a mean of 0.12 (table 4.11g). All sampling sites have mHQ < 0.5, which suggests nil to very low severity of contamination (table 2.8). The ECI for Mn (0.46) suggests uncontaminated for the sites (table 4.11h). This result was in good agreement with the results of (Benson et al., 2018).

The status of metal contamination was investigated in Asa River sediments. Pb, Cu, Co, Cr, Ni, Zn, Al, Fe and Mn concentrations were estimated in twenty-six sampling sites. The order of mean concentrations of tested heavy metals: Cr>Cu>Co>Zn>Al>Ni>Fe>Mn>Pb. The correlation analysis of mean concentrations show good to strong positive correlations among Pb, Co, Ni, Zn, Al, Fe and Mn suggesting that these metals have common sources. The EF values suggests that Asa sediments were deficient to minimal enrichment for Pb, Co, Cr, Ni, Zn, Fe and Mn while moderate enrichment for Cu and Al. According to CF, Pb, Ni, Fe and Mn shows low contamination while Cu, Co, Cr, Zn and Al face moderate contamination. The mHQ values suggests that Asa River sediments have low contamination with Pb, Zn, Fe, Mn and Al while Cu, Co, Cr and Ni have moderate severity of contamination. The calculated ECIs indicated uncontaminated to highly contaminated ecosystems. The ecological risk ranking based on percentage contribution to ECI followed the sequence Co>Cr>Ni>Al>Cu>Zn>Pb>Mn>Fe while the severity of ecosystem pollution based on the nine heavy metals decrease from KC-GS-TP-AS/SD > control/SD. In general, cobalt contributed considerably to the ecological contamination risk index of the investigated aquatic ecosystems compared to Cr, Ni and Cu. The results indicated that the mHQ and ECI are reliable and useful pollution tools state, site-specific status and aggregative contamination effects by heavy metals in aquatic ecosystems. In general, the overall total geo-accumulation indexes (I_{tot}) of the entire study area for different metals were found to be negative, table 4.11f. This suggests that concentration mean of most heavy metals in Asa sediments are lower than world surface rock average. Considering all assessing criteria, Co and Cu are responsible for significant amount of heavy metal contamination while Pb, Fe and Cr are responsible for low contamination.

Table 4.11b. Concentration of sediments quality in world standard guideline

Elements	World surface Rock average	Mean Shale Concentration	WHO	USEPA	CCME
Pb (mg/kg)	16	20	-	40	35
Cu (mg/kg)	32	11.2	25	16	35.7
Co (mg/kg)	13	29	-	-	-
Cr (mg/kg)	71	90	25	25	37.3
Ni (mg/kg)	49	68	20	16	-
Zn (mg/kg)	20	95	123	110	123
Al (mg/kg)	15.6	15.53	-	-	-
Fe (mg/kg)	35900	46700	-	30	-
Mn (mg/kg)	750	850	-	30	-

- WHO = World Health Organization, USEPA = United States Environmental Protection Agency, CCME = Canadian Council of Ministers of the Environment, SQG = Sediment Quality Guidelines, Pb = Lead, Cu = Copper, Co = Cobalt, Cr = Chromium, Zn = Zinc, Al = Aluminum, Fe =Iron and Mn = Manganese.

Table 4:11c: Pearson's correlation coefficient of heavy metals in Asa River sediments

Metal	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
Pb	1.00								
Cu	1.00	1.00							
Co	1.00	1.00	1.00						
Cr	1.00	1.00	-1.00	1.00					
Ni	1.00	-1.00	1.00	-1.00	1.00				
Zn	1.00	-1.00	1.00	-1.00	1.00	1.00			
Al	1.00	-1.00	1.00	-1.00	1.00	1.00	1.00		
Fe	1.00	-1.00	1.00	-1.00	1.00	1.00	1.00	1.00	
Mn	1.00	-1.00	1.00	-1.00	1.00	1.00	1.00	0.00	1.00

•Pb = Lead, Cu = Copper, Co = Cobalt, Cr = Chromium, Zn = Zinc, Al = Aluminum, Fe =Iron and Mn = Manganese.

Table 4.11d. Enrichment Factor (EF) values of heavy metals in Asa River Sediments

Sampling Sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
GS/SD1	0.02	5.27	1.42	0.85	0.32	0.36	1.29	0.00	0.01
GS/SD2	0.01	5.21	1.24	0.77	0.39	0.31	1.49	0.00	0.01
GS/SD3	0.02	4.67	1.27	0.80	0.43	0.37	1.34	0.00	0.01
KC/SD1	0.03	5.42	1.34	0.55	0.22	0.35	2.07	0.00	0.01
KC/SD2	0.03	4.95	1.26	0.74	0.40	0.37	1.49	0.00	0.01
KC/SD3	0.02	4.33	1.46	0.64	0.44	0.34	1.51	0.00	0.01
KC-GS/SD1	0.01	3.79	1.82	0.39	0.48	0.30	1.87	0.00	0.01
KC-GS/SD2	0.00	2.19	1.58	0.70	0.41	0.34	1.83	0.00	0.01
KC-GS/SD3	0.01	2.76	1.43	0.72	0.44	0.32	2.12	0.00	0.00
KC-GS/SD4	0.00	2.42	1.67	0.61	0.47	0.37	2.27	0.00	0.02
KC-GS-TP/SD1	0.02	4.64	1.36	0.70	0.29	0.27	2.33	0.00	0.02
KC-GS-TP/SD2	0.02	2.71	0.88	0.53	0.42	0.32	2.56	0.00	0.01
KC-GS-TP/SD3	0.02	2.54	1.68	0.59	0.38	0.33	2.19	0.00	0.01
KC-GS-TP-AS/SD	0.03	3.44	0.99	0.56	0.39	0.35	2.39	0.00	0.01
FB/SD1	0.12	5.98	1.32	0.58	0.39	0.35	1.67	0.00	0.02
FB/SD2	0.11	6.34	1.47	0.61	0.51	0.39	1.79	0.00	0.01
FB/SD3	0.02	3.47	1.11	0.63	0.30	0.37	1.84	0.00	0.02
FB-AS/SD	0.01	2.63	1.10	0.56	0.35	0.43	1.94	0.00	0.02
AS1/SD1	0.02	2.35	1.19	0.53	0.32	0.35	1.69	0.00	0.01
AS2/SD2	0.02	3.76	1.71	0.71	0.30	0.32	1.62	0.00	0.01
AS3/SD3	0.02	3.96	1.19	0.68	0.23	0.35	1.90	0.00	0.01
AS4/SD4	0.01	4.36	0.93	0.61	0.42	0.47	2.30	0.00	0.02
AS5/SD5	0.01	3.42	1.00	0.61	0.37	0.54	2.95	0.00	0.02
AS6/SD6	0.02	2.63	1.12	0.50	0.44	0.58	3.20	0.00	0.03
CONTROL1/SD	0.03	3.83	0.96	0.58	0.25	0.28	1.32	0.00	0.01
CONTROL2/SD	0.01	2.73	1.06	0.39	0.22	0.31	1.42	0.00	0.01

EF<2 = deficiency to minimal enrichment; 2≤EF≤5 = moderate enrichment; 5≤EF≤20 = significant enrichment

Table 4.11e. Contamination Factor (CF) for the heavy metals of Asa River Sediments

Sampling Sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
GS/SD1	0.03	1.84	3.17	1.07	0.45	1.73	1.28	0.00	0.01
GS/SD2	0.01	1.82	2.77	0.97	0.54	1.49	1.48	0.00	0.01
GS/SD3	0.02	1.63	2.83	1.01	0.60	1.75	1.34	0.00	0.01
KC/SD1	0.03	1.90	2.98	0.69	0.31	1.65	2.06	0.00	0.01
KC/SD2	0.03	1.73	2.81	0.93	0.55	1.76	1.48	0.00	0.01
KC/SD3	0.03	1.52	3.25	0.81	0.61	1.62	1.50	0.00	0.01
KC-GS/SD1	0.02	1.33	4.06	0.50	0.66	1.41	1.86	0.00	0.02
KC-GS/SD2	0.00	0.77	3.52	0.88	0.57	1.59	1.82	0.00	0.01
KC-GS/SD3	0.01	0.97	3.20	0.92	0.60	1.51	2.12	0.00	0.02
KC-GS/SD4	0.00	0.85	3.73	0.77	0.65	1.76	2.26	0.00	0.02
KC-GS-TP/SD1	0.02	1.63	3.04	0.89	0.41	1.28	2.32	0.00	0.01
KC-GS-TP/SD2	0.02	0.95	1.96	0.67	0.58	1.51	2.55	0.00	0.01
KC-GS-TP/SD3	0.02	0.89	3.75	0.74	0.53	1.56	2.18	0.00	0.02
KC-GS-TP-AS/SD	0.04	1.20	2.21	0.71	0.53	1.66	2.38	0.00	0.02
FB/SD1	0.15	2.09	2.94	0.74	0.55	1.65	1.67	0.00	0.01
FB/SD2	0.14	2.22	3.27	0.77	0.71	1.88	1.78	0.00	0.01
FB/SD3	0.03	1.22	2.48	0.79	0.42	1.75	1.83	0.00	0.02
FB-AS/SD	0.01	0.92	2.45	0.71	0.48	2.05	1.93	0.00	0.02
AS1/SD1	0.02	0.82	2.65	0.67	0.44	1.66	1.68	0.00	0.01
AS2/SD2	0.02	1.32	3.81	0.91	0.42	1.50	1.61	0.00	0.02
AS3/SD3	0.02	1.38	2.65	0.87	0.31	1.65	1.89	0.00	0.02
AS4/SD4	0.02	1.53	2.08	0.77	0.59	2.23	2.29	0.00	0.02
AS5/SD5	0.02	1.20	2.24	0.77	0.52	2.55	2.93	0.00	0.03
AS6/SD6	0.02	0.96	2.50	0.63	0.61	2.73	3.19	0.00	0.03
CONTROL1/SD	0.04	1.34	2.14	0.74	0.34	1.33	1.31	0.00	0.01
CONTROL2/SD	0.01	0.96	3.51	0.50	0.31	1.46	1.41	0.00	0.01
Mean	0.03	1.34	2.92	0.79	0.51	1.72	1.93	0.00	0.02

CF≤1 = low contamination; 1≤CF≤3 = moderate contamination; 3≤CF≤6 = considerable contamination

Table 4.11f: Geo-accumulation indices (I_{geo}) of heavy metals in Asa River Sediments

Samples Sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn	Itot
GS/SD1	-5.64	0.30	1.08	-0.47	-1.74	0.20	-0.23	-11.25	-7.38	-25.73
GS/SD2	-6.64	0.28	0.89	-0.62	-1.47	-0.01	-0.01	-11.57	-6.97	-26.12
GS/SD3	-5.97	0.12	0.91	-0.58	-1.32	0.23	-0.17	-11.02	-6.97	-24.77
KC/SD1	-5.64	0.33	0.99	-1.12	-2.25	0.14	0.45	-11.61	-6.97	-26.32
KC/SD2	-5.44	0.20	0.90	-0.67	-1.43	0.24	-0.01	-11.44	-6.64	-26.13
KC/SD3	-5.80	0.01	1.12	-0.89	-1.29	0.11	0.00	-11.57	-6.84	-26.99
KC-GS/SD1	-3.64	-0.18	1.44	-1.60	-1.18	-0.09	0.31	-11.32	-6.64	-28.78
KC-GS/SD2	-8.97	-0.97	1.23	-0.76	-1.40	0.08	0.28	-11.75	-6.67	-32.71
KC-GS/SD3	-7.97	-0.64	1.09	-0.71	-1.32	0.01	0.50	-11.05	-6.27	-26.36
KC-GS/SD4	-8.38	-0.84	1.32	-0.94	-1.22	0.24	0.59	-11.29	-6.38	-26.90
KC-GS-TP/SD1	-6.06	0.11	1.02	-0.76	-1.89	-0.23	0.62	-10.85	-6.95	-24.99
KC-GS-TP/SD2	-6.06	-0.67	0.39	-1.15	-1.36	0.01	0.77	-11.15	-6.98	-26.20
KC-GS-TP/SD3	-6.27	-0.76	1.32	-1.00	-1.47	0.06	0.54	-11.05	-6.69	-25.32
KC-GS-TP-AS/SD	-5.32	-0.32	0.56	-1.09	-1.47	0.15	0.67	-10.59	-6.24	-23.65
FB/SD1	-3.29	0.49	0.97	-1.03	-1.47	0.14	0.15	-11.05	-6.73	-21.82
FB/SD2	-3.44	0.57	1.12	-0.97	-1.09	0.32	0.25	-10.88	-6.80	-20.92
FB/SD3	-5.80	-0.30	0.73	-0.92	-1.84	0.23	0.29	-11.12	-6.24	-24.97
FB-AS/SD	-7.38	-0.71	0.70	-1.09	-1.64	0.45	0.37	-10.94	-6.16	-26.40
AS1/SD1	-6.06	-0.86	0.82	-1.15	-1.79	0.15	0.16	-10.88	-6.86	-26.47
AS2/SD2	-6.06	-0.18	1.34	-0.74	-1.84	0.00	0.10	-10.94	-6.51	-24.83
AS3/SD3	-6.06	-0.12	0.82	-0.79	-2.25	0.14	0.33	-10.75	-6.51	-25.19
AS4/SD4	-6.51	0.03	0.46	-0.97	-1.36	0.58	0.61	-10.80	-6.38	-24.34
AS5/SD5	-6.38	-0.32	0.58	-0.97	-1.56	0.77	0.97	-10.63	-5.88	-23.42
AS6/SD6	-6.27	-0.71	0.74	-1.25	-1.29	0.86	1.09	-10.40	-5.64	-22.87
CONTROL1/SD	-5.44	-0.16	0.52	-1.03	-2.12	-0.18	-0.18	-11.61	-7.16	-27.36
CONTROL2/SD	-7.16	-0.64	1.23	-1.56	-2.25	-0.03	-0.09	-11.32	-6.97	-28.79

Table 4.11g: Modified hazard quotients (mHQ) for heavy metals at all sites

Sampling sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
GS/SD1	0.14	1.57	1.78	1.93	1.49	0.52	1.13	0.02	0.09
GS/SD2	0.10	1.56	1.66	1.84	1.63	0.48	1.21	0.02	0.11
GS/SD3	0.13	1.48	1.68	1.88	1.72	0.52	1.16	0.02	0.11
KC/SD1	0.15	1.60	1.73	1.55	1.24	0.51	1.44	0.02	0.11
KC/SD2	0.15	1.53	1.68	1.80	1.66	0.53	1.22	0.02	0.12
KC/SD3	0.14	1.43	1.80	1.68	1.74	0.50	1.22	0.02	0.11
KC-GS/SD1	0.09	1.33	2.02	1.32	1.81	0.47	1.36	0.02	0.13
KC-GS/SD2	0.04	1.01	1.88	1.75	1.69	0.50	1.35	0.02	0.12
KC-GS/SD3	0.07	1.14	1.79	1.78	1.73	0.49	1.45	0.02	0.14
KC-GS/SD4	0.06	1.07	1.93	1.64	1.79	0.53	1.50	0.02	0.14
KC-GS-TP/SD1	0.39	1.48	1.74	1.76	1.42	0.45	1.52	0.02	0.11
KC-GS-TP/SD2	0.39	1.13	1.40	1.53	1.70	0.49	1.60	0.02	0.11
KC-GS-TP/SD3	0.12	1.09	1.94	1.61	1.62	0.50	1.48	0.02	0.12
KC-GS-TP-AS/SD	0.16	1.27	1.49	1.57	1.63	0.51	1.54	0.03	0.14

mHQ < 0.5 = nil to very low severity of contamination; 0.5 < mHQ < 1.0 = very low severity of contamination; 1.0 < mHQ <1.5 = low severity of contamination; 1.5 < mHQ < 2.0 = moderate severity of contamination

Table 4.11g (cont'd): Modified hazard quotients for heavy metals at all sites

Sampling sites	Pb	Cu	Co	Cr	Ni	Zn	Al	Fe	Mn
FB/SD1	0.33	1.68	1.72	1.60	1.64	0.51	1.29	0.02	0.12
FB/SD2	0.31	1.73	1.81	1.63	1.88	0.54	1.33	0.02	0.12
FB/SD3	0.13	1.28	1.58	1.66	1.44	0.52	1.35	0.02	0.14
FB-AS/SD	0.08	1.11	1.56	1.57	1.54	0.57	1.39	0.02	0.15
AS1/SD1	0.13	1.05	1.63	1.53	1.47	0.51	1.30	0.02	0.11
AS2/SD2	0.13	1.33	1.95	1.77	1.44	0.49	1.27	0.02	0.13
AS3/SD3	0.12	1.36	1.63	1.74	1.24	0.51	1.38	0.02	0.13
AS4/SD4	0.11	1.43	1.44	1.64	1.70	0.59	1.51	0.02	0.13
AS5/SD5	0.11	1.27	1.50	1.63	1.60	0.63	1.71	0.03	0.16
AS6/SD6	0.12	1.11	1.58	1.48	1.74	0.66	1.79	0.03	0.17
CONTROL 1/SD	0.16	1.34	1.46	1.60	1.31	0.46	1.15	0.02	0.10
CONTROL 2/SD	0.08	1.33	1.87	1.32	1.24	0.48	1.19	0.02	0.11
Mean	0.15	1.33	1.70	1.65	1.53	0.50	1.38	0.02	0.12

mHQ < 0.5 = nil to very low severity of contamination; 0.5 < mHQ < 1.0 = very low severity of contamination; 1.0 < mHQ <1.5 = low severity of contamination; 1.5 < mHQ < 2.0 = moderate severity of contamination

Table 4.11h: Ecological Contamination Index (ECI) and eigen values

Heavy metals	ECI	Eigen values
Pb	1.36	9.00
Cu	5.46	4.11
Co	6.38	3.75
Cr	3.98	2.42
Ni	1.70	1.11
Zn	1.70	3.39
Al	1.50	1.09
Fe	0.07	3.14
Mn	0.46	3.92

ECI < 2 = uncontaminated; 2 < ECI < 3 = uncontaminated to slightly contaminated; 3 < ECI < 4 = slightly to moderately contaminated; 4 < ECI < 5 = moderately to considerable contaminated; 5 < ECI < 6 = considerably to highly contaminated; 6 < ECI < 7 = highly contaminated

4.3.2 Correlation of surface water and sediment for heavy metal contaminants

The table 4.12 to 4.14 reveals the correlation analysis of heavy metal parameter from surface water to sediment. 10 is degree of freedom at 5% significant level with critical table value = 0.553. Lead concentrations reveal $r_{cal}>r_{table}$ for sampling sites GS-1, TP-2, FB-1, KC-GS, KC-GS-TP, AS5, AS6 therefore null hypothesis was rejected and concluded that this parameter in sediment do have influence on the surface water while the other sites do not have influence. Copper concentrations reveal $r_{cal}>r_{table}$ for sampling sites GS-1, TP-2, KC-3, KC-GS, AS6 therefore null hypothesis was rejected and concluded that this parameter in sediment do have influence on the surface water while the other sites do not have influence. Chromium concentrations reveal $r_{cal}>r_{table}$ for sampling sites GS-1, TP-2, KC-3, FB-2, KS-GS, KC-GS-TP, AS4, AS5, AS6, CTR-1 therefore null hypothesis was rejected and concluded that this parameter in sediment do have influence on the surface water while site FB-1 do not have influence.

4.4 Groundwater quality assessment

Groundwater which occurs beneath the earth surface is considered free from contamination; hence usable bur anthropogenic as well as natural factors are affecting the quality as well as quantity of this valuable resource. It has been estimated that once pollution enters the subsurface environment, it may remain concealed for many years, becoming dispersed over wide areas of groundwater aquifer and rendering groundwater supplies unsuitable for consumption on and other uses. Therefore, understanding the potential influences of human activity on groundwater is important for protection and sustainable use of groundwater resources (Jehagir *et al.*, 2011). Shallow wells are normally located in the valley, where the groundwater is relatively high (1-4 m below ground level) and infiltration of rain and river water plays a main part in groundwater recharge (Pritchard *et al*., 2008).

Table 4:12: Correlation of surface water and sediment for lead concentration in selected sampling sites

SITES	GS-1	TP-2	KC-3	FB-4a	FB-4c	KC-GS	KC-GS-TP	AS-4	AS-5	AS-6	CTR 1
GS-1	1										
TP-2	0.80	1									
KC-3	0.17	0.80	1								
FB-4a	0.69	0.17	0.80	1							
FB-4c	0.14	0.69	0.17	0.80	1						
KC-GS	0.63	0.14	0.69	0.17	0.80	1					
KC-GS-TP	0.86	0.63	0.14	0.69	0.17	0.80	1				
AS-4	0.52	0.86	0.63	0.14	0.69	0.17	0.80	1			
AS-5	0.98	0.52	0.86	0.63	0.14	0.69	0.17	0.80	1		
AS-6	0.87	0.98	0.52	0.86	0.63	0.14	0.69	0.17	0.80	1	
CTR 1	0.05	0.87	0.98	0.52	0.86	0.63	0.14	0.69	0.17	0.80	1

Table 4:13: Correlation of surface water and sediment for copper concentration in selected sampling sites

SITES	GS-1	TP-2	KC-3	FB-4a	FB-4c	KC-GS	KC-GS-TP	AS-4	AS-5	AS-6	CTR 1
GS-1	1										
TP-2	0.97	1									
KC-3	0.95	0.97	1								
FB-4a	0.44	0.95	0.97	1							
FB-4c	0.44	0.44	0.95	0.97	1						
KC-GS	0.91	0.44	0.44	0.95	0.97	1					
KC-GS-TP	0.21	0.91	0.44	0.44	0.95	0.97	1				
AS-4	0.06	0.21	0.91	0.44	0.44	0.95	0.97	1			
AS-5	0.37	0.06	0.21	0.91	0.44	0.44	0.95	0.97	1		
AS-6	0.85	0.37	0.06	0.21	0.91	0.44	0.44	0.95	0.97	1	
CTR 1	-0.30	0.85	0.37	0.06	0.21	0.91	0.44	0.44	0.95	0.97	1

Table 4:14: Correlation of surface water and sediment for Chromium concentration in selected sampling sites

SITES	GS-1	TP-2	KC-3	FB-4a	FB-4c	KC-GS	KC-GS-TP	AS-4	AS-5	AS-6	CTR 1
GS-1	1										
TP-2	0.78	1									
KC-3	0.90	0.78	1								
FB-4a	0.20	0.90	0.78	1							
FB-4c	0.63	0.20	0.90	0.78	1						
KC-GS	0.60	0.63	0.20	0.90	0.78	1					
KC-GS-TP	0.80	0.60	0.63	0.20	0.90	0.78	1				
AS-4	-0.75	0.80	0.60	0.63	0.20	0.90	0.78	1			
AS-5	0.81	-0.75	0.80	0.60	0.63	0.20	0.90	0.78	1		
AS-6	-0.94	0.81	-0.75	0.80	0.60	0.63	0.20	0.90	0.78	1	
CTR 1	-0.81	-0.94	0.81	-0.75	0.80	0.60	0.63	0.20	0.90	0.78	1

Groundwater contamination is the result of polluted water infiltrating through the soil and rock and eventually reaching the groundwater. This process might take many years and might take place at varying distances from various wells where such contaminations are found. Once the groundwater is contaminated, it is very difficult to remediate. No doubt that the new technologies will always reduce the pollution level (Geetha *et al*., 2008). Human health, agricultural development and the ecosystems are all at risk unless water and land systems are effectively managed (Kehinde *et al*., 2009).

Pollution of groundwater refers to any deterioration in the quality of the water resulting from the activities of man. This definition also includes apparently natural processes like salt water encroachment into freshwater-bearing aquifers in coastal areas resulting from the artificial lowering of groundwater heads. Most pollution of groundwater results from the disposal of domestic, municipal and industrial wastes on the land surface, in shallow excavations including septic tanks, or through deep wells and mines; the use of fertilizers and other agricultural chemicals; leaks in sewers, storage tanks, and pipelines; and animal feedlots. The magnitude of a pollution problem depends on the size of the affected area, the amount of the pollutant involved, the solubility, toxicity and density of the pollutant, the mineral composition and hydraulic characteristics of the soils and rocks through which the pollutant moves and the effect or potential effect on groundwater use.

Depending on the area under study, underground water quality in basins are based on various factors such as influx of industrial effluents, influx of water through rainfall, soil, agriculture pattern etc. Therefore we can say that by these factors, the underground water quality can be varied qualitatively and quantitatively. The aim of this aspect is to evaluate the source of portable water from the six locations and to clarify the concerns about the quality and safety of water used as drinking water within the locality.

4.4.1 pH and alkalinity

pH and alkalinity results recorded for six sampling sites are revealed in table 4.15. The acidity or basicity of domestic water is expressed as pH (<7.0 acidic; >7.0 basic). The normal pH range for domestic or drinking water is from 6.5 to 8.5 according to (WHO, 2004b). The highest value of pH recorded during the dry season was at FB/GW and GS/GW. Statistical analysis showed pH to be higher during the wet seasons than the dry season. The values generally were found to be within the recommended range for WHO and NSWDQ respectively for both seasons (figure 4.8).

Abnormally, low pHs are not common in Nigeria, but where observed to occur, it may cause accelerated corrosion of the various metal mediums where the water may be stored for future use. High pHs above 8.5 are often caused by high bicarbonate (HCO_3^-) and trioxocarbonate (CO_3^{2-}) concentrations. High carbonates cause Calcium and Magnesium ions to form insoluble minerals leaving Sodium as the dominant ion in solution. This is in conformity with the findings of (Musa and Ahanonu, 2013) on shallow groundwater in Patigi Local Government, Kwara State.

4.4.2 Colour

Colour results recorded for six sampling sites are revealed in table 4.15. The appearance of water can be significant factor in consumer satisfaction. Low levels of colour are important for drinking water.

The two seasons colour was within the permissible level recommended by (WHO, 2004b) which is 15 Hu for drinking water. Only site AS5/GW recorded a value higher than the recommended value of 15 Hu which is 16.0 Hu. The source of colour in water can include natural metallic ions (Iron and Manganese), humic and fulvic acids from humus and peat materials, plankton, dissolved plant components, Iron and Sulphur bacteria, and industrial wastes or the dissolved soil particles within the areas where it is high as most of the soil as either clay or loam soils. This is in conformity with the works of (Adejuwon and Adeniyi, 2011). Pure drinking and domestic water is a colourless liquid. Therefore, colour in water is suggestive of the presence of foreign, water-soluble substances (organic and inorganic). Thus, the coloured appearance of water obtained from the well during the rainy season from AS5/GW suggest contamination, which may have its origin in dissolved products of the decay dead natural vegetation as rainwater infiltrates to the groundwater table or it may be due to surface runoffs making input into poorly covered or lined wells.

4.4.3 Turbidity

Turbidity results recorded for six sampling sites are revealed in table 4.15.Clarity of water is said to be a major factor in consumer satisfaction. Thus, turbidity has been used over many years as an indicator of drinking water quality and as an indicator of the efficiency of drinking water coagulation and filtration processes. Thus the results from the seven study wells during the rainy and dry season for the period of two years of sampling were found to be higher than the recommended values of (WHO, 2004b and NSWDQ, 2007). In general, this result corresponds with the works of (Zamxaka *et al.*, 2004) except for dry season.

Turbidity has been described as a relatively crude method of detecting a wide variety of particles from a wide assortment of sources as it provides no information about the nature of the particles. Turbidity in water is caused by the presence of colloidal and suspended matter (such as clay, silt, finely divided organic and inorganic matter, plankton, and other microscopic organisms). The added presence of turbidity increases the apparent, but not the true colour of water.

4.4.4 Total solid, total dissolved solid and suspended solid

The solids results recorded for six sampling sites are revealed in table 4.15.The total suspended solid concentration was found to be high in all the underground water within the considered study areas. Although in both seasons, the observed suspended solids were found to be in range with the recommended values for WHO, 2004b and NSWDQ, 2007). This finding followed a similar trend with the works of (Adejuwon and Adeniyi, 2011). It was observed that total solid and dissolved solid had higher values recorded in the rainy season than in the dry season.

4.4.5 Total hardness, Calcium hardness and Magnesium hardness

The hardness results recorded for six sampling sites are revealed in table 4.15.Hardness is generally defined as the sum of the polyvalent cations present in water and expressed as an equivalent quantity of calcium carbonate ($CaCO_3$). The most common cations are Calcium and Magnesium. This can also be defined to be a measure of the capacity of the water for precipitating soap. It is this aspect of hard water that is the most perceptible to consumers. From the various samples collected, it was revealed that wet season had a higher value than the dry season throughout the sampling period. These values were found to be lower than the recommended value of (NSWDQ, 2007) which is stated to be 15.0 mg/L $CaCO_3$ while the (WHO, 2004b) did not have any specified value. This reveals that all the groundwater are soft waters and satisfactory for as drinking facility, this is contrary to what was observed in Patigi shallow underground waters by (Musa and Ahanonu, 2013).

Table 4.15: Range and mean concentrations of groundwater physicochemical parameters

PARAMETERS		GS/GW	TP/GW	KC/GW	FB/GW	AS5/GW	AS6/GW
pH	Range	7.10-7.20	6.80-7.30	6.80-7.30	7.10-7.30	6.30-6.50	6.30-6.50
	mean±SD	7.15±0.06	6.98±0.22	6.98±0.22	7.20±0.08	6.40±0.08	6.40±0.08
Alkalinity (mg/L)	Range	45.00-70.00	55.00-65.00	45.00-65.00	55.00-65.00	45.00-50.00	45.00-55.00
	mean±SD	57.50±11.9	60.00±4.08	55.00±9.13	60.00±4.08	47.50±2.89	51.25±4.79
Colour (Hu)	Range	4.00-6.00	5.00-8.00	4.00-6.00	4.00-6.00	10.00-22.00	8.00-13.00
	mean±SD	4.75±0.96	5.75±1.50	4.75±0.96	4.75±0.82	16.00±5.89	10.50±2.38
Turbidity (NTU)	Range	3.00-6.00	4.00-6.00	3.00-6.20	4.00-6.00	8.00-13.50	8.50-13.00
	mean±SD	4.50±1.29	5.00±0.82	4.55±1.37	5.00±0.82	10.75±2.66	10.88±2.21
TS (mg/L)	Range	95.00-101.00	100.00-105.00	106.00-110.00	95.00-104.00	246.00-292.00	284.00-365.00
	mean±SD	98.00±2.94	102.50±2.38	107.75±1.71	99.75±4.92	268.75±25.71	324.50±46.19
TDS (mg/L)	Range	68.00-73.00	71.00-77.00	69.00-72.00	72.00-74.00	180.00-219.00	234.00-298.00
	mean±SD	70.50±2.38	74.00±2.94	70.75±1.50	72.75±0.96	119.50±21.95	265.50±35.82
SS (mg/L)	Range	17.00-28.00	28.00-29.00	36.00-38.00	22.00-32.00	66.00-73.00	50.00-70.00
	mean±SD	25.00±5.35	28.50±0.58	37.00±0.82	27.00±4.76	69.25±3.77	59.00±10.52
TH (mg/L)	Range	43.00-50.00	45.00-52.00	38.00-50.00	51.00-55.00	63.00-70.00	70.00-78.00
	mean±SD	46.50±3.11	49.75±4.03	44.00±5.89	52.50±1.73	66.25±3.30	74.00±3.65
MgH (mg/L)	Range	16.00-19.00	18.00-26.00	14.00-22.00	21.00-26.00	28.00-28.00	35.00-36.00
	mean±SD	17.25±1.50	22.00±4.16	20.25±4.35	23.75±2.06	28.0±0.00	35.75±0.50
CaH (mg/L)	Range	25.00-34.00	27.00-40.00	17.00-28.00	24.00-30.00	28.00-42.00	35.00-42.00
	mean±SD	29.25±4.43	30.75±6.18	22.25±5.56	27.75±2.63	35.25±5.74	38.25±3.30

Table 4.16: Mean concentration of groundwater physicochemical parameters for dry and rainy season over sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV. 2014 – APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014-OCT.2014]
pH	6.81±0.21	6.89±0.92
Alkalinity	52.86±28.28	60.36±24.75
Colour	6.07±2.12	9.00±7.07
Turbidity	5.57±0.11	7.63±4.10
Total solid	146.64±2.12	168.29±5.66
Total dissolved solid	110.64±0.71	126.29±5.66
Suspended solid	35.29±8.49	42.00±11.31
Total hardness	53.14±7.07	57.71±11.31
Magnesium hardness	24.36±3.54	24.93±2.12
Calcium hardness	28.79±3.54	32.07±6.36

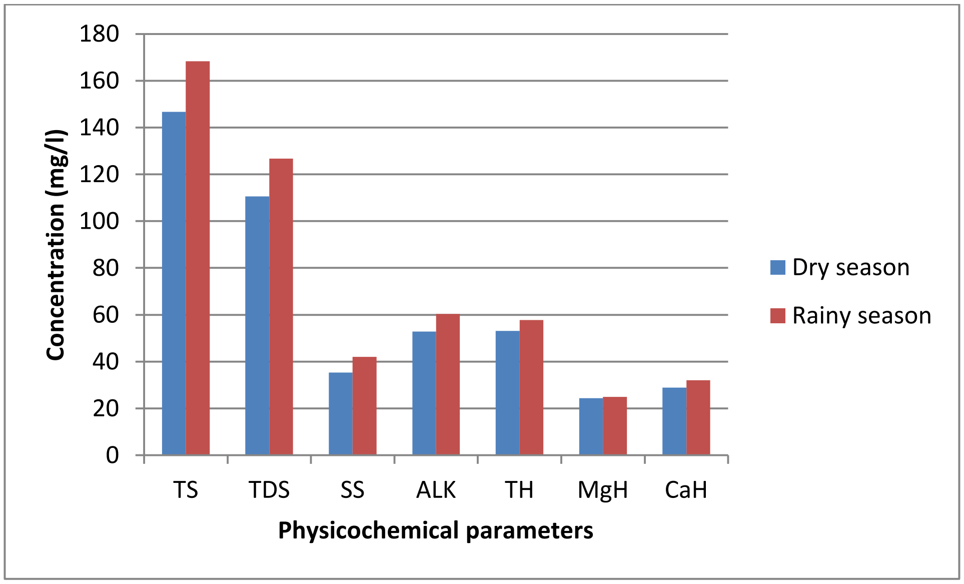

Figure 4.8: Seasonal variations in the concentrations of physicochemical parameters of groundwater samples

4.4.6 Nutrient loading of groundwater

Nutrient loading results recorded for six sampling sites are revealed in table 4.16 and 4.17 respectively. Sulphate values for both dry and wet season (figure 4.9) were observed to be below the recommended values of both WHO and NSWDQ. Sulphate is a naturally occurring anion. High concentration of sulphate in drinking water may cause transitory diarrhea (Nowak *et al*., 2006). However, toxicity is rarely a problem, except at very high concentrations where high sulphate may interfere with uptake of other nutrients. Sulphate in irrigation water has fertility benefits, and irrigation water in Colorado often has enough sulphate for maximum production for most crops.

Nitrate had mean values of rainy season relatively higher compared with the recommended values of (WHO, 2004b) and (NSWDQ, 2007). This can be attributed to high rate of inorganic fertilizer and chemical application on the surrounding farmLands. Nitrate is one of the major anions in natural waters, but concentrations can be greatly elevated due to leaching of Nitrogen from fertilizers. The mean concentration of nitrate nitrogen (NO_3-N, nitrate measured as nitrogen in testing) in a typical surface water supply would be around 0.2 to 2 mg/L; however, the individual wells considered in this study showed a significantly higher concentrations during the wet season and dry season respectively. This is also in conformity with the study carried out by (Akiwumi *et al*., 2012) on groundwater of Ilorin environs and (Musa and Ahanonu, 2013).

Chloride concentrations revealed in this study was lower for both dry and rainy seasons when compared with the WHO recommended permissible level of 250 mg/l throughout that of NSWDQ was not available. Chloride is one of the constituents found in human excreta. Like nitrate, the chloride in the samples could be possibly traced to fecal contamination of shallow wells.

Phosphate levels in this research work were below the permissible level of 5 mg/l required by (WHO, 2004b). The elevated phosphate concentrations in water have been linked to increasing rates of plant growth, changes in species composition and proliferation of plank tonic and epiphytic and epibenthic algae, resulting in shading of higher plant which was not in conformity with the research carried out in this study.

Ammonia is the initial product of the decay of nitrogenous organic waste and its presence frequently is indicative of such waste. Consequently, the increasing concentration of ammonia-nitrogen downstream strongly indicates continuous addition of nitrogenous organic waste mainly from domestic and industrial sources downstream (Adebayo and Usman, 2009). The permissible level of ammonia is 0.2 mg/L but all the values in this study were below the permissible level. Ammonia in drinking water is not of immediate health relevance and therefore no health-based guideline value is proposed. However, ammonia can compromise disinfection efficiency, result in nitrite formation in distribution systems, cause the failure of filters for the removal of Manganese and cause taste and odour problems.

Table 4.17: Range and mean concentrations of groundwater nutrient loadings

PARAMETERS		GS/GW	TP/GW	KC/GW	FB/GW	AS5/GW	AS6/GW
Sulphate (mg/L)	Range	7.10-8.00	7.60-10.00	8.20-9.00	8.00-10.00	12.00-16.50	12.00-17.00
	mean±SD	7.45±2.45	8.60±1.12	8.53±1.57	9.00±0.82	14.25±2.10	14.50±2.61
Ammonia (mg/L)	Range	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00	0.02-0.04	0.01-0.03
	mean±SD	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.03±0.01	0.02±0.01
Nitrate (mg/L)	Range	0.20-0.60	0.30-0.70	0.60-1.00	0.50-0.70	0.90-1.30	0.70-1.45
	mean±SD	0.40±2.62	0.50±2.54	0.80±0.18	0.60±0.08	1.10±0.18	1.10±0.38
Phosphate (mg/L)	Range	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00	0.10-0.30	0.15-0.40
	mean±SD	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.20±0.83	0.26±0.11
Chloride (mg/L)	Range	5.90-8.10	6.00-10.00	6.00-7.2	6.90-7.60	11.00-14.00	11.00-13.00
	mean±SD	7.00±1.21	8.00±1.83	6.80±0.54	7.25±0.35	12.63±1.38	11.63±1.38

Table 4.18: Mean and standard deviation of groundwater nutrient loading for dry and rainy season over sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT. 2014]
Sulphate	9.27±2.83	11.29±3.54
Ammonia	0.01±0.00	0.01±0.01
Nitrate	0.59±0.49	0.86±0.49
Phosphate	0.02±0.04	0.09±0.14
Chloride	8.20±0.85	9.97±1.84

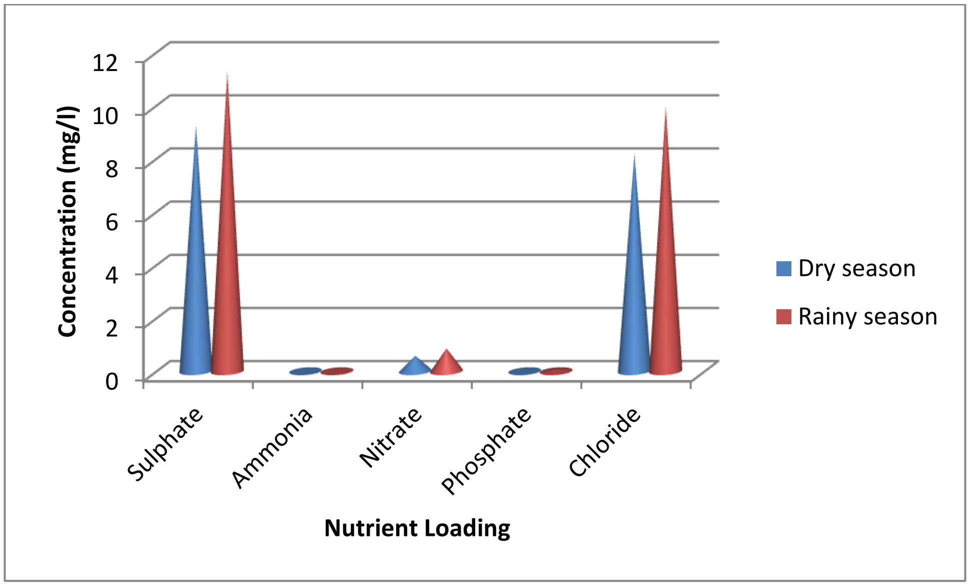

Figure 4.9: Seasonal variations in the concentrations of nutrient loading parameters of groundwater samples

4.4.7 Metals and heavy metals

Metals and heavy metals results recorded for six sampling sites are revealed in table 4.18 and 4.19 respectively. Water containing Sodium (Na^+) with carbonate and chloride or sulphate is termed as alkali or saline water respectively. Sodium is a naturally occurring constituent of drinking water. Food is the major source of sodium. Of a suggested maximum daily intake of 2400 mg drinking water at a typical concentration of 20 mg/L, contributes less than 2% assuming consumption of 2 L/day. Average adult intake is 1000 mg/day. The sodium value obtained in both dry and rainy seasons are far below the permissible level of WHO standard of 200 mg/L. Iron concentration values of some groundwater bodies considered in this study were above the permissible level of WHO standard which is 0.3 mg/L and the sites are FB/GW, AS5/GW and AS6/GW while the rest are below the WHO standard for drinking water quality. The ones high can be attributed to the washing of some iron materials around the edge of the well which will find their ways into the same. The samples analysed during the wet season was significantly higher than that of the dry season (figure 4.10) but still within the permissible limit of 0.3 mg/L that is based on taste and appearance rather than detrimental to health effect. Iron is not considered hazardous to health. In fact, it is an essential element for good health because it transports Oxygen in the blood. Iron is considered a secondary anesthetics contaminant (WHO, 2004b).

Copper is commonly found in drinking water (Eze *et al*., 2017) though it is a nutritional requirement. Insufficient copper causes anemia, skeletal defects, nervous system degeneration and reproductive abnormalities. For both wet and dry seasons (figure 4.10), the values were observed not to be higher than recommended values of 1.3 mg/L for (WHO, 2004b) and 1.0 ppm for (NSDWQ, 2007). When the values were further compared against the seasons, it was observed that the values obtained during the rainy season were higher than that of the dry season.

Zinc commonly occurs in source waters and may leach into finished waters through corrosion of galvanised metal roofing sheets which mostly used in these areas. The zinc

content during the dry season and rainy season were within the WHO standard for drinking water quality. Drinking water containing zinc typically contributes to the basic requirement of 15 mg/L for male and12 mg/L for female as recommended by WHO.
Cadmium was not detected in all the water samples analysed throughout the period of sampling and this reveals that impurity in zinc which is mostly used as roofing materials have not found their way into the groundwater bodies.

Lead occurs in drinking water primarily from corrosion of lead pipe, solders and faucets constructed with leaded brass, especially in areas of soft or acidic water. The values obtained during the dry and art season were compared with the standards of WHO, 2004b) and (NSWDQ, 2007), it was observed that the values obtained during the wet and dry season were below the recommended values which again could be linked to the effect of runoff and infiltration activities. Health effects of lead are generally correlated with blood test levels. Infants and young children absorb ingested lead more readily than do older children and young adults. Lead exposure across a broad range of blood lead levels is associated with a continuum of path physiological effects, including interference with heme synthesis necessary for formation of red blood cells, anemia, kidney damage, impaired reproductive function, interference with vitamin D metabolism, impaired cognitive performance, delayed neurological and physical development, and elevations in blood pressure (Brown, 2007).

Chromium in water primary sources are usually from mining areas, wastes from electroplating operations which is not a common practice in all the sites considered for this study and garbage or refuse dump sites which is very much common in all the study areas. The Chromium values for both dry and rainy season were lower compared to the recommended (NSWDQ, 2007) value. This could be linked also to the rate of runoff and infiltration activities within the various sites. Chromium in excess is toxic thus leading to liver and kidney damage, internal hemorrhage, and respiratory disorders, as well as causing cancer in humans and animals through inhalation exposure, but it has not been shown to be carcinogenic through ingestion exposure (Eze *et al*., 2017; Pandey *et al*., 2014).

Table 4.19: Range and mean concentrations of groundwater metals and heavy metals loadings

PARAMETERS		GS/GW	TP/GW	KC/GW	FB/GW	AS5/GW	AS6/GW
Calcium (mg/L)	Range	12.40-12.90	11.00-11.20	7.80-9.70	11.10-11.40	14.20-17.00	14.20-17.00
	mean±SD	12.65±0.24	11.10±0.12	8.78±1.16	11.23±0.13	15.40±1.34	15.40±1.34
Magnesium (mg/L)	Range	4.40-5.30	8.00-8.60	7.40-8.50	8.00-8.20	8.40-8.80	12.00-12.20
	mean±SD	4.89±0.44	8.25±0.30	7.98±0.56	8.10±2.71	8.60±1.13	12.00±0.12
Sodium (mg/L)	Range	0.60-0.90	0.50-0.90	1.00-1.30	0.70-0.80	1.30-1.70	1.10-1.45
	mean±SD	0.78±0.15	0.70±0.18	1.15±0.13	0.75±0.06	1.50±0.18	1.28±0.16
Iron (mg/L)	Range	0.10-0.20	0.10-0.30	0.00-0.20	0.20-0.35	0.30-0.70	0.45-0.90
	mean±SD	0.15±0.04	0.19±0.09	0.09±0.10	0.26±0.06	0.50±0.18	0.66±0.22
Copper (mg/L)	Range	0.00-0.00	0.00-0.00	0.00-0.04	0.00-0.00	0.10-0.30	0.00-0.20
	mean±SD	0.00±0.00	0.00±0.00	0.02±0.02	0.00±0.00	0.22±0.09	0.08±0.10
Zinc (mg/L)	Range	0.50-0.80	0.30-0.60	0.30-0.60	0.30-0.40	1.00-1.30	0.80-2.00
	mean±SD	0.65±0.13	0.45±0.13	0.45±0.13	0.35±0.06	1.15±0.13	1.23±0.53
Cadmium (mg/L)	Range	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00
	mean±SD	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00
Lead (mg/L)	Range	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.03
	mean±SD	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00	0.013±1.73
Chromium (mg/L)	Range	0.00-0.00	0.01-0.02	0.01-0.03	0.00-0.00	0.12-0.20	0.02-0.04
	mean±SD	0.00±0.00	0.01±0.00	0.02±0.01	0.00±0.00	0.15±0.04	0.12±0.01

Table 4.20: Mean and standard deviation of groundwater metals and heavy metals loading for dry and rainy season over sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT. 2014]
Calcium	11.99±0.85	12.74±1.70
Magnesium	8.29±0.57	8.63±0.28
Sodium	0.89±0.21	1.11±0.42
Iron	0.22±0.18	0.39±0.42
Copper	0.03±0.08	0.07±0.18
Zinc	0.56±0.07	0.76±1.10
Cadmium	0.00±0.00	0.00±0.00
Lead	0.00±0.00	0.00±0.01
Chromium	0.03±0.01	0.04±0.05

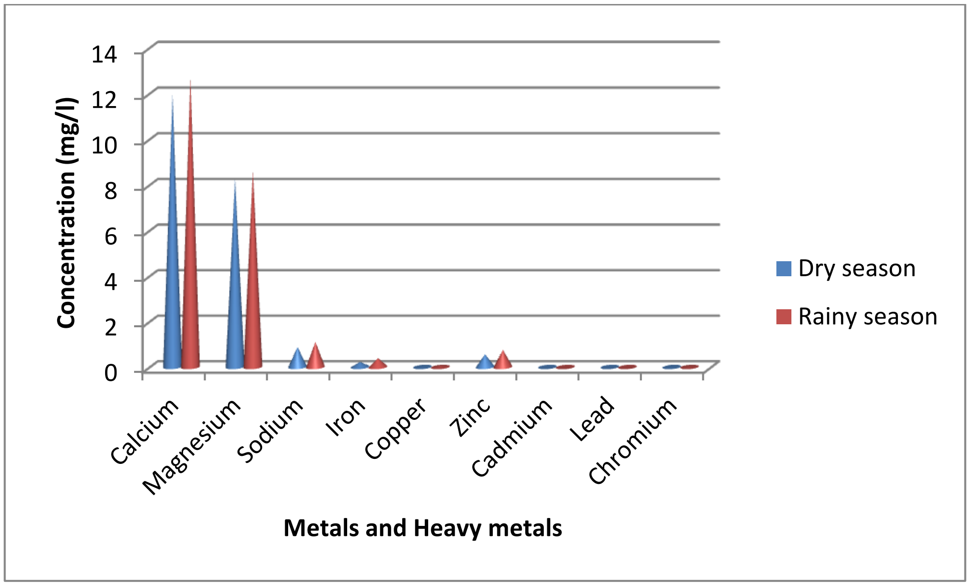

Figure 4.10: Seasonal variations in the concentrations of metals and heavy metals parameters of groundwater samples

4.5 Organic compounds in water and sediment samples

Organic compounds are chemicals that have high vapour pressure at ordinary room temperature conditions. Their high vapour pressure results from a low boiling point, which causes large numbers of molecules to evaporate or sublimate from the liquid or solid form of the compound and enter the surrounding air.

Volatile organic compounds are numerous, varied and ubiquitous (Goldstein and Galbally, 2007). They include both human-made and naturally occurring chemical compounds. Volatile organic compounds are primary precursors to the formation of ground level ozone and particulate matter in the atmosphere, which are main ingredients of air pollutant referred to as smog. The major anthropogenic sources of concern are transportation sector, the use of solvents and solvent containing products, and industrial sources (Behr and Johnen, 2009).

In this research, our focus is on Asa River, which was pointed out that the river is subject to high level of eutrophication due to organic matter and industrial discharge into it (Eletta and Adekola, 2005). It was also reported that Asa River catchment was found to have high precipitation and sediment yields when analysed yearly for a period of seven years (Jimoh and Ajao, 2009).

It is based on the findings that the researcher seeks to analyse the limitation, which has not been reviewed or given attention by any researcher on Asa River, Kwara State that is volatile organic compounds and its hazards to health and environment.

This study was carried out on river water samples and sediment of Ilorin environs based on three sampling zones, which are New Yidi/Asa dam zone, Unity zone, and Amilegbe zone respectively in Kwara state, Nigeria. These areas are highly industrialised and commercialised; also, discharge of effluents from various companies into water bodies occurs majorly in these zones. Concentration at 0.01 µg/L, 0.02µg/L and 0.05 µg/L were obtained to generate a good recovery and repeatability. Correlation analysis was done to ascertain interaction between river and sediment samples (Akiwumi and Oderinde, 2013).

4.5.1 Quality Assurance and Quality Control

Quality control and quality assurance (QC/QA) include method detection limit (MDL), Gas chromatograph retention times (RT), and reproducibility for all compounds analysed. In table 4.21, a list of forty – six OCs with their physical properties is displayed. Method detection limit were betwixt 0.2 and 0.7 ppbv for organic compounds analysed. Standard deviation was betwixt 0.6% - 5.0% which is well within the limit of ±30%. 30% of the samples were analysed in triplicate for quality assurance. Percentage quality reported is the amount present in the sample.

4.6 Recovery study model for OCs in water and sediment

Recovery study was performed on investigated compounds from spiked river zone and sediment samples along Asa River route at three concentration levels. Recovery mean±SD of alkanes, alkenes, aromatics and carboxylic acids (acetic acid) can be observed in table 4.22 and 4.23 respectively.

Table 4.21: Properties, quality assurance and quality control for targeted Organic Compounds in river and sediment samples of three zones

Groups	OCs Species	MW	Bp (^oC)	Mp (^oC)	MDL	RSD	%Quality	RT
Alkanes	1, 1-dichloro-2, 2-difluoroethane	135	60	N/A	0.3	3.7	91	3.327
	Bromodichloromethane	164	87	-55	0.2	3.2	96	3.362
	Trichloromethane	119	60.5	-63	0.5	1.5	96	3.327
	Oxybis [dichloromethane]	184	39.8	N/A	0.2	0.3	96	3.785
	1, 2-dimethyl-cis cyclopentane	98	99	N/A	0.5	1.5	62	8.992
	1, 2-dimethyl-trans cyclopentane	98	92	N/A	0.5	1.5	62	8.992
	Bromomethane	94	4	-94	0.3	1.0	96	10.073
	Methylene cyclobutane	68	42	N/A	0.5	2.0	81	5.192
	2-isocyanato propane	85	74	<-75	0.3	1.0	81	3.413
	2-cyclo propyl propane	84	58	N/A	0.5	2.5	81	3.550
	Ethyl cyclobutane	84	70.7	N/A	0.5	3.6	96	4.357
	Methyl cyclopentane	98	101	-126	0.5	0.6	95	4.592
	1, 3-dimethyl-cis cyclopentane	84	80.7	6.5	0.2	3.5	53	9.016
	1, 3-dimethyl-trans cyclopentane	98	91	N/A	0.5	3.3	58	9.016
	2-chloro-1, 1, 1-trifluoroethane	119	6.9	-106	0.5	3.5	91	7.144
	1-methyl-2-octyl cyclopropane	154	203.3	n/a	0.2	3.3	62	25.975
	1, 2-diethyl cyclobutane	112	N/A	N/A	0.5	2.0	73	25.975
	1, 3-dimethyl cyclopentane	98	N/A	N/A	0.5	2.0	64	8.935
Alkenes	2-Pentene (E)	70	37	-40	0.3	2.7	93	3.613
	2-methyl-1-butene	70	31	-137	0.2	1.0	93	3.648
	2-Pentene	70	37	N/A	0.3	2.0	93	3.676
	2-Pentene (Z)	70	38	-180	0.3	1.0	93	3.699
	1, 2-dichloroethene (Z)	97	60.3	-81	0.4	1.5	57	6.697
	2-Hexene (E)	84	62	N/A	0.4	1.5	55	6.978
	3, 4-dimethyl-1-pentene	98	N/A	N/A	0.5	1.5	77	7.464
	3, 7-dimethyl-1-octane	140	156	N/A	0.5	1.0	77	7.464
	4-ethenyl cyclohexene	108	N/A	N/A	0.2	2.0	53	25.855
	1-Nonene	126	146	-81	0.5	1.6	65	26.038
	2-Butene (E)	56	1	-105	0.5	1.0	91	4.883
	2-Butene (Z)	56	3.7	-139	0.4	2.8	91	4.557
	2-Butene	56	N/A	N/A	0.3	1.5	91	4.906
	Cycloheptene	96	112	N/A	0.2	0.6	57	27.840
	1-chloro-Z-2-heptene	13.3	N/A	N/A	0.4	4.6	50	5.740
	1-Hexene	84	64	-140	0.3	1.0	90	4.929

MW = Molecular Weight; Bp = boiling point; Mp = melting point; MDL = Method Detection Limit; RSD = Relative Standard Deviation; % quality = percentage quality; RT = Retention Time

Table 4.21 (Cont'd): Properties, quality assurance and quality control for targeted OCs in river and sediment samples of three zones

Groups	OCs Species	MW	Bp (^oC)	Mp (^oC)	MDL	RSD	%Quality	RT
Aromatics	Fluorobenzene	96	85	-42	0.2	3.8	91	6.697
	2, 3, 4, 5-tetrahydropyridine	83	N/A	N/A	0.4	2.5	53	6.692
	Pyridine-D5	84	115	N/A	0.6	3.2	50	6.108
	2-chlorothiophene	119	127	N/A	0.7	4.4	62	7.018
	3-chlorothiophene	119	137	N/A	0.7	3.2	62	7.018
	Indan-1, 2, 3-trione	178	N/A	250	0.5	5.0	53	26.581
	Ninhydrin	178	N/A	250	0.5	2.5	62	26.581
Carboxylic Acids	2, 6-diamino-4-hexenoic acid	144	N/A	N/A	0.3	1.0	53	26.261
	Dichloroacetic acid	129	194	9	0.3	3.8	91	3.459
	Non-3-enyl ester acetic acid	184	234	N/A	0.3	2.0	50	28.858
	Fluroacetic acid	78	165	33	0.5	1.0	95	7.584
	2-cyano ethyl ester hexanoic acid	169	N/A	N/A	0.5	1.0	54	25.820

MW = Molecular Weight; Bp = boiling point; Mp = melting point; MDL = Method Detection Limit; RSD = Relative Standard Deviation; % quality = percentage quality; RT = Retention Time

Table 4.22: Mean recoveries and standard deviation for river zones sampled

VOCs	Concentration (µg/L)	RW-AS-1	RW-UN-2	RW-AM-3
Alkanes				
(Pentane)	0.01	101.80±3.70	102.70±3.20	100.30±1.50
	0.02	97.10±3.20	96.70±1.50	97.70±1.50
	0.05	104.00±1.00	99.00±2.00	104.00±1.00
Alkenes				
(Butene)	0.01	101.20±2.70	103.00±1.00	102.00±2.00
	0.02	102.00±1.00	103.30±1.50	98.70±1.50
	0.05	103.00±1.50	95.00±1.00	103.30±1.50
Aromatics				
(Benzene)	0.01	99.60±3.80	99.70±2.50	101.70±3.20
	0.02	99.60±4.40	101.30±3.20	100.00±5.00
	0.05	101.30±2.52	91.00±3.61	101.30±1.50
Carboxylic Acids				
(Acetic acid)	0.01	102.00±1.00	99.00±1.00	102.00±1.00
	0.02	102.30±3.80	103.00±2.00	99.00±1.00
	0.05	103.00±1.00	90.00±1.00	100.00±1.00

Table 4.23: Mean recoveries and standard deviation for sediment zones sampled

VOCs	Concentration (µg/L)	SD-AS-1	SD-UN-2	SD-AM-3
Alkanes				
(Pentane)	0.01	97.70±2.50	101.80±3.60	98.90±0.60
	0.02	97.30±3.50	99.10±3.30	103.10±2.00
	0.05	99.10±2.00	105.00±3.00	92.00±6.30
Alkenes				
(Pentene)	0.01	100.00±2.00	99.70±1.60	104.00±1.00
	0.02	100.30±2.80	102.60±1.50	103.00±0.60
	0.05	90.00±4.60	104.00±1.70	90.00±1.00
Aromatics				
(Benzene)	0.01	101.70±0.60	104.00±1.70	100.80±3.20
	0.02	102.00±0.70	99.10±0.50	99.20±1.10
	0.05	85.00±2.70	102.00±2.70	85.00±6.60
Carboxylic Acids				
(Acetic acid)	0.01	102.70±2.20	103.70±0.70	97.30±2.20
	0.02	102.80±1.80	101.60±1.60	103.70±1.20
	0.05	92.00±5.30	101.00±2.00	85.00±8.70

4.6.1 Recovery study on river zones

A known volume of standard volatile organic compounds infused in the coupon before evocation to check how much was rediscovered after culmination exercise is termed recovery study.

Volatile organic compounds reformation from spicate river zones inhabit at three concentrations altitude, at each strength level; three occurrences exist, recorded at 0.01 μg/L, 0.02 μg/L and 0.05 μg/L respectively. RW-AS-1 observed mean reformation distend and standard deviation of [97.1±3.2 - 104±1.0], RW-UN-2 [90.0±1.0 – 103.3±1.5] while RW-AM-3 obtained [97.7±1.5 - 104±1.0] (Figure 4.11 -4.13)

4.6.2 Recovery study on sediment zones

Volatile organic compounds recoveries from spiked sediment were carried out at three levels of concentration (0.01 μg/L, 0.02 μg/L and 0.05 μg/L respectively). At each level, three resolutions were done. A mean recovery and standard deviation of [90.0±4.6 – 102.8±1.8] was observed at SD-AS-1; [99.1±0.5 – 104.0±1.7] at SD-UN-2 while, 85.0±6.6 – 103.7±1.2 at SD-AM-3 (Figure 4.14 -4.16).

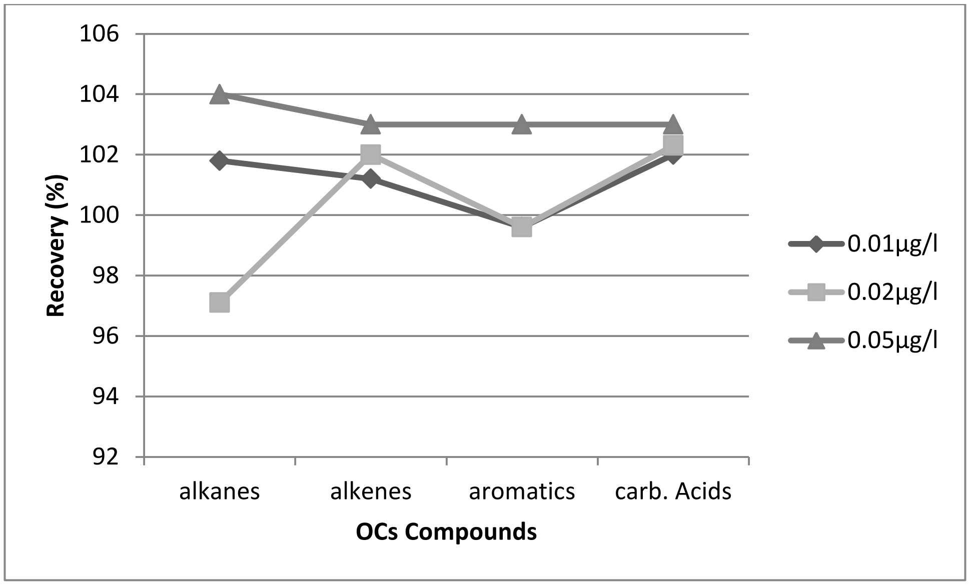

Figure 4.11: Recoveries of organic compounds from spiked surface water (RW-AS-1) with three fortification levels using liquid-liquid extraction method [n=3]

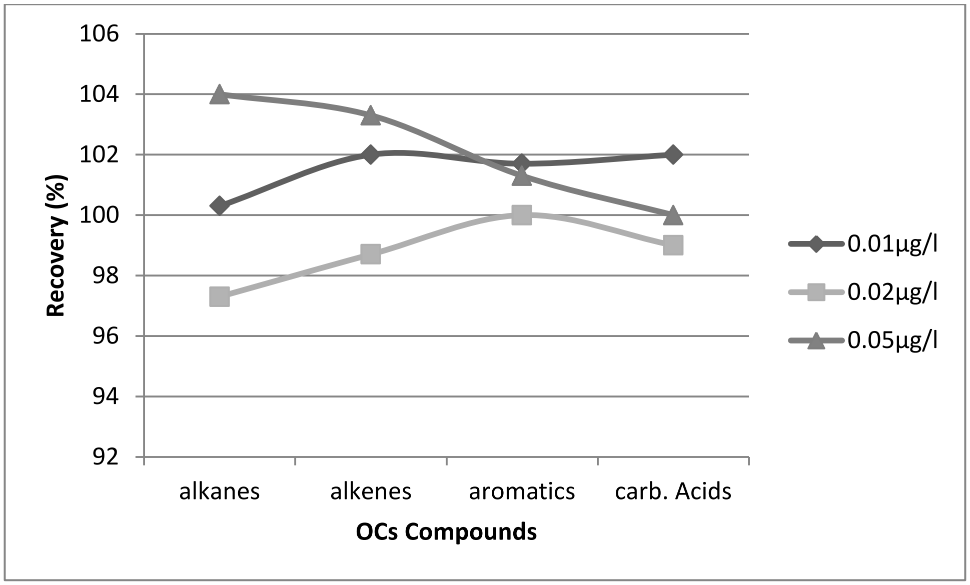

Figure 4.12: Recoveries of organic compounds from spiked surface water (RW-UN-2) with three fortification levels using liquid-liquid extraction method [n=3]

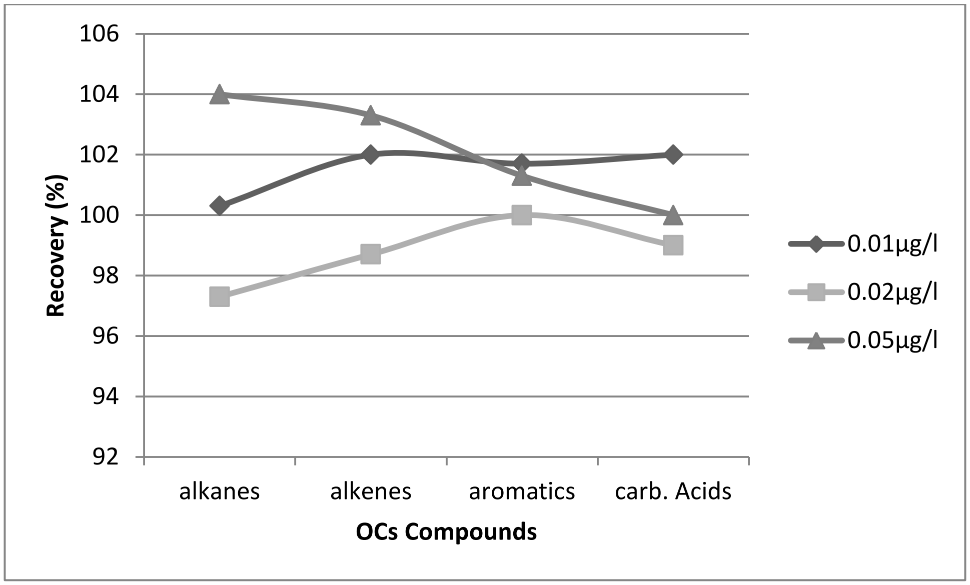

Figure 4.13: Recoveries of organic compounds from spiked surface water (RW-AM-3) with three fortification levels using liquid-liquid extraction method [n=3]

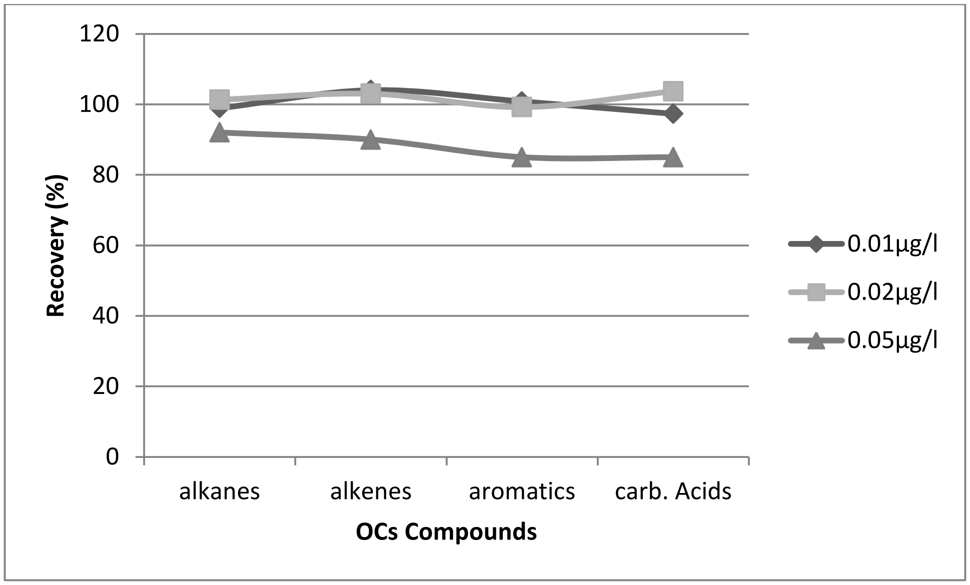

Figure 4.14: Recoveries of organic compounds from spiked sediment (SD-AS-1) with three fortification levels using liquid-liquid extraction method [n=3]

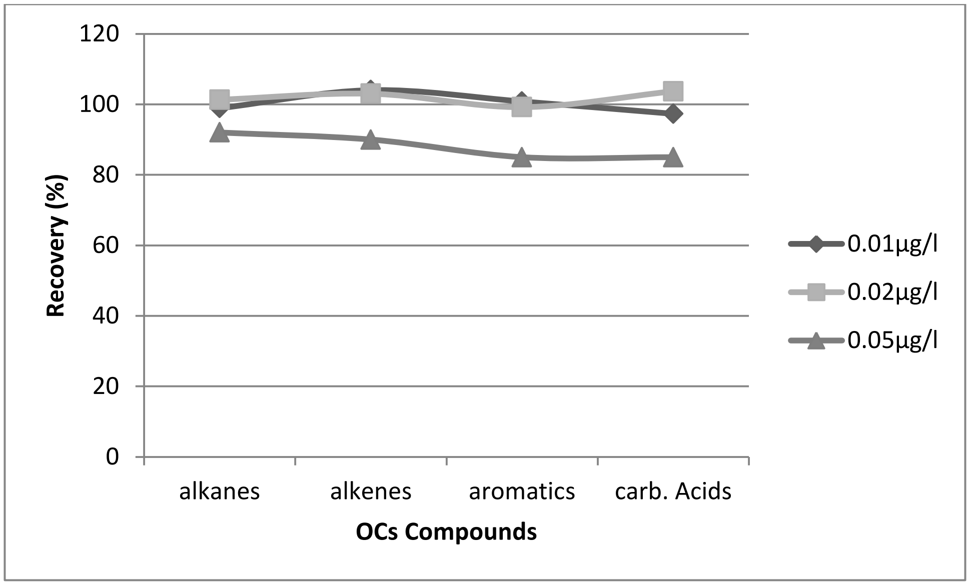

Figure 4.15: Recoveries of organic compounds from spiked sediment (SD-UN-2) with three fortification levels using liquid-liquid extraction method [n=3]

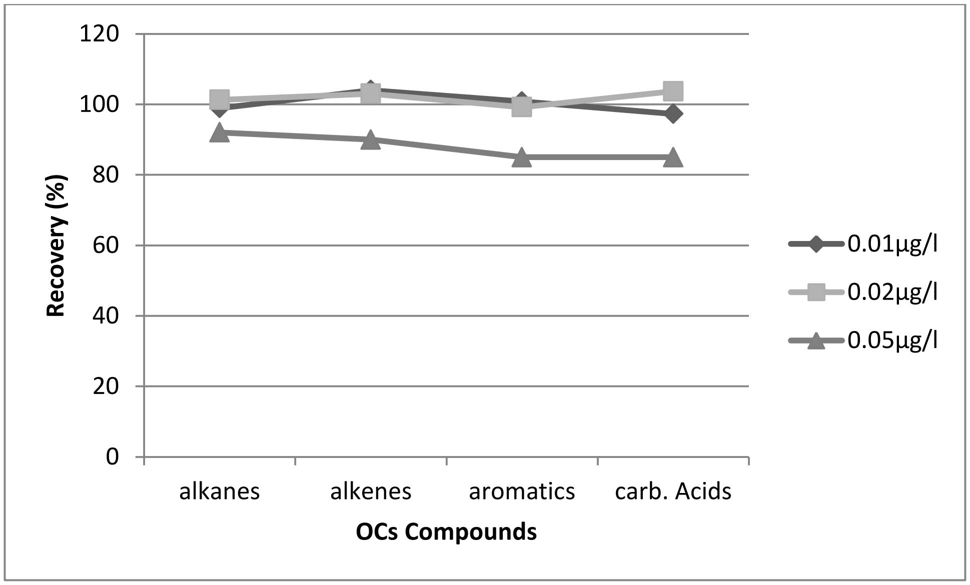

Figure 4.16: Recoveries of organic compounds from spiked sediment (SD-AM-3) with three fortification levels using liquid-liquid extraction method [n=3]

4.6.3 Correlation model of OCs recovery concentration

Table 4.24 reveals organic compounds targeted using correlation analysis at river zones in relation to sediment. 5 is the degree of freedom at 5% significant level with critical table value = 0.754. RW-SD-AS-1, RW-SD-UN-2 and RW-SD-AM-3 at 0.01µg/l recorded range of (-0.26 – 0.30), while at 0.02 µg/L for RW-SD-AM-3 was 0.74 which indicated that r_{cal} is less than r_{table} therefore Ho is accepted and this concludes that there is no association between organic compound of river and sediment at that concentration. At 0.02 µg/L, RW-SD-AS-1 and RW-SD-UN-2 obtained range (0.76 - 0.77), while at 0.05 µg/L, RW-SD-AS-1, RW-SD-UN-2 and RW-SD-AM-3 recorded range (0.91 – 0.98) and revealed that $r_{cal} > r_{table}$ therefore the Ho is rejected and it is summarised that positive association exist betwixt river zone and sediment at those concentration. Figure 4.17-4.19, which reveals the correlation analysis pattern at 0.05 µg/L, also affirmed the interaction between the river and sediment zones. The R^2 determined on the graph account for the reliability of the extraction method used based on recovery studies.

The extraction method was performed on the river and sediment zones to confirm their applicability on Ilorin environs, Kwara State that acquire common crystal clear element to consider. Previous experiment had shown that the type and quantity of dissolving agent keep upturn the coating compositions. Therefore, hexane: dichloromethane was used for liquid-liquid extraction. The recovery experiments were carried out for optimization of liquid-liquid extraction for organic compounds and the following summaries were made: For river samples at 0.05 µg/L recorded 90.0±1.0% – 104.0±1.0% while sediment samples obtained (85.0±8.7% - 105.0±3.0%).

Both the river and sediment zones revealed a derivative of benzene (Fluorobenzene) which is a human carcinogen and a chemic compound found in ecological smoking mixture, gathered combustibles and tires from vehicles. It again found to adulterate edible material and aqua, when digested can surpass to inborn reflex, giddiness, somnolence, fast systole and at immense levels, mega death

Table 4.24: Correlation model of Organic Pollutants based on recovery concentration

Concentration (µg/L)	RW-SD-AS-1	RW-SD-UN-2	RW-SD-AM-3
0.01	-0.26	-0.91	0.30
0.02	0.76	0.77	0.74
0.05	0.91	0.98	0.96

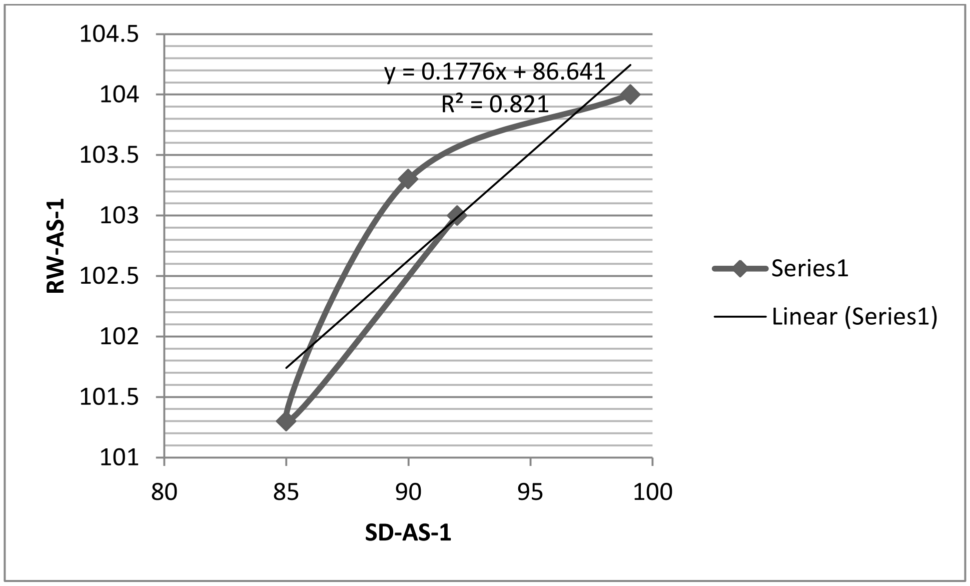

Figure 4.17: Correlation model of river zone and sediment at 0.05µg/l (RW-SD-AS-1)

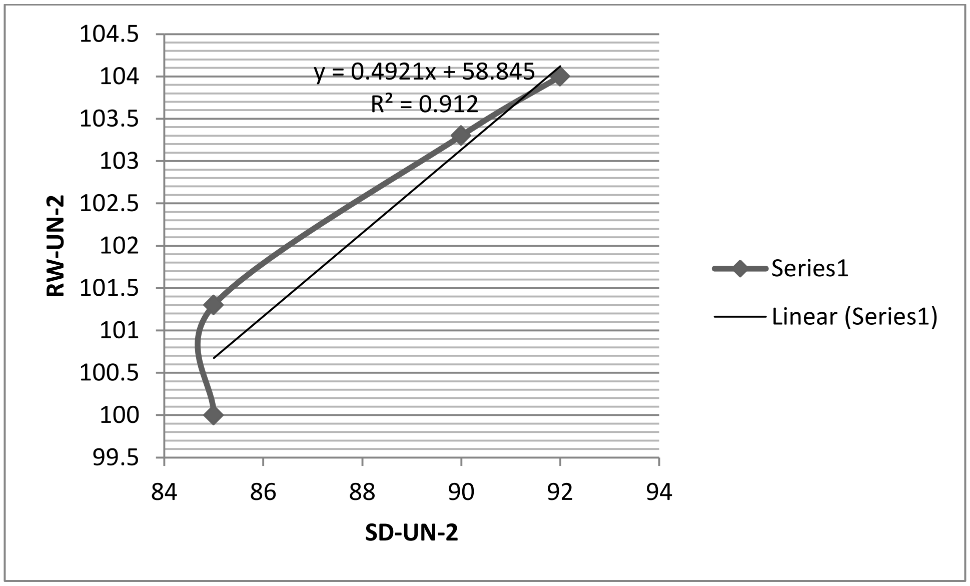

Figure 4.18: Correlation model of river zone and sediment at 0.05µg/l (RW-SD-UN-2)

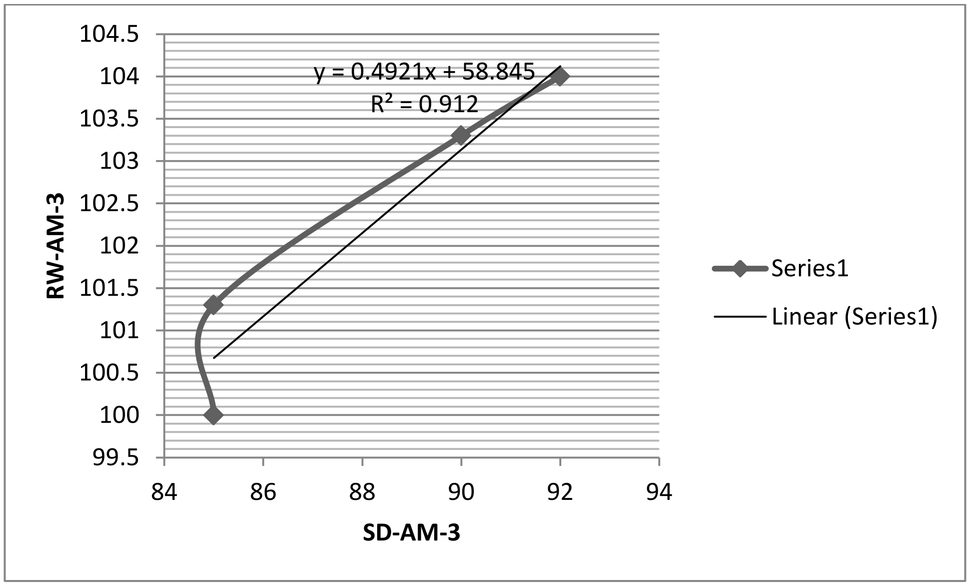

Figure 4.19: Correlation model of river zone and sediment at 0.05µg/l (RW-SD-AM-3)

could occur. Other organic compounds like chlorofluorocarbons and chlorocarbons also determined in this experiment are harmful to health and should be thoroughly monitored because this is the river that serves as drinking water source for Kwara state. People who could not afford tap water undergo direct intake through surface water, which could cause the aforementioned health hazards to an individual. Industrial companies which directly or indirectly pour their waste into the water bodies should also be monitored by environmental protection agencies.

4.7 FTIR analysis

Fourier Transform Infra-red spectrometry is used to detect functional groups presents in organic compounds already analyse using GC-MS.

This study was carried out on effluent and surface water samples of Ilorin environs based on eight sampling sites which are EW-GS-1, EW-TP-2, EW-KC-3, EW-FB-4, GS/SW1, KC-GS-TP/SW1, KC/SW1 and FB/SW1 respectively. These sites are highly industrialised and commercialised; also discharge of effluents from various companies into water bodies occurs majorly in these areas.

From the figure IR 1 and IR 2 (appendix), it can be seen that EW-GS-1 and GS/SW1 array present apparent apex in the succeeding amplitudes. 3447.07-3454.2 cm^{-1}; 2075.52-2964cm^{-1}; 1636.96-1741.12 cm^{-1}; 1378.2-1461 cm^{-1}; 1032.2-1378.2 cm^{-1}; 744.73-764.22 cm^{-1} and 384.43-427.97cm^{-1}.

The ample and energetic bandeau stationed in the bounds 3447.07-3454.2 cm^{-1} can be ascribed to primary amines of –N-H distends. The bandeau separating the bounds 2075.52-2964 cm^{-1} is assigned to the –C-H expands oscillations. The energetic peaks of 1636.96 cm^{-1} for effluent water, while 1621.9 cm^{-1} and 1741.12 cm^{-1} are for surface water respectively could be as a result of a –C=O distends in carboxylic or acetamide bands indicative of 1,3-diketones. -C≡C stretching weak absorption at 2075.52 cm^{-1} for effluent water. –C-O-C stretching at bands 1102.62 cm^{-1} for effluent water and 1032.2 cm^{-1} and 1110.2 cm^{-1} for surface water indicative of aliphatic ethers.

All the peaks found in these sampling sites were expected due to the raw materials used by the effluent companies such as sodium benzoate, caustic soda, fatty alcohols, alkyl benzenes and carboxy methyl cellulose.

From the figure IR 3 and IR 4 (appendix), it can be observed that EW-TP-2 and KC-GS-TP/SW1 spectrum present specific apex in the succeeding amplitude: 3449.3-3897.2 cm^{-1}, 2879.2-2964.72 cm^{-1}, 1617-1745.3 cm^{-1}, 1256.4-1467.7 cm^{-1}, 1032.2-1154 cm^{-1}, 505.94-754.97 cm^{-1}, 371.83-391.33 cm^{-1}. C=C-H stretching for unconjugated alkenes was observed at 3449.3 cm^{-1}, C-H stretching situated at 2964.7cm^{-1} for effluent water and 2965.05 cm^{-1} for surface water as asymmetrical stretching indicative of straight chains alkanes. The strong and broad absorption overtone band at 1382 cm^{-1} and 1378 cm^{-1} respectively is assigned to C≡C-H distends. The band observed at 1258.7 cm^{-1} for effluent water and 1256.4 cm^{-1} for surface water was assigned to –C-H bend overtone of alkynes. The peaks observed at 1154 cm^{-1} and 1032.2 cm^{-1} is attributed to –C-O stretching resonance indicative of tertiary and primary alcohols respectively and also the bands ranges at 1276-1738.9 cm^{-1} indicated –C-O stretching of alcohols.

Bands at 1466 cm^{-1} is assigned to –C-C stretch indicative of aromatic hydrocarbons for benzene ring. The strong characteristic bands observed at 1046.2 cm^{-1} for effluent water and 1032.2 cm^{-1} for surface water is assigned to –C-O-C stretching due to the strong dipole moment. The strong peaks at 1258.7 cm^{-1} for effluent water and 1256.4 cm^{-1} for surface water are attributed to asymmetrical stretch of alkyl aryl ethers.

The intense band at 1745.3 cm^{-1} and 1738.9 cm^{-1} is assigned to C=O stretch indicative of ketones (esters), acids, lactones and lactams (1738.9 cm^{-1}). Crest at 1276 cm^{-1} and 1256.4 cm^{-1} are indicative of α, β unsaturated esters. The peaks at 1467.7 cm^{-1}, 1382 cm^{-1} for effluent water and 1466 cm^{-1}, 1378.2 cm^{-1} for surface water was attributed to alkyl nitrite. The bands at 750.07 cm^{-1} for surface water and 754.97 cm^{-1} for surface water were assigned to-C-C stretching of mononuclear aromatic hydrocarbons which is benzene.

From the figure IR 5 and IR 6 (appendix), it can be observed that EW-KC-3 and KC/SW1 spectrum present specific crest in the succeeding amplitude: 3449.3-3897.2 cm^{-1}, 2879.2-2965.80 cm^{-1}, 1617-1745.3 cm^{-1}, 1256.4-1461 cm^{-1}, 1032.2-1154 cm^{-1}, 569.3-754.97 cm^{-1} and 391.43 cm^{-1} respectively.

The bandeau observed at 3449.3 cm^{-1} was indicative of C=C-H stretching for unconjugated alkenes. C-H stretching situated at 2964.7cm^{-1} for effluent water and 2965.05 cm^{-1} for surface water as asymmetrical stretching indicative of straight chains alkanes. The strong and broad absorption overtone band at 1382 cm^{-1} and 1378 cm^{-1} respectively is assigned to C≡C-H stretching. The band observed at 1258.7 cm-1 for effluent water and 1256.4 cm^{-1} for surface water was assigned to –C-H bend overtone of alkynes. The peaks observed at 1154 cm^{-1} and 1032.2 cm^{-1} is attributed to –C-O stretching oscillations indicative of tertiary and primary alcohols respectively and also the bands ranges at 1276-1738.9 cm^{-1} indicated –C-O distends of alcohols.

Apex at 1466 cm^{-1} is attached to –C-C stretch indicative of aromatic hydrocarbons for benzene ring. The strong characteristic bands observed at 1046.2 cm^{-1} for effluent water and 1032.2 cm^{-1} for surface water is assigned to –C-O-C stretching due to the strong dipole moment. The strong peaks at 1258.7 cm^{-1} for effluent water and 1256.4 cm^{-1} for surface water are attributed to asymmetrical stretch of alkyl aryl ethers.

The intense band at 1745.3 cm^{-1} and 1738.9 cm^{-1} is assigned to C=O stretch indicative of ketones (esters), acids, lactones and lactams (1738.9 cm^{-1}). Alps at 1276 cm^{-1} and 1256.4 cm^{-1} are indicative of α, β unsaturated esters. The peaks at 1467.7 cm^{-1}, 1382 cm^{-1} for effluent water and 1466 cm^{-1}, 1378.2 cm^{-1} for surface water was attributed to alkyl nitrite. The bands at 750.07 cm^{-1} for surface water and 754.97 cm^{-1} for surface water were assigned to-C-C stretching of mononuclear aromatic hydrocarbons which is benzene.

All peaks found in this sampling site were expected due to the raw materials used by the effluent company of pharmaceuticals such as benzene, methanol, glycerin, acetone, hydrochloric acid, starches and sugar.

From the figure IR 7 and IR 8 (appendix), it can be seen that EW-FB-4 and FB/SW1 spectrum present specific crest in the succeeding amplitude: 3439.6-3444.5 cm^{-1}, 2850-2964.96 cm^{-1}, 1617-1743.7 cm^{-1}, 1227.2-1466 cm^{-1}, 1032.2-1159 cm^{-1}, 749.6-764.22 cm^{-1} and 371.85-391.39 cm^{-1}.

Crest of 2964 cm^{-1} and 2928 cm^{-1} are assigned to C-H stretching and the range of 2850-2964 cm^{-1} indicated $–CH_3$ and $–CH_2$ of alkanes asymmetrical stretching respectively. C-C stretches was indicated at peaks 1154 cm^{-1} and 1032.2 cm^{-1} with the band range of 1032.2-1159 cm^{-1} indicated alkanes. The peak range at 3439.6-3444.5 cm^{-1} is assigned to C=C-H stretching indicative of alkenes and also intermolecular hydrogen bonding occurs as concentration increases, accompanied by a shift to lower frequency at the expense of the free OH bend. The intense bands observe at 1743.7 cm^{-1}, 1617 cm^{-1} is designated to C=O distends of carbonyls for lactones, aldehydes, acids, esters and acid halides. The broad and strong absorption bandeau from amplitude 1227.2-1466 cm^{-1} is imputed to -C≡C-H bending. Alps 1466 cm^{-1} is imputed for –C-C distends for aromatic, while the peaks at 1271 cm^{-1}, 1261.3 cm^{-1}, 1154 cm^{-1} and 1032.2 cm^{-1} respectively were assigned to C-H stretching in plane bends of aromatics.

The peak 1738.9 cm^{-1}, 1667 cm^{-1} for primary alcohol and 1466 cm^{-1} and 1373 cm^{-1} for tertiary alcohol were assigned to C-O stretching vibrations for alcohols. The energetic alp at 1271 cm^{-1} is assigned to –C-O-C distends indicative of alkyl aryl ether because of strong dipole moment.

All the peaks found in these sampling sites both in effluent and surface waters were expected due to the raw materials used by the battery company and other accompany companies nearby which uses paraffin waxes, catechols, sulphur, acids, sodium chloride and tar.

4.8 Surface water modelling

The surface water of Asa River was modeled using Regression and ANOVA models respectively.

(A) Regression model

Ho: Null hypothesis H1: Alternative hypothesis

Fitted model of regression of surface water loads on Distance (DT)

$$Y = \alpha + \beta Xi$$

$$YP = b1X3 + b2X2 + b3X + C$$

Where Y = Dependent variables, α = Intercept, β = Regression coefficient

Xi = Independent variable, i = Number of variables P = Parameters

Hypothesis: $Ho = \beta = 0 \, vs \, H1: \beta \neq 0$

Ho: β = 0 this implies that the regression coefficient is not significantly different from zero.

Decision Rule: Accept Ho if p-value contains zero and reject Ho if p-value does not contain zero.

(i) Effect of distance on the total solid (TS) collected from selected sampling sites of Asa River surface water?

$$TSi = \alpha + \beta DTi$$

$$TSi = 3.92308 + 0.230DTi$$

The overall mean of TS_i is 3.92308. However, for every increase in DT, TS_i increases by a function of 0.230. The p-value does not contain zero therefore, we reject Ho and can conclude that effect of DT on TS is significant.

(ii) Effect of distance on the total hardness (THS) collected from selected sampling sites of Asa River surface water?

$$THSi = \alpha + \beta DTi$$

$$THSi = 5.35385 + 0.503DTi$$

The overall mean of this is 5.35385. However, for every increase in DT, this increases by a function of 0.503.The p-value does not contain zero therefore, we reject Ho and can conclude that effect of DT on THS is significant.

(iii) Effect of distance on alkalinity (ALK) collected from selected sampling sites of Asa River surface water?

$$ALKi = \alpha + \beta DTi$$

$$ALKi = 7.46731 - 0.104DTi$$

The overall mean of ALK_i is 7.46731. However, for every increase in DT, ALK_i decreases by a function of 0.104. The p-value does contain zero therefore, we do not reject Ho and can conclude that effect of DT on ALK is not significant.

(iv) How does distance has effect on Dissolved Oxygen (DOX) of selected sampling sites on Asa River surface water?

$$DOXi = \alpha + \beta DTi$$

$$DOXi = 5.86731 - 0.375DTi$$

The overall mean of DOX_i is 5.86731. However, for every unit increase in DT, DOX_i decreases by a function of 0.375. The p-value does contain zero therefore, Ho is not rejected and effect of DT is not significant. This summarizes that distance has no effect on DOX.

(v) Biochemical Oxygen Demand (BOD) loadings and DT of selected sampling sites from Asa River surface water has effect on each other?

$$BODi = \alpha + \beta DTi$$

$$BODi = 4.39327 + 0.034DTi$$

The overall mean of BOD_i is 4.43592. However, for every unit increase in DT, BOD_i increases by a function of 0.133. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant. This summarizes that distance has effect on the BOD_i.

(vi) Chemical Oxygen Demand (COD) and distance from selected sampling sites of Asa River surface water has effect on each other?

$$CODi = \alpha + \beta DTi$$

$$CODi = 5.999712 + 0.075DTi$$

The overall mean of COD_i is 5.999712. However, for every increase in DT, COD_i increases by a function of 0.075. The p-value does not contain zero therefore, we reject Ho and can conclude that effect of DT is significant.

(vii) Effect of distance on sulphate (SULP) of selected sampling sites from Asa River surface water?

$$SULPi = \alpha + \beta DTi$$

$$SULPi = 2.42827 + 0.161DTi$$

The overall mean of $SULP_i$ is 2.42827. However, for every increase in DT, $SULP_i$ increases by a function of 0.161. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant.

(viii) Effect of distance on nitrate (NIT) loadings of selected sampling sites from Asa River surface water?

$$NITi = \alpha + \beta DTi$$

$$NITi = 4.28654 - 0.008DTi$$

The overall mean of NIT_i is 4.28654. However, for every increase in DT, NIT_i decreases by a function of 0.008. The p-value contains zero therefore, Ho is not rejected and effect on distance is not significant.

(ix) Ammonia (AMO) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$AMOi = \alpha + \beta DTi$$

$$AMOi = 0.04348 - 0.079DTi$$

The overall mean of AMO_i is 0.04348. However, for every increase in DT, AMO_i decreases by a function of 0.079. The p-value contains zero therefore, Ho is not rejected and effect on distance is not significant.

(x) Effect of distance on phosphate (PHO) of selected sampling sites from Asa River surface water?

$$PHOi = \alpha + \beta DTi$$

$$PHOi = 0.97019 + 0.0023DTi$$

The overall mean of PHO_i is 0.97019. However, for every increase in DT, PHO_i increases by a function of 0.0023. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant.

(xi) Effect of distance on Calcium (Ca) loadings of selected sampling sites from Asa River surface water?

$$Cai = \alpha + \beta DTi$$

$$Cai = 1.22827 - 0.338DTi$$

The overall mean of Ca_i is 1.22827. However, for every unit increase in DT, Ca_i decreases by a function of 0.338. The p-value contains zero therefore, Ho is not rejected and effect of DT is not significant. This summarizes that distance has no effect on the Calcium loadings.

(xii) Magnesium (Mg) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Mgi = \alpha + \beta DTi$$

$$Mgi = 7.42019 + 0.223DTi$$

The overall mean of Mg_i is 7.42019. However, for every unit increase in DT, Mg_i increases by a function of 0.223. The p-value does not contain zero therefore, Ho is rejected and effect of DT is significant. This summarizes that distance has effect on Mgi.

(xiii) Sodium (Na) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Nai = \alpha + \beta DTi$$

$$Nai = 2.34471 + 0.222DTi$$

The overall mean of Na_i is 2.34471. However, for every increase in DT, Na_i decreases by a function of 0.222. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant.

(xiv) Iron (Fe) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Fei = \alpha + \beta DTi$$

$$Fei = 2.29135 + 0.104DTi$$

The overall mean of Fe_i is 2.29135. However, for every unit increase in DT, Fe increases by a function of 0.104. The p-value does not contain zero therefore, Ho is rejected and effect of DT is significant. This summarizes that distance as effect on Fe_i.

(xv) How does distance has effect on Copper (Cu) loadings of selected sampling sites from Asa River surface water?

$$Cui = \alpha + \beta DTi$$

$$Cui = 0.57981 + 0.061DTi$$

The overall mean of Cu_i is 0.57981. However, for every increase in DT, Cu_i increases by a function of 0.061. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant.

(xvi) Zinc (Zn) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Zni = \alpha + \beta DTi$$

$$Zni = 3.71058 - 0.035DTi$$

The overall mean of Zn_i is 3.71058. However, for every increase in DT_i, Zn_i decreases by a function of 0.035.The p-value contains zero therefore, Ho is not rejected and effect on distance is not significant.

(xvii) Cadmium (Cd) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Cdi = \alpha + \beta DTi$$

$$Cdi = 0.00460 + 0.182DTi$$

The overall mean of Cd_i is 0.00460. However, for every increase in DT, Cd_i increase by a function of 0.182. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant.

(xviii) Effect of DT on Lead (Pb) loadings from selected sampling sites of Asa River surface water?

$$Pbi = \alpha + \beta DTi$$

$$Pbi = 0.62346 - 0.068DTi$$

The overall mean of Pb_i is 0.62346. However, for every increase in DT, Pb_i decrease by a function of 0.068. The p-value contains zero therefore, Ho is not rejected and effect on distance is not significant.

(xix) Chromium (Cr) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Cri = \alpha + \beta DTi$$

$$Cri = 0.45490 + 0.128DTi$$

The overall mean of Cr_i is 0.45490. However, for every increase in DT_i, Cr_i increases by a function of 0.128.The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant.

(xx) Chloride (Cl) loadings and distance from selected sampling sites of Asa River surface water has effect on each other?

$$Cli = \alpha + \beta DTi$$

$$Cli = 3.22163 + 0.310DTi$$

The overall mean of Cl_i is 3.22163. However, for every increase in DTi, Cl_i decrease by a function of 0.310. The p-value does not contain zero therefore, Ho is rejected and effect on distance is significant. In other words, there is significant relationship between Cl and DT.

A lot of labour on field sampling and sample analysis of river quality will be reduced if regression model is constructed for each determinable analyte. It was reported that regression modelling assists in monitoring and controlling water pollution issues in rivers (Chung et al., 2009). This is because the models relate the distance downstream independently with each characteristic of water. The regression model developed for Asa River is limited in their applications. This is because the estimating equations have to be revised and updated frequently. Moreover, they are not transferable to other river (Chung et al., 2009). It was reported that the model is inadequate when significant changes in river quality take place over time (Sharp et al., 2006). Also, the regression model becomes questionable if the distance further than the field sampling point is excessively long, with variation in water quality within the distance under consideration.

Table 4.25: Regression equation showing the distribution of parameters levels to downstream of Asa River receiving effluent from detergent company.

Equation	Regression coefficient
$Y_{TS} = 0.034x^3 + 1.18x^2 - 8.252x + 392.516$	0.748
$Y_{THS} = 0.003x^3 -1.293x^2 - 2.415x + 48.656$	0.506
$Y_{ALK} = 0.011x^3 - 5.877x^2 + 4.722x + 106.065$	0.442
$Y_{DOX} = 0.001x^3 - 4.002x^2 + 2.752x + 5.358$	0.380
$Y_{BOD} = 0.002x^3 - 3.371x^2 + 1.998x + 2.675$	0.268
$Y_{COD} = 0.000x^3 + 6.962x^2 - 4.675x + 5.728$	0.132
$Y_{SO4}^{2-} = -0.004x^3 + 1.216x^2 - 9.326x + 26.152$	0.060
$Y_{NO3}- = 0.000x^3 - 2.276x^2 - 5.412x + 3.283$	0.270
$Y_{PO4}^{3-} = -6.105x^3 - 1.027x^2 + 2.278x + 0.977$	0.288
$Y_{NH3} = -1.532x^3 + 4.427x^2 - 2.961x + 0.047$	0.465
$Y_{Ca} = 0.000x^3 + 6.002x^2 - 6.165x + 13.138$	0.051
$Y_{Mg} = 0.000x^3 + 2.498x^2 - 1.660x + 7.592$	0.524
$Y_{Na} = 0.000x^3 + 1.963x^2 -1.440x + 2.612$	0.289
$Y_{Fe} = 0.002x^3 +3.858x^2 - 2.015x +3.792$	0.787
$Y_{Cu} = 0.000x^3 + 5.051x^2 - 2.634x + 0.717$	0.475
$Y_{Zn} = 0.002x^3 + 5.928x^2 - 4.310x + 6.426$	0.073
$Y_{Cd} = 6.412x^3 - 1.547x^2 + 1.035x + 0.000$	0.500
$Y_{Pb} = -5.187x^3 + 2.070x^2 - 1.125x + 0.528$	0.324
$Y_{Cr} = 0.000x^3 + 5.168x^2 - 3.282x + 0.495$	0.524
$Y_{Cl-} = 0.010x^3 - 7.068x^2 - 5.691x + 19.407$	0.468

●TH = Total Hardness; TS = Total Solids; SO_4^{2-} = Sulphate ion; NO_3^-= Nitrate ion; NH_3= Ammonia; PO_4^{3-} = Phosphate ion; Cl^- = Chloride ion

● Six parameters yielded strong relationship with distance along the river network

Table 4.26: Regression equation showing the distribution of parameters levels to downstream of Asa River receiving effluent from pharmaceutical company A

Equation	Regression Coefficient
$Y_{TS} = 0.031x^3 + 0.000x^2 – 1.495x + 278.949$	0.712
$Y_{THS} = 0.005x^3 +0.000x^2 – 4.806x + 41.721$	0.317
$Y_{ALK} = 0.061x^3 + 4.456x^2 + 0.000x + 264.425$	0.633
$Y_{DOX} = 0.002x^3 + 9.590x^2 + 0.000x + 10.581$	0.268
$Y_{BOD} = 0.000x^3 + 2.525x^2 + 0.000x + 6.540$	0.232
$Y_{COD} = 0.001x^3 + 0.000x^2 – 3.507x + 3.601$	0.173
$Y_{SO4}{}^{2-} = 0.016x^3 – 1.214x^2 + 0.000x – 20.046$	0.152
$Y_{NO3}- = 0.002x^3 – 1.248x^2 + 0.000x -0.322$	0.160
$Y_{NH3} = 3.470x^3 – 2.419x^2 + 0.000x -0.067$	0.633
$Y_{PO4}{}^{3-} = 1.835x^3 + 1.344x^2 + 0.000x + 0.736$	0.388
$Y_{Ca} = 0.001x^3 + 0.000x^2 – 1.231x + 7.724$	0.146
$Y_{Mg} = 3.046x + 6.391$	0.586
$Y_{Na} = 0.002x^3 – 1.330x^2 + 0.000x – 2.782$	0.371
$Y_{Fe} = 0.001x^3 + 0.000x^2 – 1.874x – 1.885$	0.911
$Y_{Cu} = 0.000x^3 – 1.238x^2 + 0.000x – 0.376$	0.600
$Y_{Zn} = 0.002x^3 + 0.000x^2 – 1.440x -1.885$	0.082
$Y_{Cd} = 3.417x^3 + 2.418x^2 + 0.000x + 0.017$	0.426
$Y_{Pb} = 0.000x^3 – 1.156x^2 + 0.000x – 0.149$	0.289
$Y_{Cr} = 0.000x^3 – 1.088x^2 + 0.000x – 0.263$	0.501
$Y_{Cl-} = 0.014x^3 + 0.000x^2 – 1.614x – 5.356$	0.448

●TH = Total Hardness; TS = Total Solids; SO_4^{2-} = Sulphate ion; $NO3^-$= Nitrate ion; NH_3 = Ammonia; PO_4^{3-} = Phosphate ion; Cl^- = Chloride ion

● Seven parameters yielded strong relationship with distance

Table 4.27: Regression equation showing the distribution of parameters levels to downstream of Asa River receiving effluent from Pharmaceutical company B

Equation	Regression Coefficient
$Y_{TS} = 0.032x^3 + 1.130x^2 -7.900x + 391.702$	0.743
$Y_{THS} = 0.008x^3 – 1.003x^2 + 3.098x + 42.700$	0.520
$Y_{ALK} = 0.070x^3 – 1.854x^2 + 1.285x + 26.652$	0.311
$Y_{DOX} = 1.000x + 7.322$	0.520
$Y_{BOD} = 0.001x^3 – 2.550x^2 + 1.516x + 3.393$	0.163
$Y_{COD} = 0.001x^3 + 3.403x^2 – 2.203x + 7.251$	0.125
$Y_{SO4}{}^{2-} = 0.008x^3 + 2.268x^2 – 1.657x + 30.129$	0.078
$Y_{NO3}{}^{-} = 0.002x^3 + 4.379x^2 – 2.983x + 6.264$	0.071
$Y_{NH3} = 2.039x^3 + 6.009x^2 – 4.153x + 0.048$	0.509
$Y_{PO4}{}^{3-} = 6.304x^3 + 1.148x^2 + 5.417x + 0.937$	0.297
$Y_{Ca} = 0.000x^3 + 1.930x^2 – 1.734x + 12.617$	0.053
$Y_{Mg} = 0.000x^3 + 1.310x^2 – 8.581 + 7.047$	0.409
$Y_{Na} = 0.001x^3 + 3.056x^2 – 2.179x + 3.095$	0.287
$Y_{Fe} = 0.003x^3 + 5.930x^2 – 3.483x + 4.383$	0.507
$Y_{Cu} = 0.000x^3 + 8.083x^2 – 4.829x + 0.781$	0.488
$Y_{Zn} = 0.001x^3 + 4.521x^2 – 3.544x +0.413$	0.053
$Y_{Pb} = 8.298x^3 – 2.257x^2 + 1.289x + 0.273$	0.389
$Y_{Cr} = 0.00x^3 + 3.752x^2 – 2.468x + 0.360$	0.571
$Y_{Cd} = 3.356x^3 – 9.088x^2 + 6.327x + 0.004$	0.256
$Y_{Cl-} = 0.012x^3 – 9.724x^2 – 4.095x + 17.009$	0.447

●TH = Total Hardness; TS = Total Solids; SO_4^{2-} = Sulphate ion; NO_3^-= Nitrate ion; NH_3 = Ammonia; PO_4^{3-} = Phosphate ion; Cl^- = Chloride ion

● Six parameters yielded strong relationship along the river network dispersion channels.

Table 4.28.: Regression equation showing the distribution of parameters levels to downstream of Asa River receiving effluent from Battery Company.

Equation	Regression Coefficient
$Y_{TS} = 0.043x^3 – 2.480x^2 + 0.000x + 270.218$	0.769
$Y_{THS} = 0.004x^3 – 2.454x^2 + 0.000x + 39.833$	0.753
$Y_{ALK} = 0.003x^3 + 1.851x^2 + 0.000x + 74.124$	0.022
$Y_{DOX} = 1.000x + 0.139$	0.852
$Y_{BOD} = 9.711x^3 + 0.000x^2 – 2.120x + 4.089$	0.126
$Y_{COD} = 0.000x^3 + 0.000x^2 – 2.032x + 5.337$	0.148
$Y_{SO4}{}^{2-} = 0.000x^3 – 2.021x^2 + 2.615 + 25.322$	0.013
$Y_{NO3}{}^{-} = 0.000x^3 + 0.000x^2 + 6.527x + 2.555$	0.583
$Y_{NH3} = 4.948x^3 – 1.254x^2 + 0.000x + 0.022$	0.710
$Y_{PO4}{}^{3-} = 1.000x + 1.993$	0.546
$Y_{Ca} = 0.001x^3 + 0.000x^2 – 6.591 + 8.737$	0.642
$Y_{Mg} = 0.067x + 7.090$	0.598
$Y_{Na} = 0.000x^3 + 1.607x^2 – 4.723x + 2.062$	0.281
$Y_{Fe} = 0.000x^3 – 2.923x^2 + 0.000x + 1.934$	0.876
$Y_{Cu} = 9.576x^3 + 0.000x^2 + 4.487x + 0.536$	0.484
$Y_{Zn} = 0.138x + 1.100$	0.384
$Y_{Cd} = 1.403x^3 – 7.330x^2 + 0.000x – 0.001$	0.873
$Y_{Pb} = 4.787x^3 + 0.000x^2 + 4.964x + 0.982$	0.016
$Y_{Cl}{}^{-} = -0.002x^3 + 0.000x^2 + 1.160x + 31.080$	0.092

●TH = Total Hardness; TS = Total Solids; SO_4^{2-} = Sulphate ion; NO_3^-= Nitrate ion; NH_3 = Ammonia; PO_4^{3-} = Phosphate ion; Cl^- = Chloride ion

● Eleven parameters yielded strong relationship with distance.

In receiving effluents from industries, concentration of effluent pollutants tend to be much greater at the discharge point than downstream location possibly due to dispersion along the river. Holvoet et al., 2007 noted that the transformations occurring in rivers are difficult to identify and quantify. Also, the problems of determining the levels of analytes at locations far beyond the last downstream sampling points without intensive water quality determination have been a challenge to many water quality modelers. In view of these challenges, simple relationship between each water quality parameter and distance downstream of discharge point was developed as linear regression model. This is one of the mathematical models that adequately describe the water quality of polluted river. Therefore, the main interest of this regression model is to obtain the best fit of estimating equations for predicting the concentrations of water quality characteristics at distances further than field sampling points. A stepwise regression procedure involving use of the SPSS 16.0 package was employed in this study for the construction of regression models.

This procedure is based on the maximum likelihood method, which yield the best regression equations justified by the values of R^2 (Montgomery et al., 2015).

The procedure is as follows:

a. The set of data for the measured parameter and variable (the distance from the discharge point) are input into two separate columns of SPSS package.
b. The data is fitted to obtain the best fit of mathematical model for estimating the measured parameter as a function of the distance from the discharge point.
c. In fitting the data, another set of data which is referred to as predicted data is generated by the SPSS package.
d. The set of predicted data and corresponding measured values for a particular parameter are replotted against the distance from the discharge point.

Calculating R^2 (the proportion of the initial variance accounted for by the model) assessed goodness of fit of the models. The maximum value of R^2 is unity. The closer the R^2 value to +1 or -1, the better the fitted models as a description of the relationship between the water quality parameters and the distance downstream. This also gives evidence of the validity of the fitted models. The resulted R^2 values and the temporal regression model for each measured parameters are given in table 4.25 to 4.28.

These regression curves, which describe the relation between the means of the probability distribution of the levels of each parameter and the distance from the discharge point, are curvilinear. The values of R^2 for water quality characteristics ranged between 0.500 and 0.787 for detergent company to Asa River, 0.501 and 0.911 for pharmaceutical company A to Asa River, 0.507 and 0.743 for pharmaceutical company B to Asa River while Battery Company to Asa River ranged from 0.546 – 0.876. It is worth noting that most of these R2 values for water quality characteristics of industrial companies to Asa River were high and very close to +1. The regression model for each parameter was developed with the input data value for water quality characteristics as far as 8628 m downstream of discharge points of Asa River.

(B) ANOVA model

Summary of A-One Way ANOVA

Variation	Sum of Squares	Df	Mean of Squares	F
Group	Vr	$K-1$	$Sr = Vr/K-1$	Sr/Se
Residual	Ve	$N-K$	$Se = Ve/N-K$	
Total	V	$N-1$		$Df = (K-1, N-K)$

Sum of Squares

$$Vr = \sum ni\,Xi2 - [\sum niXi]2 / N$$

$$Ve = \sum (ni - 1)Si2$$

$$V = Vr + Ve$$

Where

$Xi = \sum Xij/ni$ (Mean of groups)

K = number of groups/treatments

n_i = sizes of groups i (i =1,2, 3……K)

N = total observation

Research Question: which of the industries polluted most in all of the parameters used in this research work with respect to distance?

1. Total Solids (TS)

Variation	SS	Df	MS	F-ratio
Group	170924.029	21	8139.239	6.920
Residual	96450.125	82	1176.221	
Total	267374.154	103		

F-ratio calculated = 6.920 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the TS loading are dependent on distance. Hence, the null hypothesis is rejected. From the mean plot it was observed that AS1/SW1, AS2/SW2 and AS3/SW3 (668 m, 1162 m and 1192 m) recorded high concentration per distance while from sites KC-GS/SW2 to AS5/SW5 (3976 m to 7652 m) there was decrease down the slope as shown in figure 4.20 and 4.21.

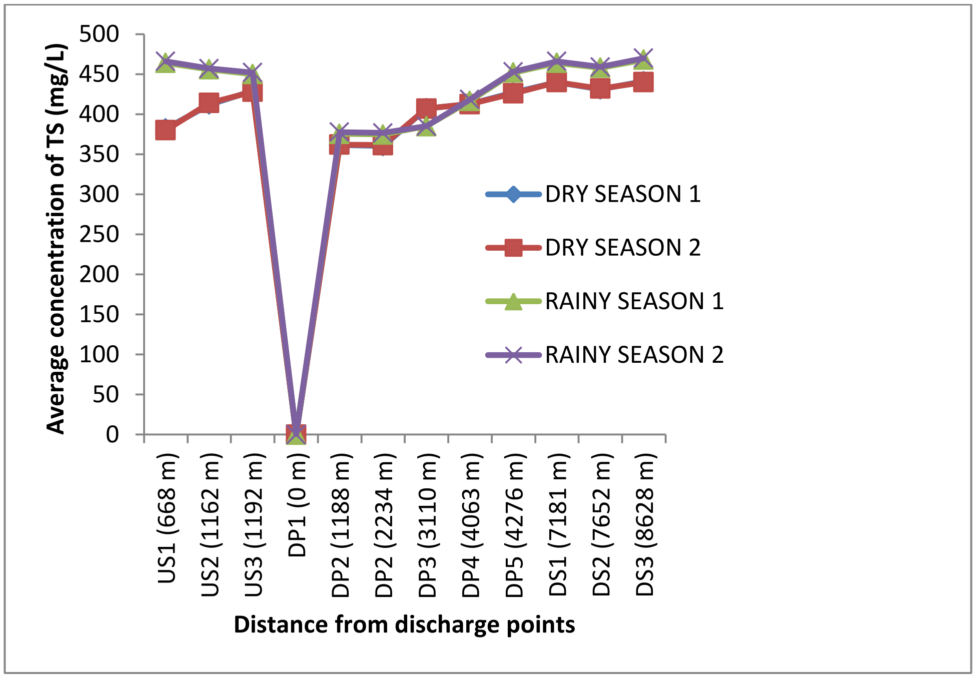

Figure 4.20: Seasonal distribution of total solids from detergent, pharmaceutical company A and B discharge points to Asa River (upstream and downstream).

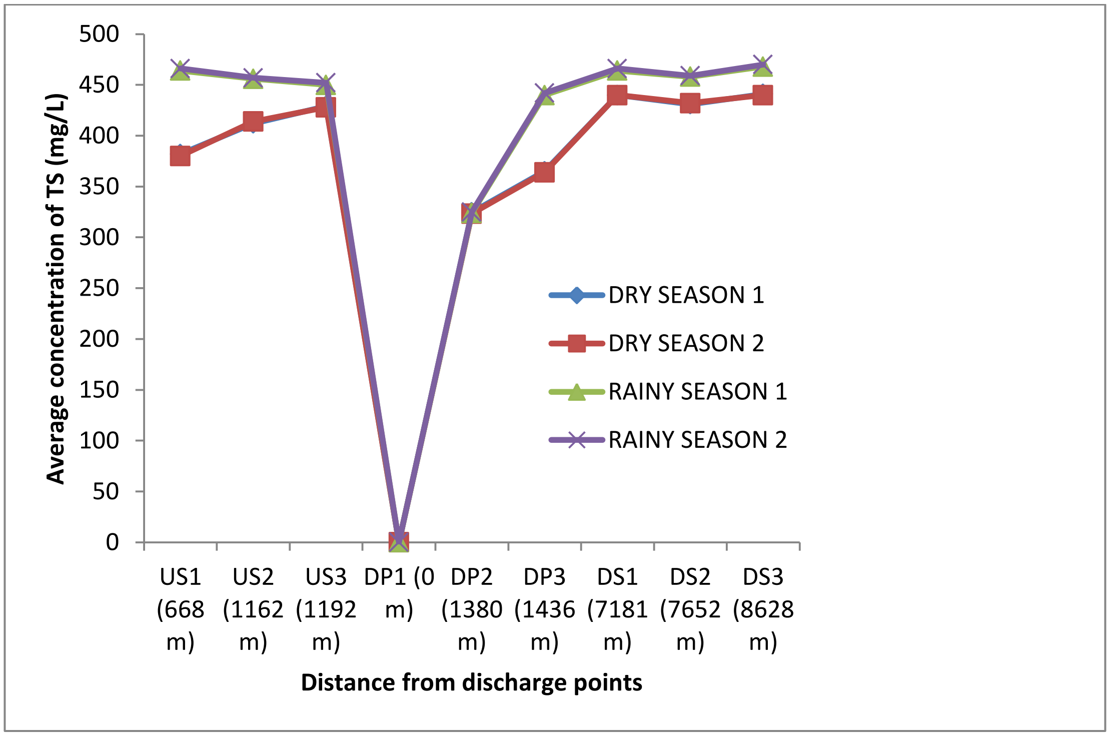

Figure 4.21: Seasonal distribution of total solids from Battery Company discharge points to Asa River (upstream and downstream).

2. Total hardness (THS)

Variation	SS	Df	MS	F-ratio
Group	4443.346	21	211.588	24.911
Residual	696.500	82	8.494	
Total	5139.846	103		

F-ratio calculated = 24.911> the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the THS loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plots affirm AS1/SW1, AS2/SW2, KC/SW3, AS3/SW3 and GS/SW2 (668 m,1162 m 1188 m, 1192m and 1240 m) recorded high concentration per distance while from sites GS/SW3 to KC-GS/SW4 (1856 m to 4595 m) it decreases slightly then at sites KC-GS-TP/SW1 to KC-GS-TP/SW3 (4846 m - 5255 m) there was increase and from 7181 m - 8628 m there was decrease downstream which were sites AS4/SW4, AS5/SW5 and AS6/SW6 respectively (Figure 4.22 and 4.23).

3. Alkalinity (ALK)

Variation	SS	Df	MS	F-ratio
Group	66283.093	21	3156.338	12.933
Residual	20011.792	82	244.046	
Total	86294.885	103		

F-ratio calculated = 12.933 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the alkalinity loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot revealed that sites GS/SW1, KC/SW3 and KC-GS/SW1 (553 m, 1188 m and 3701 m) increase in concentration per distance while sampling sites KC-GS/SW2 to AS6/SW6 (3976 m – 8628 m) decrease in concentration down the stream (Figure 4.24 and 4.25).

4. Dissolved Oxygen (DOX)

Variation	SS	Df	MS	F-ratio
Group	72.164	21	3.436	6.715
Residual	41.965	82	0.512	
Total	114.129	103		

F-ratio calculated = 6.715> the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the dissolved oxygen concentration is dependent on distance. Hence, the null hypothesis is rejected. The mean plot observed that sites GS/SW1, KC/SW1, GS/SW2 and KC-GS-TP/SW1 (553m 889 m, 1240 m and 4846 m) recorded high concentration per distance while sampling sites from KC-GS-TP/SW2 to AS6/SW6 (5042 m – 8628 m) noted decrease down the slope (Figure 4.26 and 4.27).

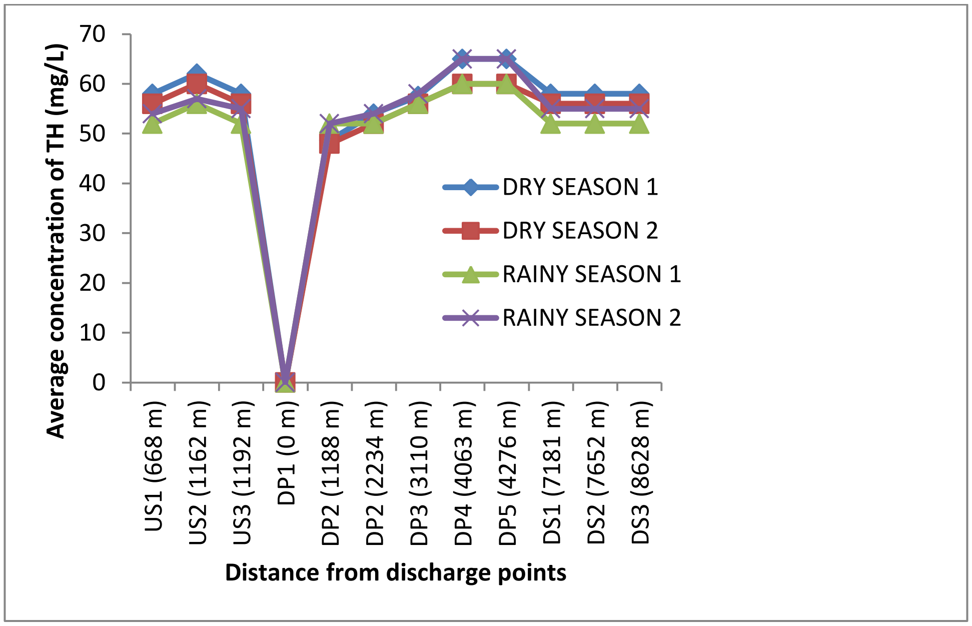

Figure 4.22: Seasonal distribution of total hardness from detergent, pharmaceutical company A and B discharge points to Asa River (upstream and downstream).

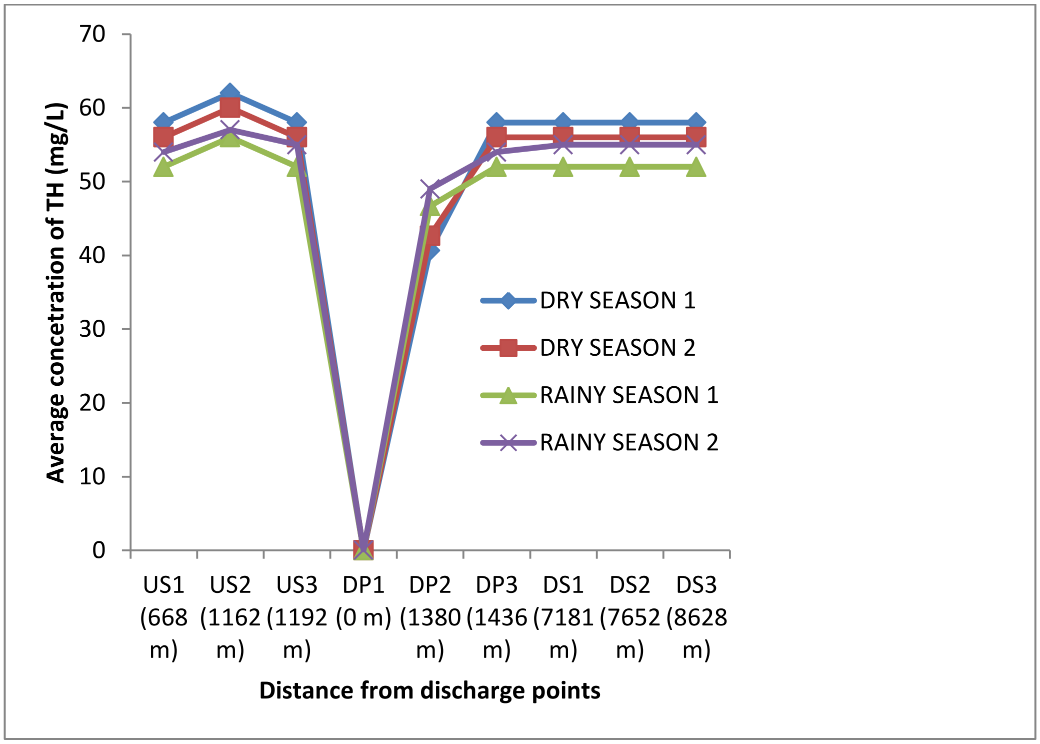

Figure 4.23: Seasonal distribution of total hardness from Battery Company discharge points to Asa River (upstream and downstream).

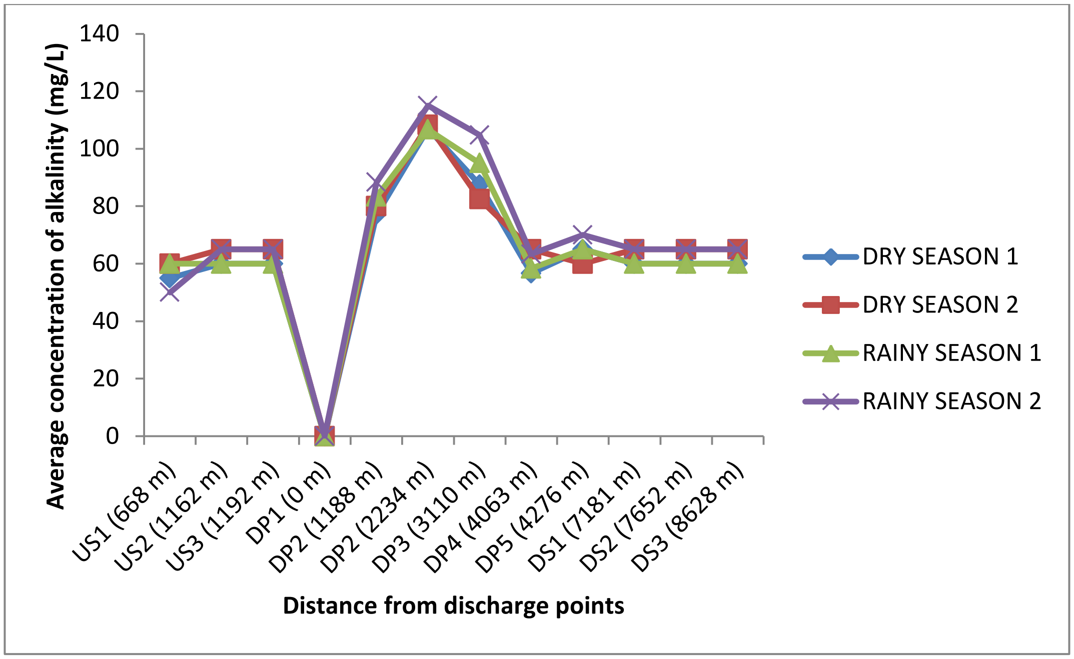

Figure 4.24: Seasonal distribution of alkalinity from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream)

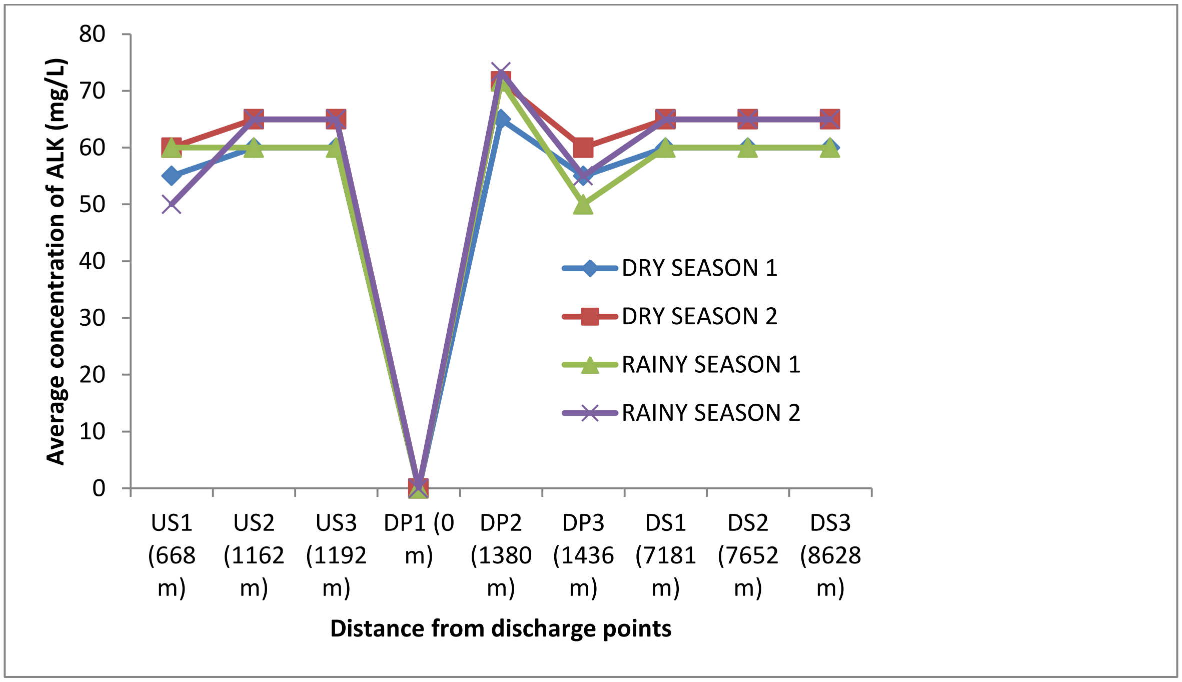

Figure 4.25: Seasonal distribution of alkalinity from Battery Company discharge points to Asa River (upstream and downstream).

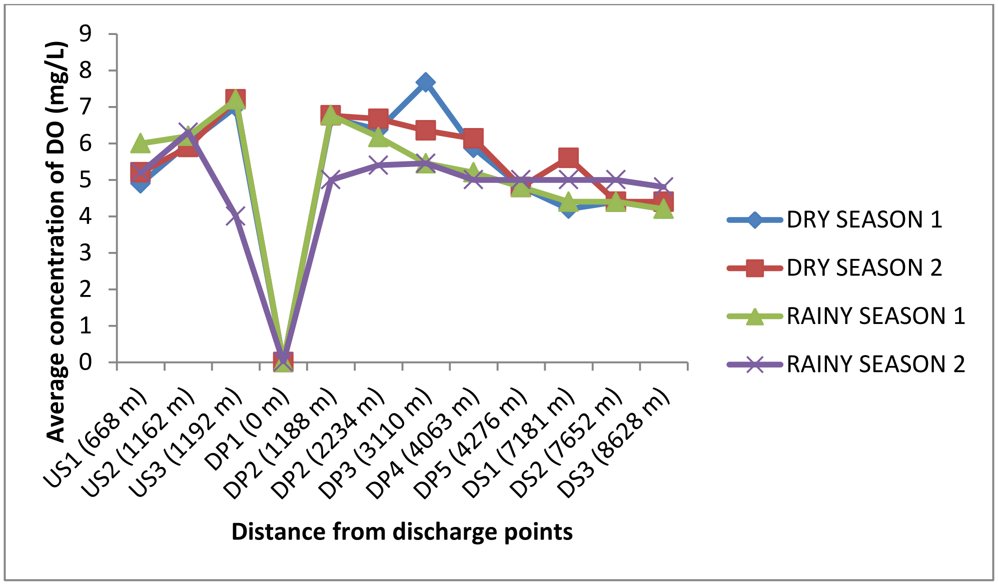

Figure 4.26: Seasonal distribution of Dissolved Oxygen from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream to downstream).

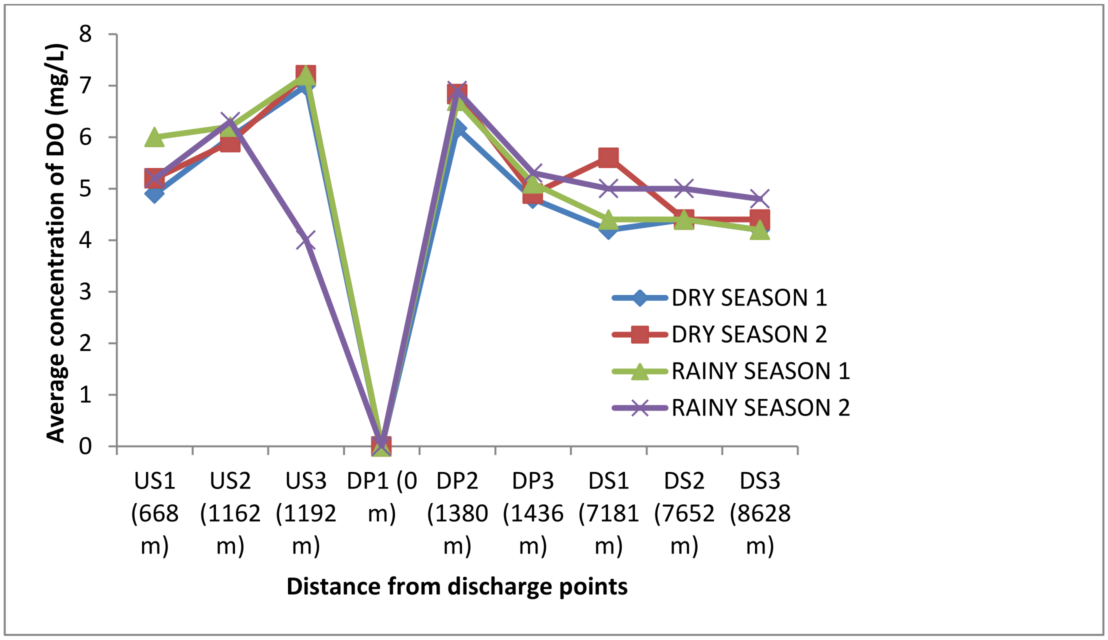

Figure 4.27: Seasonal distribution of Dissolved Oxygen from Battery Company discharge points to Asa River (upstream and downstream).

5. Biochemical Oxygen Demand (BOD)

Variation	SS	Df	MS	F-ratio
Group	31.211	21	1.486	3.150
Residual	38.694	82	0.472	
Total	69.905	103		

F-ratio calculated = 3.150 < the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is not significant. That is, the biochemical oxygen demand loading is not dependent on distance. Hence, the null hypothesis cannot be rejected. The mean plot affirms that sampling sites AS1/SW1, AS2/SW2, AS3/SW3 and KC-GS-TP/SW1 (668 m, 1162m, 1192 m and 4846 m) reveal increase in concentration per distance while from sites KC-GS-TP/SW2 to AS6/SW6 (5042 m – 8628 m) decrease in concentration per distance downstream (Figure 4.28 and 4.29).

6. Chemical Oxygen Demand (COD)

Variation	SS	Df	MS	F-ratio
Group	24.899	21	1.185	2.718
Residual	35.760	82	0.436	
Total	60.649	103		

F-ratio calculated = 2.718 < the table value F (21, 82) = 3.93 at 5% level then the effect of distance is not significant. That is the chemical oxygen demand loading is not dependent on distance. Hence, the null hypothesis cannot be rejected. The mean plot reveals that sites KC/SW1,GS/SW3, KC-GS/SW4 and AS5/SW5 (889 m, 1856 m, 4595 m and 7652 m) increase in concentration per distance while decrease was observed at sampling sites KC-GS-TP/SW1 to AS6/SW6 (4846 m – 8628 m) (Figure 4.30 and 4.31).

7. Sulphate (SULP)

Variation	SS	Df	MS	F-ratio
Group	1348.323	21	64.206	2.303
Residual	2286.026	82	27.878	
Total	3634.349	103		

F-ratio calculated = 2.303 < the table value F (21, 82) = 3.93 at 5% level, then the effect of distant is not significant. That is, the sulphate loading is not dependent on distance. Hence, the null hypothesis cannot be rejected. The mean plot using Duncan graph explains that there was decrease in concentration per distance at sites control1/SW, FB-AS, AS4/SW4 and AS5/SW5 (1217 m, 1436 m, 7181 m and 7652 m) respectively while GS/SW3 and KC-GS-TP/SW3 (1856 m and 5255 m) reveal increase (Figure 4.32 and 4.33).

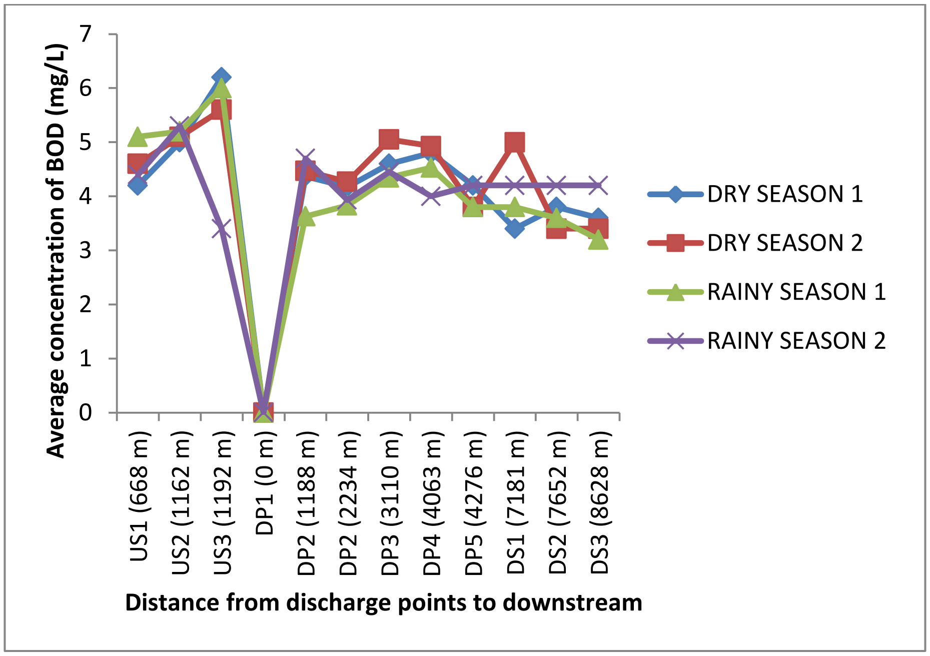

Figure 4.28: Seasonal distribution of Biochemical Oxygen Demand from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

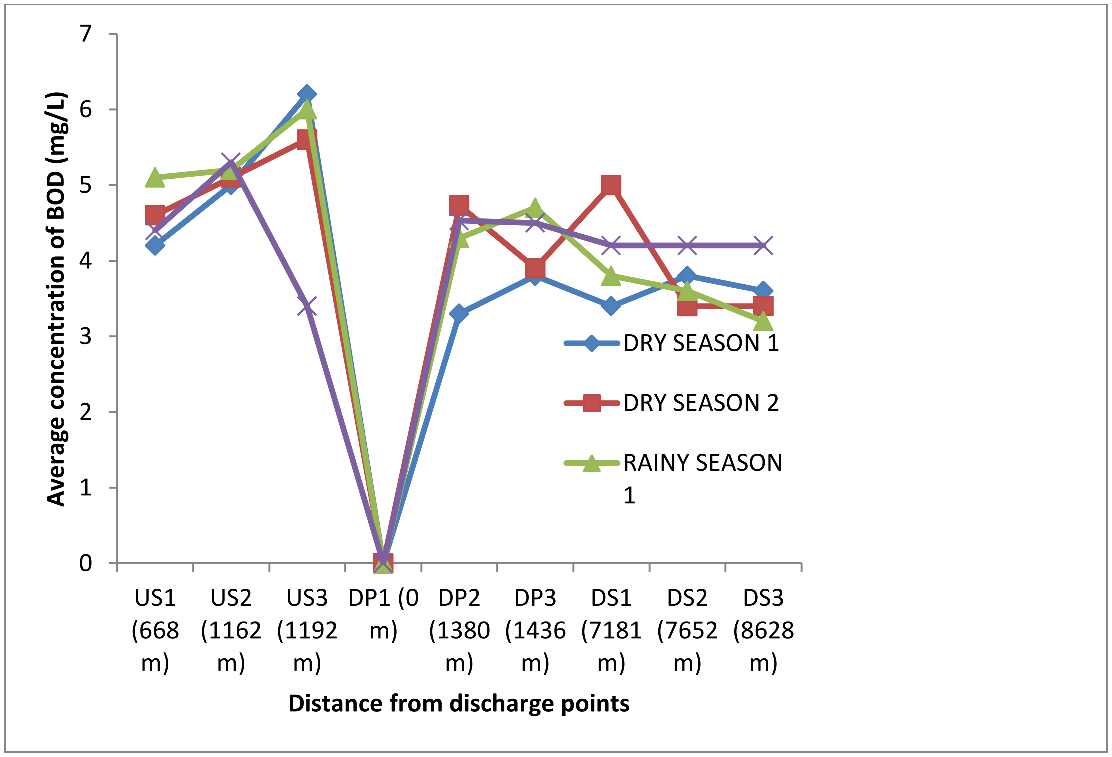

Figure 4.29: Seasonal distribution of Biochemical Oxygen Demand from Battery Company discharge points to Asa River (upstream and downstream).

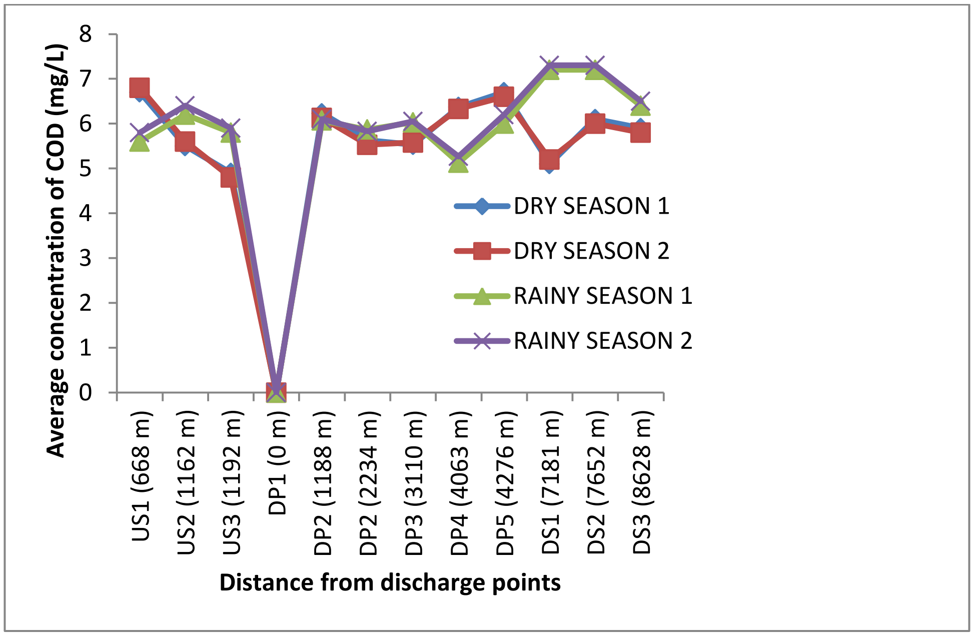

Figure 4.30: Seasonal distribution of Chemical Oxygen Demand from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

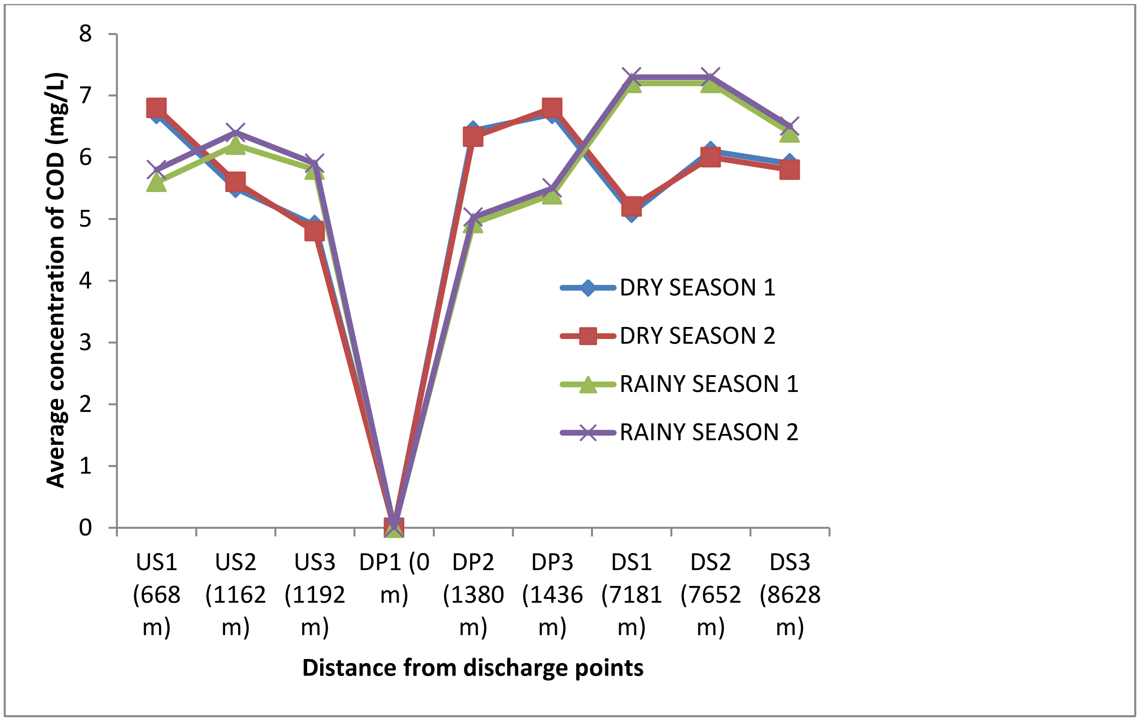

Figure 4.31: Seasonal distribution of Chemical Oxygen Demand from Battery Company discharge points to Asa River (upstream and downstream).

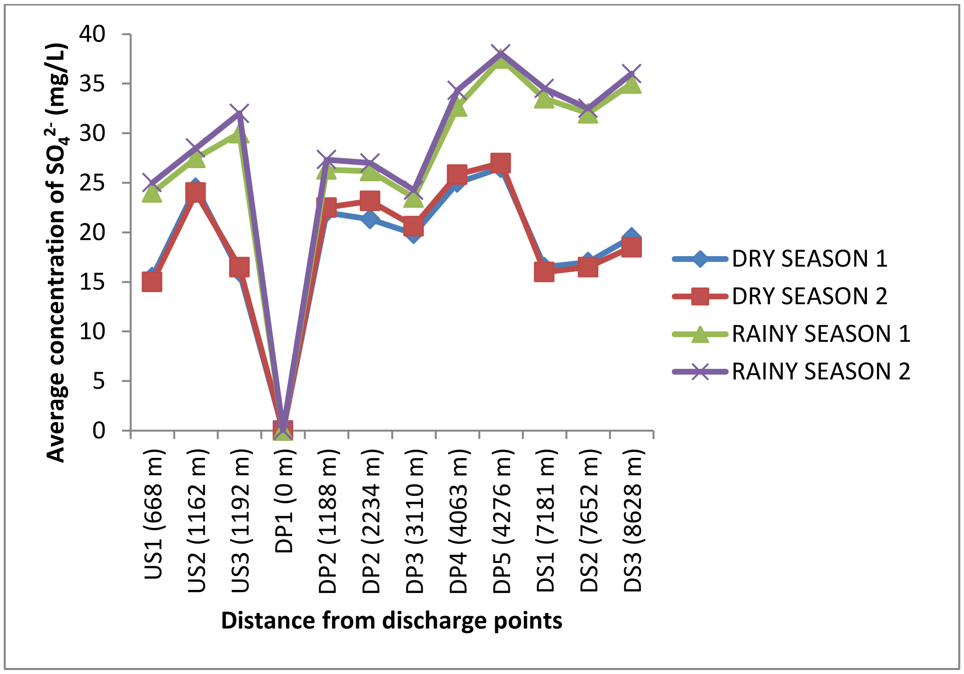

Figure 4.32: Seasonal distribution of sulphate from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

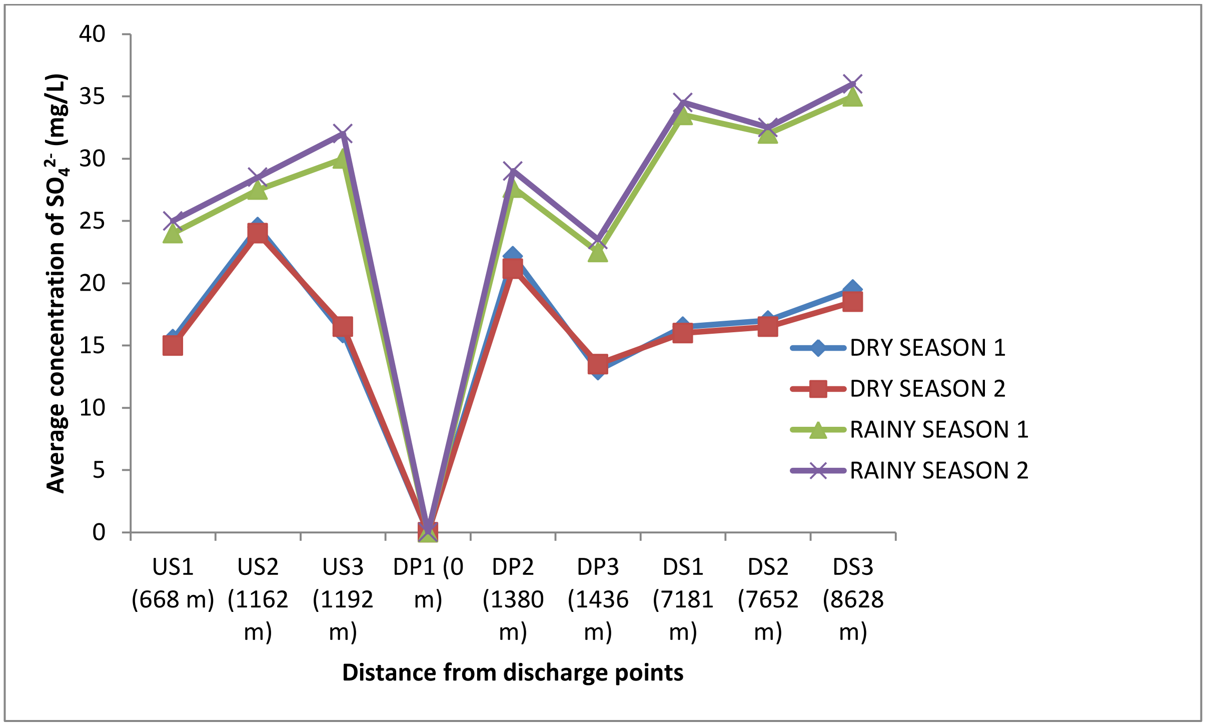

Figure 4.33.: Seasonal distribution of sulphate from Battery Company A and B discharge points to Asa River (upstream and downstream).

8. Nitrate (NIT)

Variation	SS	Df	MS	F-ratio
Group	58.759	21	2.798	4.187
Residual	54.802	82	0.668	
Total	113.561	103		

F-ratio calculated = 4.187 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the nitrate loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot confirms that KC/SW1 (889 m) increase in concentration per distance compared to the other sampling sites, which decrease downstream (Figure 4.34 and 4.35).

9. AMMONIA (AMO)

Variation	SS	Df	MS	F-ratio
Group	0.038	21	0.002	1.432
Residual	0.104	82	0.001	
Total	0.142	103		

F-ratio calculated = 1.432 < the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is not significant. That is, the ammonia loading is not dependent on distance. Hence, the null hypothesis cannot be rejected. The mean plot confirms that site AS1/SW1 (668 m) increase in concentration per distance compared to other sampling sites, which decreases downstream (Figure 4.36 and 4.37).

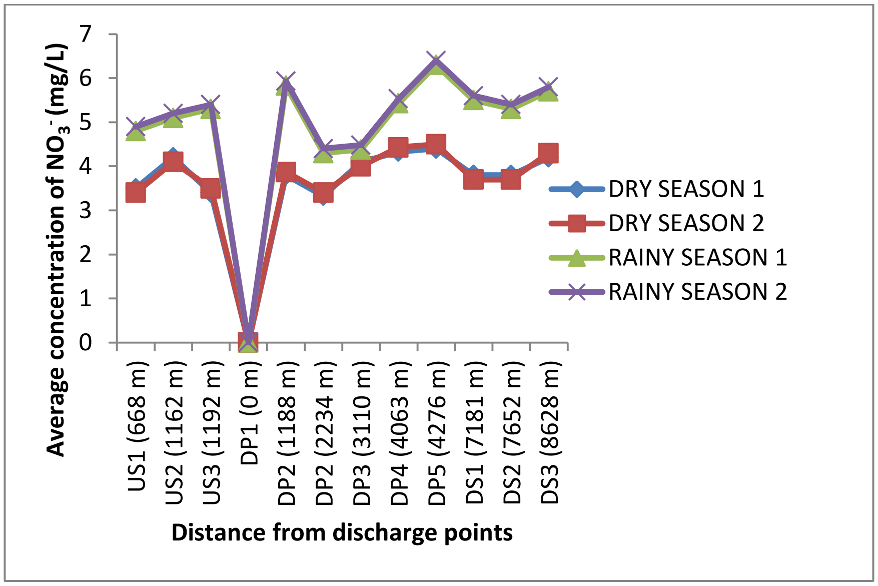

Figure 4.34: Seasonal distribution of nitrate from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

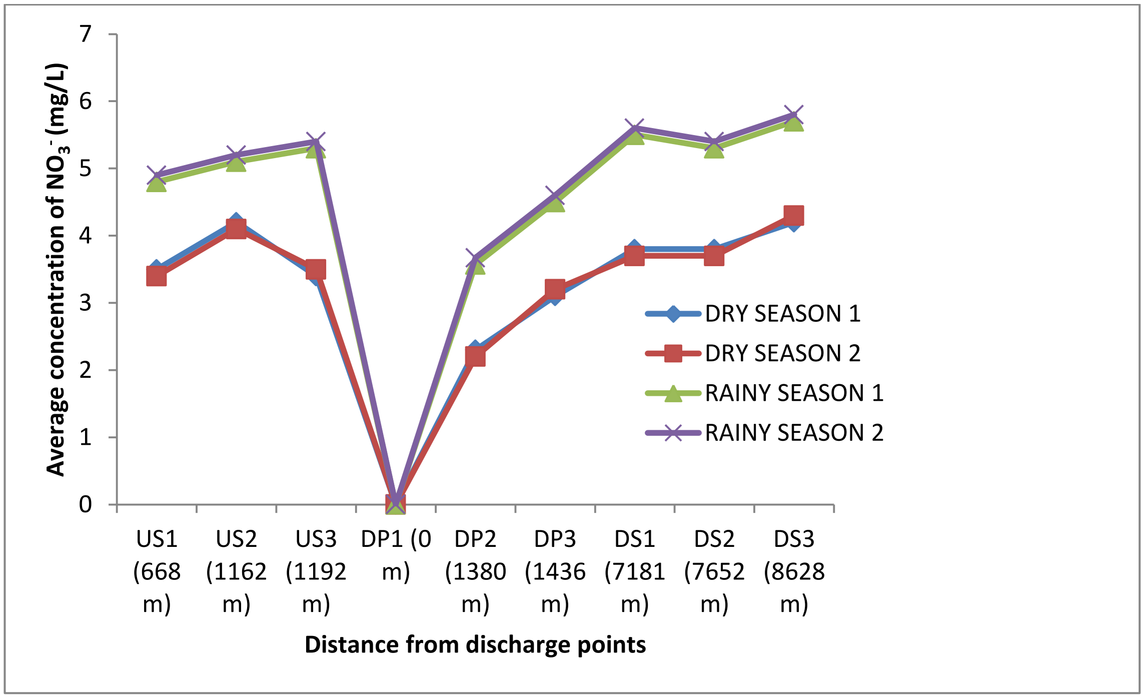

Figure 4.35: Seasonal distribution of nitrate from Battery Company discharge points to Asa River (upstream and downstream)

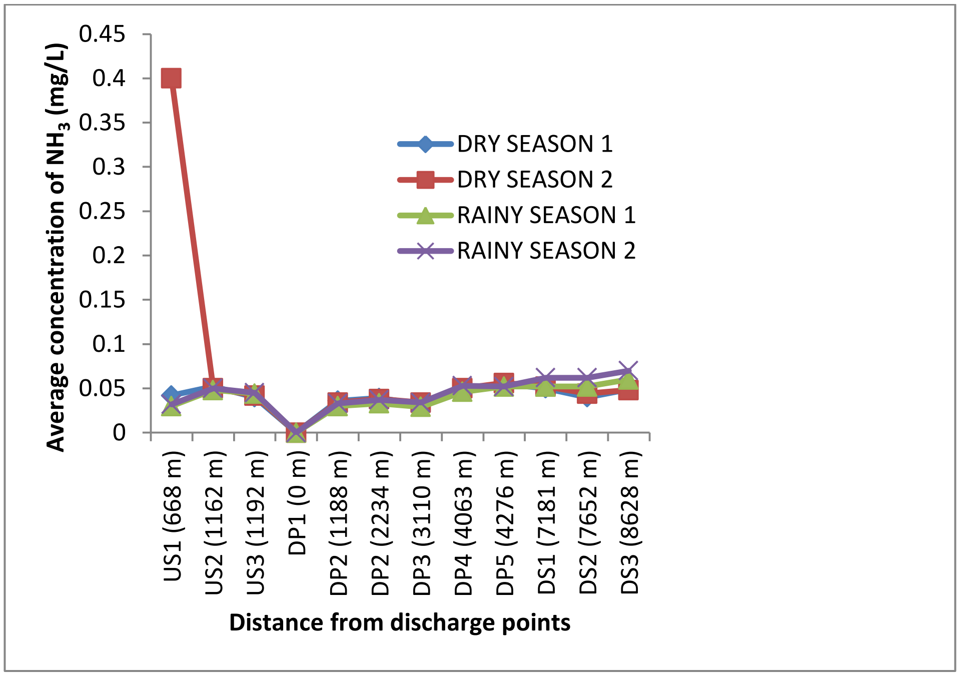

Figure 4.36: Seasonal distribution of ammonia from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

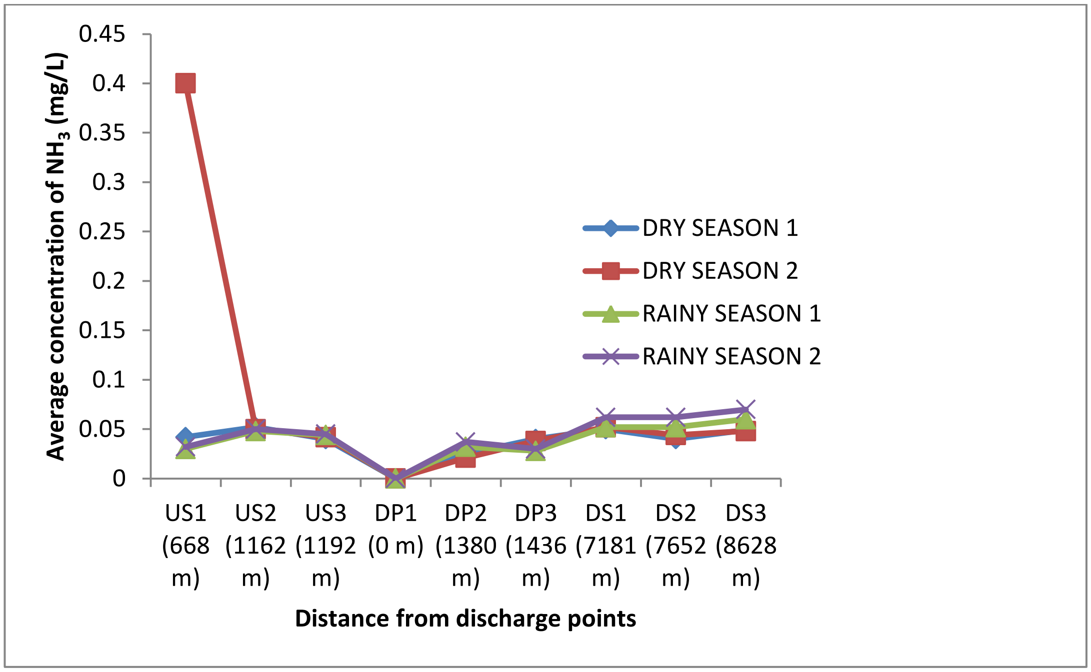

Figure 4.37: Seasonal distribution of ammonia from Battery Company discharge points to Asa River (upstream and downstream).

10. Phosphate (PHO)

Variation	SS	Df	MS	F-ratio
Group	7.551	21	0.360	3.184
Residual	9.262	82	0.113	
Total	16.813	103		

F-ratio calculated = 3.184 < the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is not significant. That is, the phosphate concentration is not dependent on distance. Hence, the null hypothesis cannot be rejected. The mean plot affirms that increase in concentration per distance was observed at sampling sites AS1/SW1, AS2/SW2, AS3/SW3 and also downstream (Figure 4.38 and 4.39).

11. Calcium (Ca)

Variation	SS	Df	MS	F-ratio
Group	207.357	21	9.874	12.054
Residual	67.172	82	0.819	
Total	274.579	103		

F-ratio calculated = 12.054 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Calcium loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot affirms that sampling sites KC/SW2 and GS/SW2 (1039 m and 1240 m) reveal high concentration per distance while sites AS4/SW4 and AS6/SW6 decrease downstream (Figure 4.40 and 4.41).

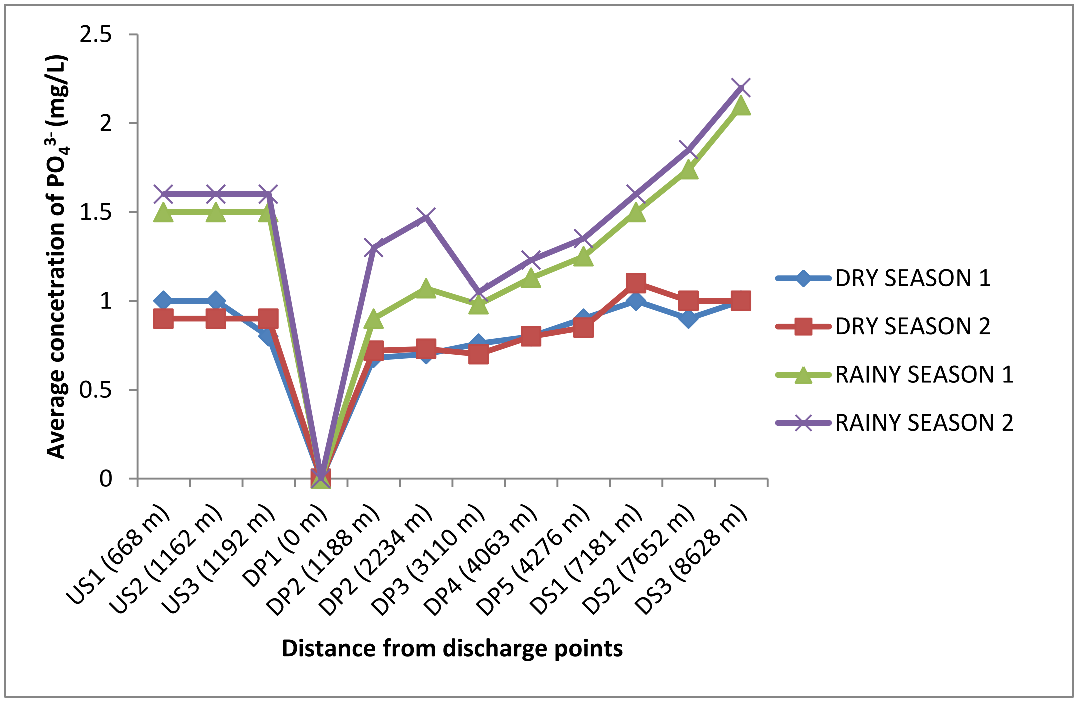

Figure 4.38: Seasonal distribution of phosphate from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

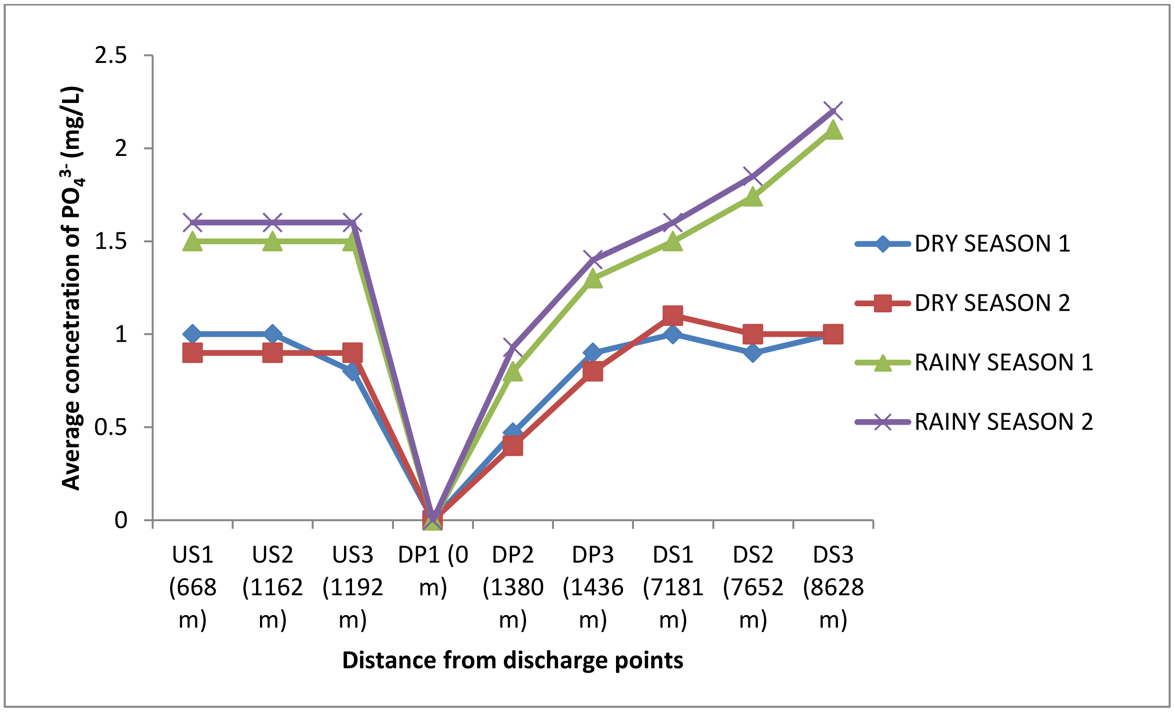

Figure 4.39: Seasonal distribution of phosphate from Battery Company discharge points to Asa River (upstream and downstream).

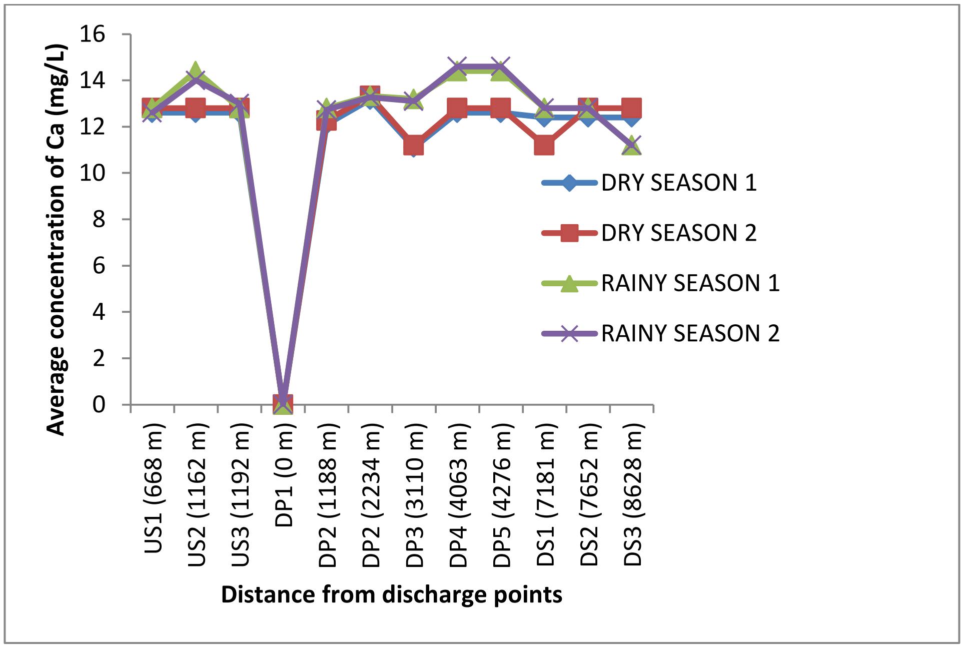

Figure 4.40: Seasonal distribution of Calcium from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

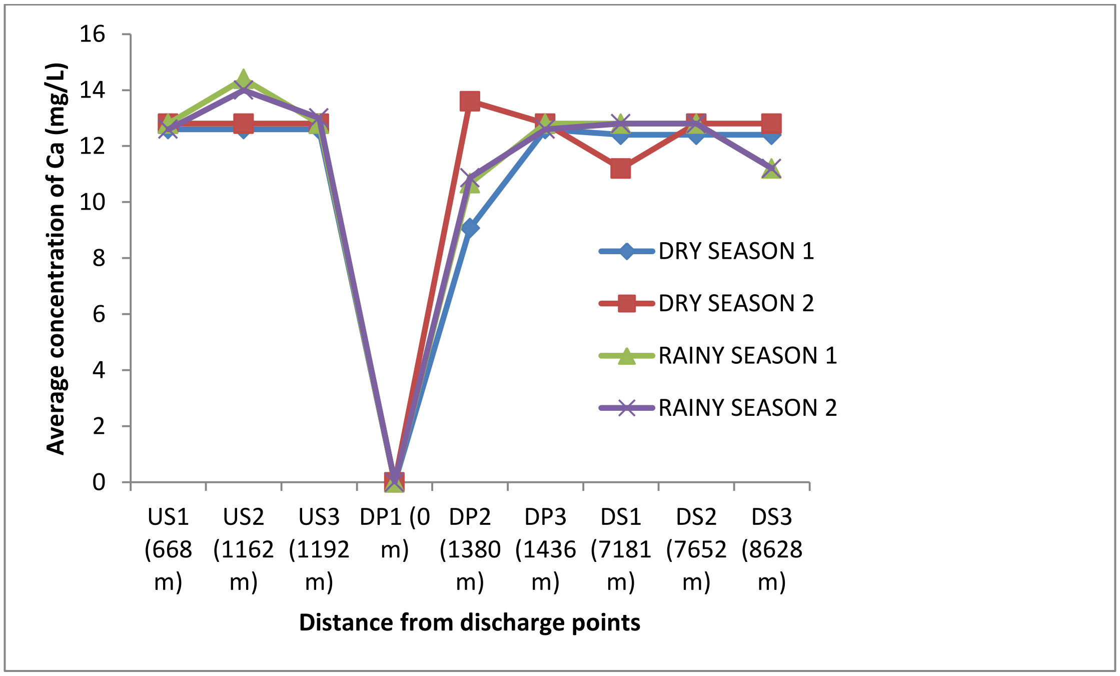

Figure 4.41: Seasonal distribution of Calcium from Battery Company discharge points to Asa River (upstream and downstream).

12. Magnesium (Mg)

Variation	SS	Df	MS	F-ratio
Group	31.653	21	1.507	5.967
Residual	20.714	82	0.253	
Total	52.368	103		

F-ratio calculated = 5.967 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the magnesium loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot affirms that AS2/SW2 and AS3/SW3 (1162 m and 1192 m) shows increase upstream while the downstream sampling sites reduce (Figure 4.42 and 4.43).

13. Sodium (Na)

Variation	SS	Df	MS	F-ratio
Group	24.526	21	1.168	6.151
Residual	15.569	82	0.190	
Total	40.095	103		

F-ratio calculated = 6.151 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the sodium loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot confirms that sampling sites GS/SW1, KC/SW1, AS2/SW2 and AS3/SW3 (553 m, 889 m, 1162 m and 1192 m) increase in concentration per distance at the discharge points and upstream points while slight decrease at site AS4/SW4 (7181 m) (figure 4.44 and 4.45).

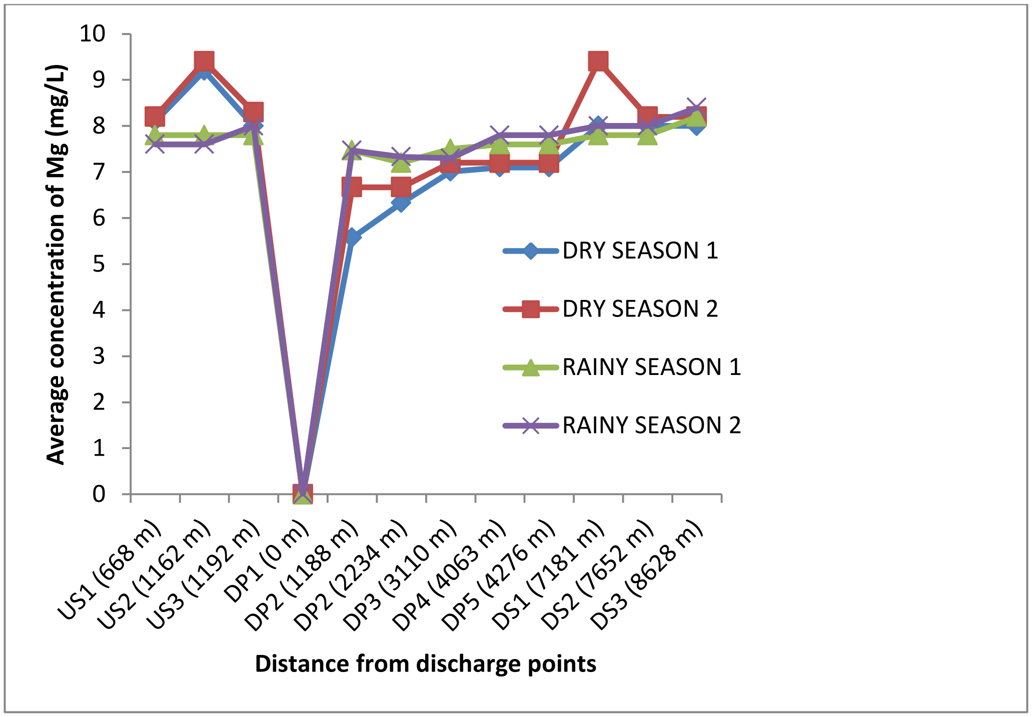

Figure 4.42: Seasonal distribution of Magnesium from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

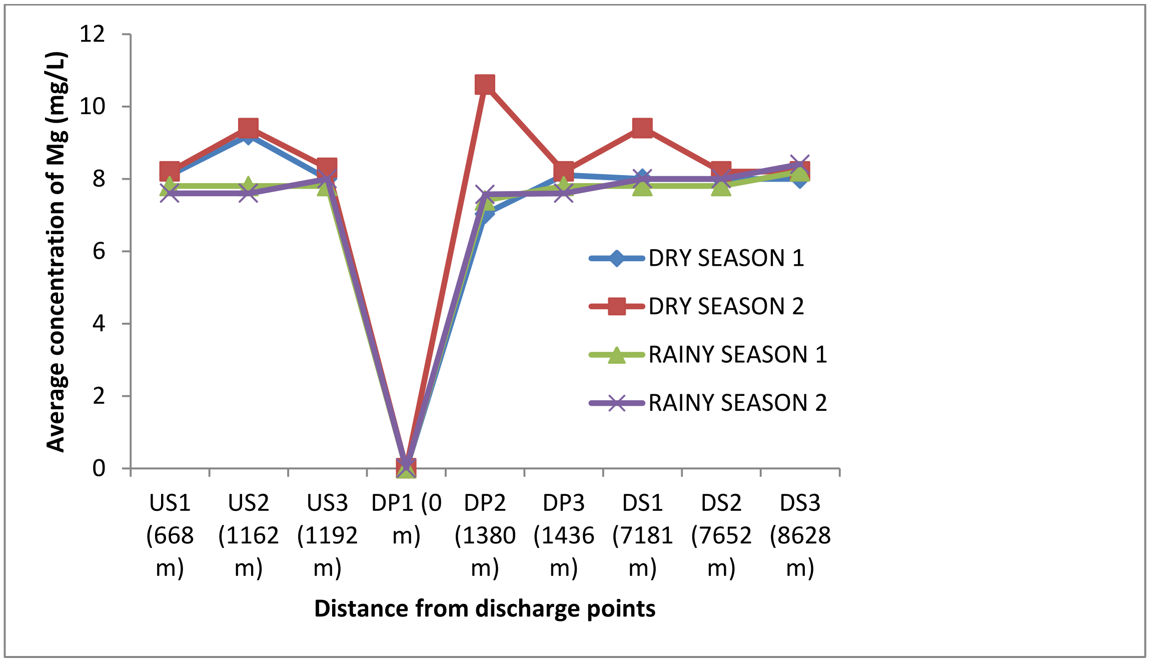

Figure 4.43: Seasonal distribution of Magnesium from Battery Company discharge points to Asa River (upstream and downstream).

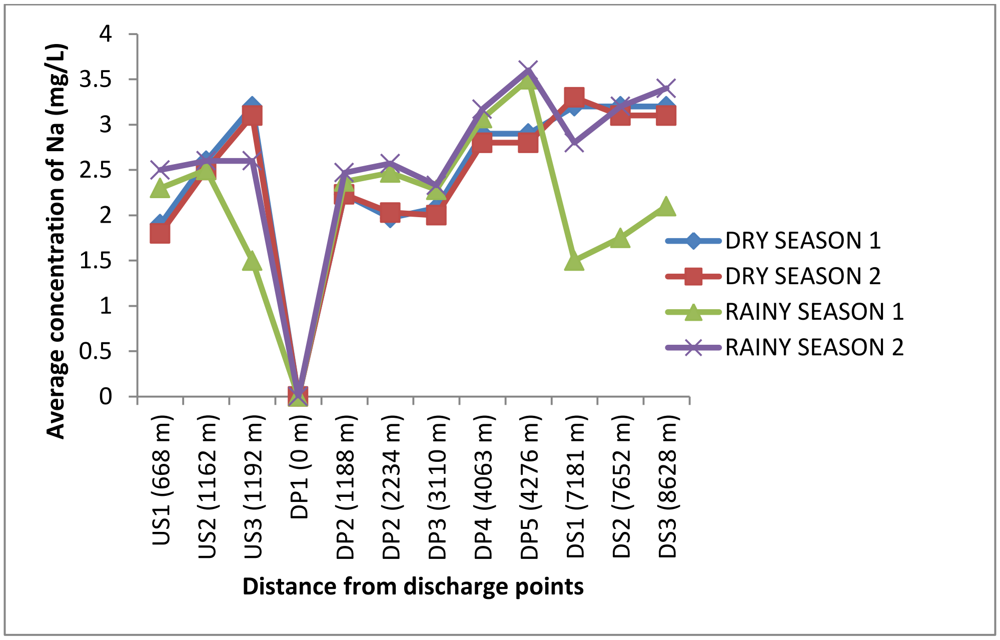

Figure 4.44: Seasonal distribution of Sodium from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

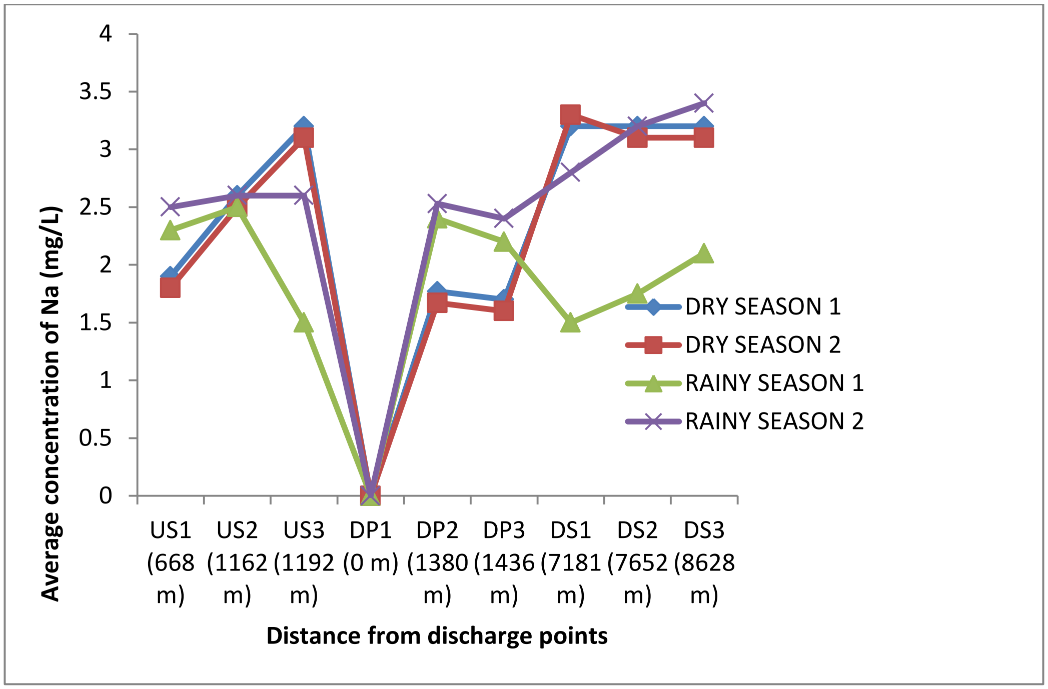

Figure 4.45: Seasonal distribution of Sodium from Battery Company discharge points to Asa River (upstream and downstream).

14. Iron (Fe)

Variation	SS	Df	MS	F-ratio
Group	71.203	21	3.391	7.452
Residual	37.309	82	0.455	
Total	108.512	103		

F-ratio calculated = 7.452 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Iron loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot revealed that sampling sites AS1/SW1, KC/SW2, AS2/SW2, AS3/SW3, GS/SW2 and FB-AS (668 m, 1039 m, 1192 m, 1240 m and 1436 m) increase in concentration per distance compare to site AS5/SW5 which reduces downstream (Figure 4.46 and 4.47).

15. Copper (Cu)

Variation	SS	Df	MS	F-ratio
Group	2.908	21	0.138	7.830
Residual	1.450	82	0.018	
Total	4.358	103		

F-ratio calculated = 7.830 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Copper loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot sampling sites AS1/SW1,AS2/SW2, AS3/SW3, GS/SW2 and FB-AS (668 m, 1162 m, 1192 m, 1240 m and 1436 m) revealed increase in concentration per distance compared to AS4/SW4 and AS5/SW5 which decrease downstream (Figure 4.48 and 4.49)

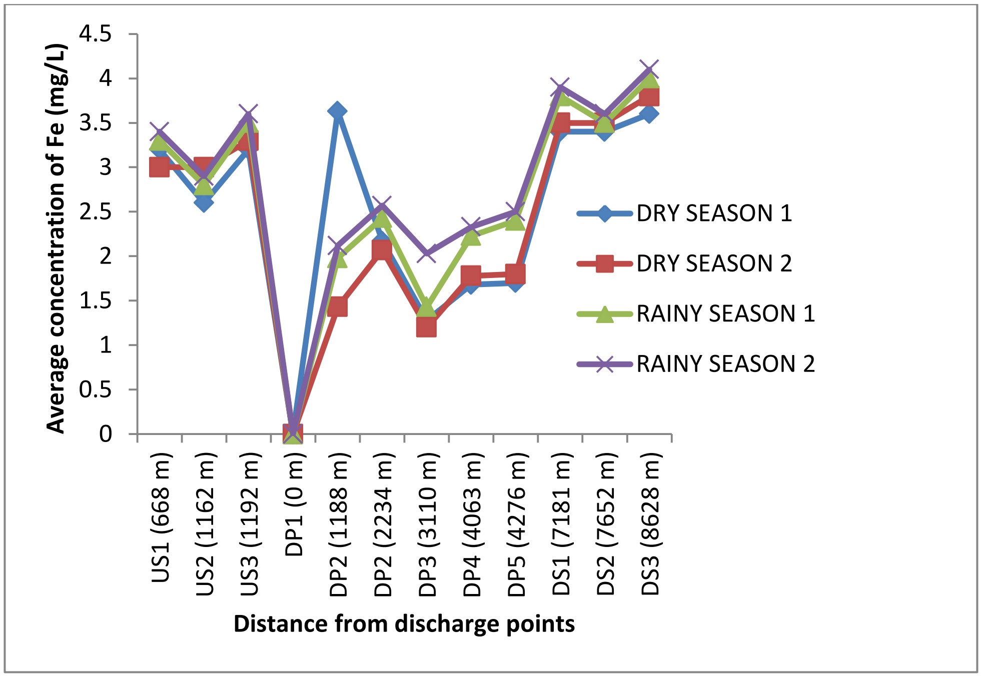

Figure 4.46: Seasonal distribution of Iron from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

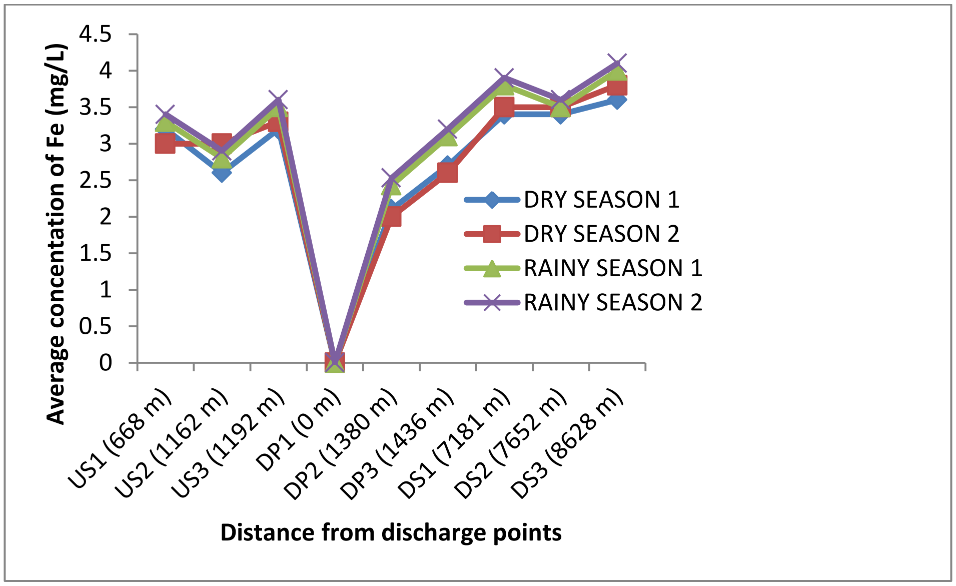

Figure 4.47: Seasonal distribution of Iron from Battery Company discharge points to Asa River (upstream and downstream)

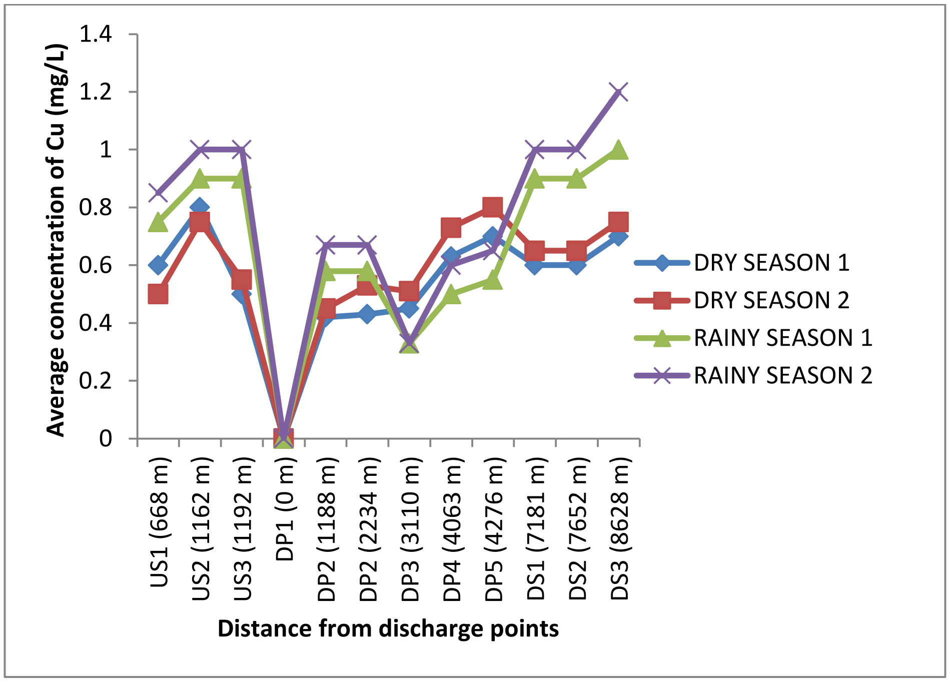

Figure 4.48: Seasonal distribution of Copper from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

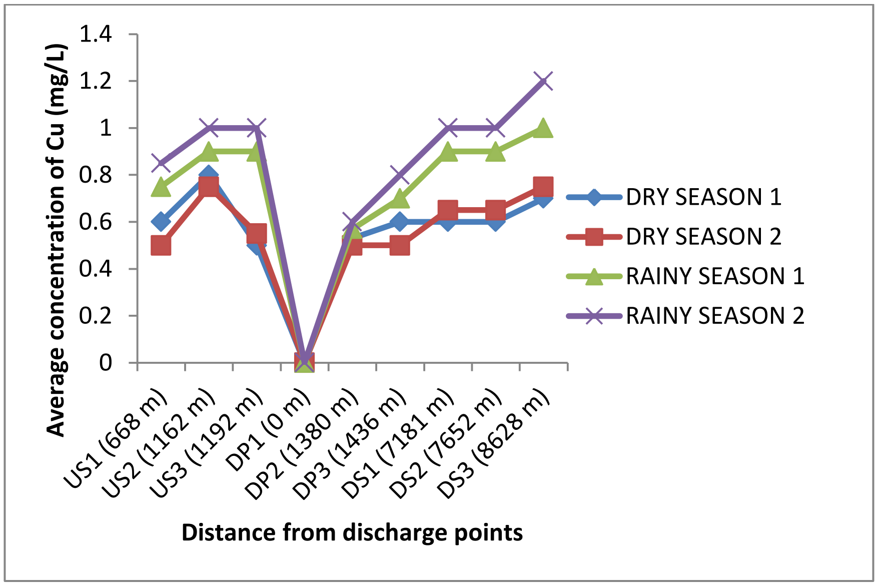

Figure 4.49: Seasonal distribution of alkalinity from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

16. Zinc (Zn)

Variation	SS	Df	MS	F-ratio
Group	168.708	21	8.034	5.893
Residual	111.790	82	1.363	
Total	280.498	103		

F-ratio calculated = 5.893 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Zinc loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot observed at sampling sites GS/SW1, KC/SW2, GS/SW2 and KC-GS-TP/SW3 (553 m, 1039 m, 1240 m and 5255 m) increase in concentration per distance at the discharge points compared to downstream which reveal decrease at sites AS4/SW4, AS6/SW6 and control1/SW (Figure 4.50 and 4.51).

17. Cadmium (Cd)

Variation	SS	Df	MS	F-ratio
Group	0.001	21	0.000	16.671
Residual	0.000	82	0.000	
Total	0.001	103		

F-ratio calculated = 16.671 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Cadmium loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot at sampling sites KC/SW1, KC/SW3 and GS/SW3 (889 m, 1188 m and 1856 m) affirms increase in concentration per distance at the discharge points compare to downstream and control site which shows decrease (Figure 4.52 and 4.53).

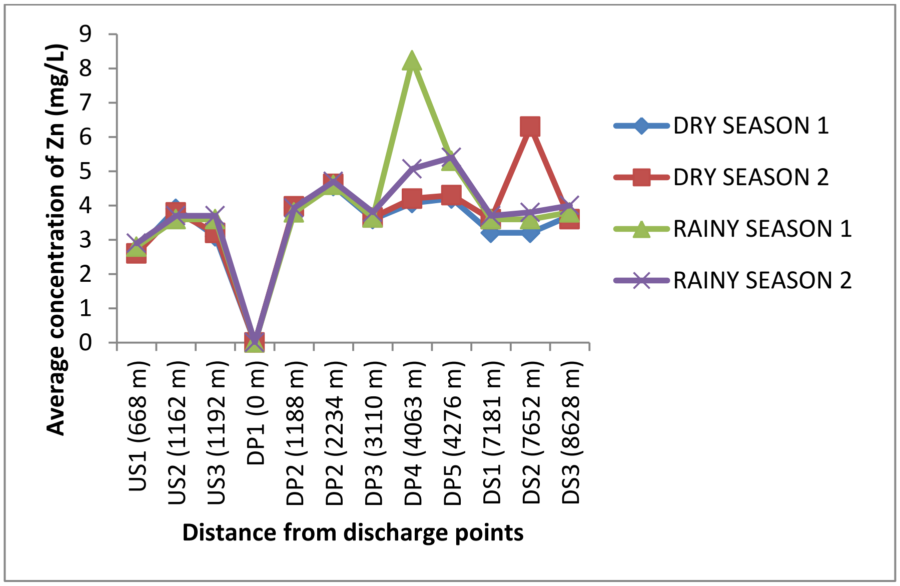

Figure 4.50: Seasonal distribution of Zinc from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

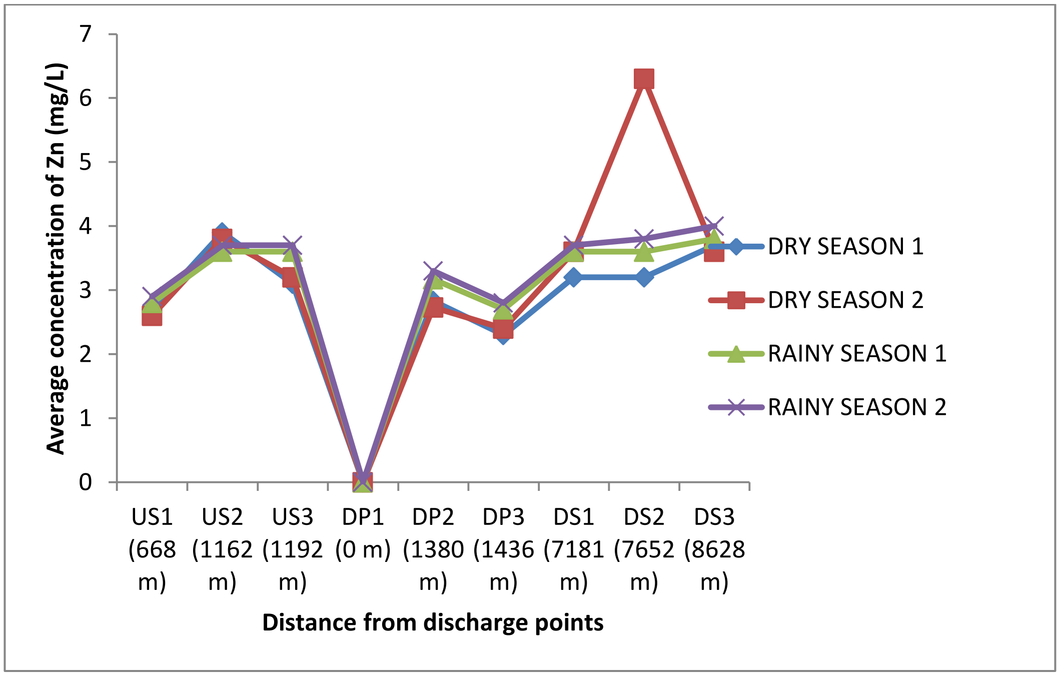

Figure 4.51: Seasonal distribution of Zinc from Battery Company discharge points to Asa River (upstream and downstream)

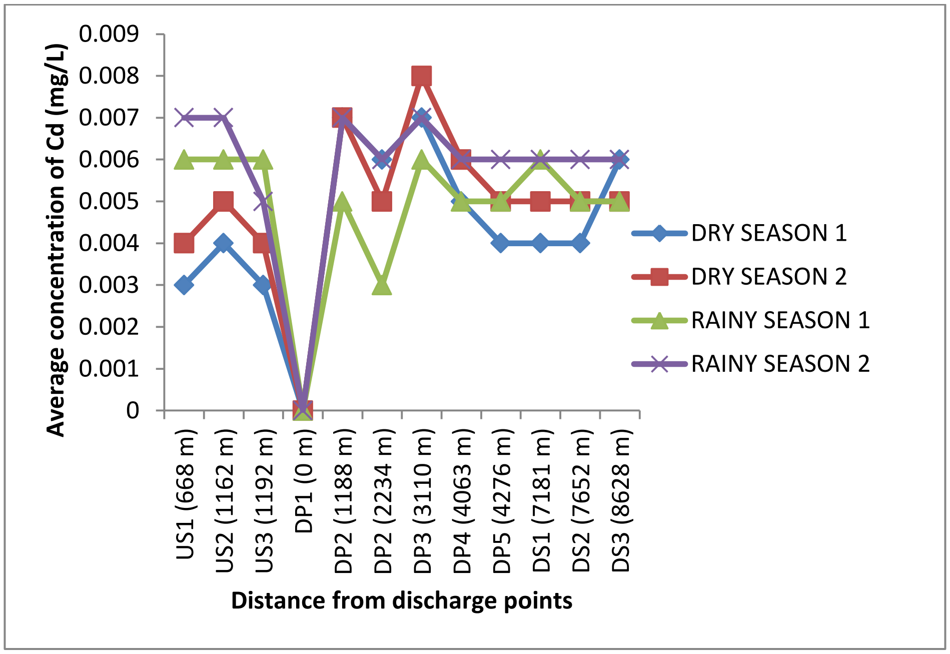

Figure 4.52: Seasonal distribution of Cadmium from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

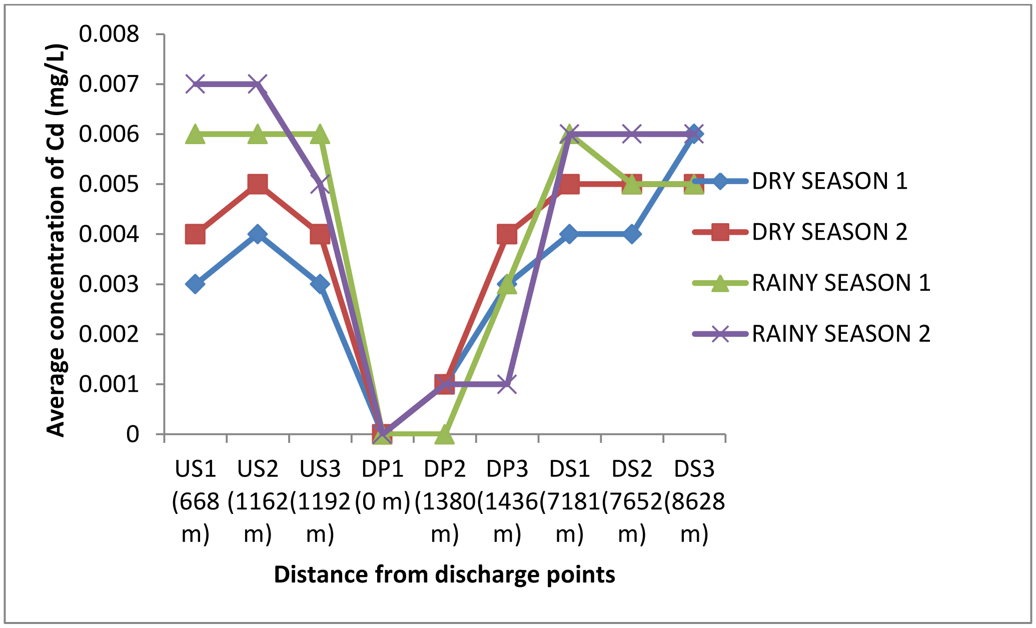

Figure 4.53: Seasonal distribution of Cadmium from Battery Company discharge points to Asa River (upstream and downstream).

18. Lead (Pb)

Variation	SS	Df	MS	F-ratio
Group	5.333	21	0.254	5.105
Residual	4.079	82	0.050	
Total	9.412	103		

F-ratio calculated = 5.105 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Lead loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot confirms that sampling sites AS1/SW1, AS2/SW2, AS3/SW3 and FB/SW1 (668 m, 1162 m, 1192 m, and 1380 m) increase in concentration per distance at upstream and discharge points while decrease was observed at downstream and control sites (Figure 4.54 and 4.55).

19. Chromium (Cr)

Variation	SS	Df	MS	F-ratio
Group	2.430	21	0.116	10.067
Residual	0.952	82	0.011	
Total	3.372	103		

F-ratio calculated = 10.067 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Chromium loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot confirms that sampling sites AS1/SW1, AS2/SW2, AS3/SW3 and FB-AS (668 m, 1162 m, 1192 m and 1436 m) increase in concentration per distance upstream points and entry into Asa River while sites AS4/SW4 and AS5/SW5 decrease compared to the upstream points (Figure 4.56 and 4.57).

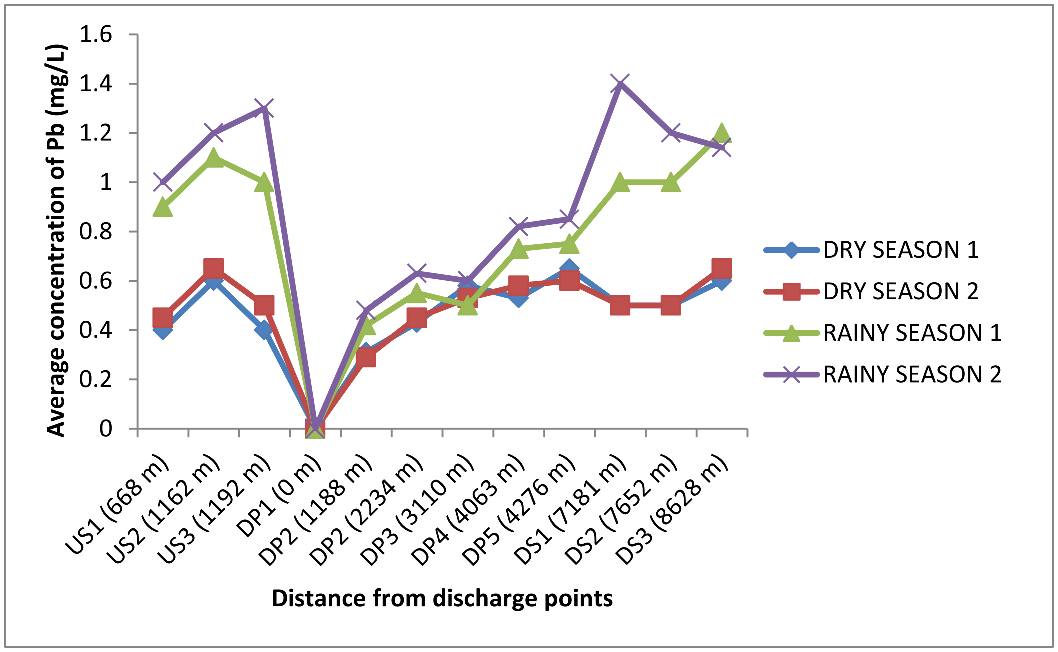

Figure 4.54: Seasonal distribution of Lead from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream).

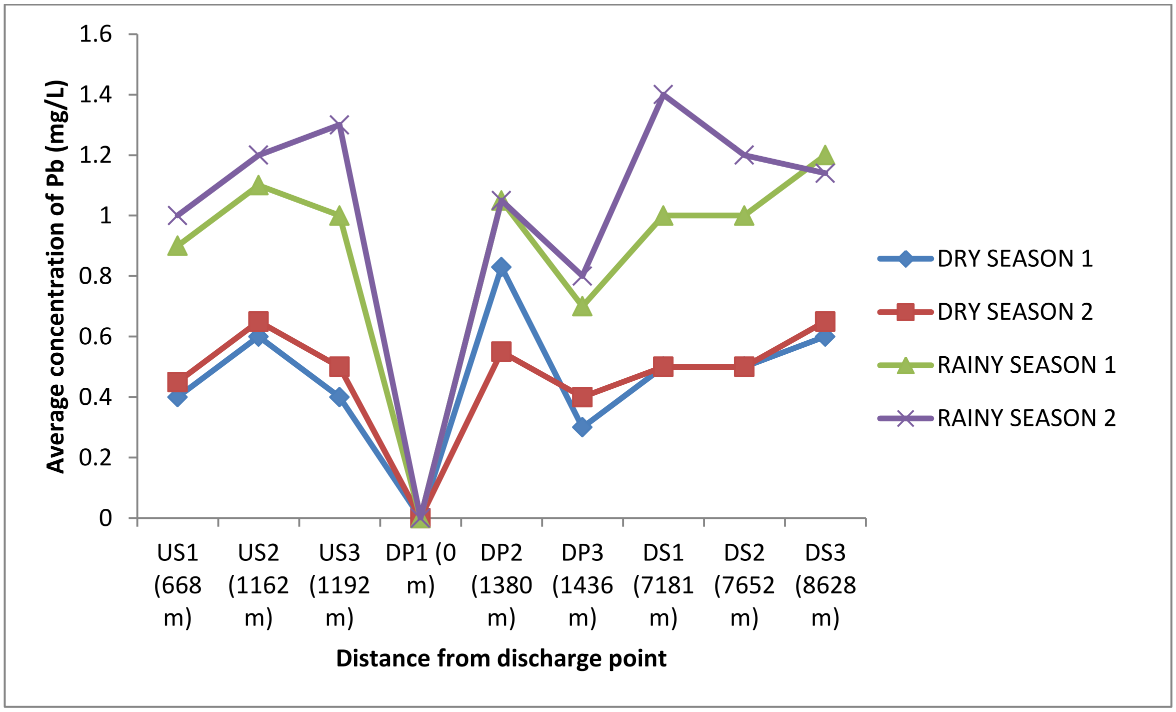

Figure 4.55: Seasonal distribution of Lead from Battery Company discharge points to Asa River (upstream and downstream).

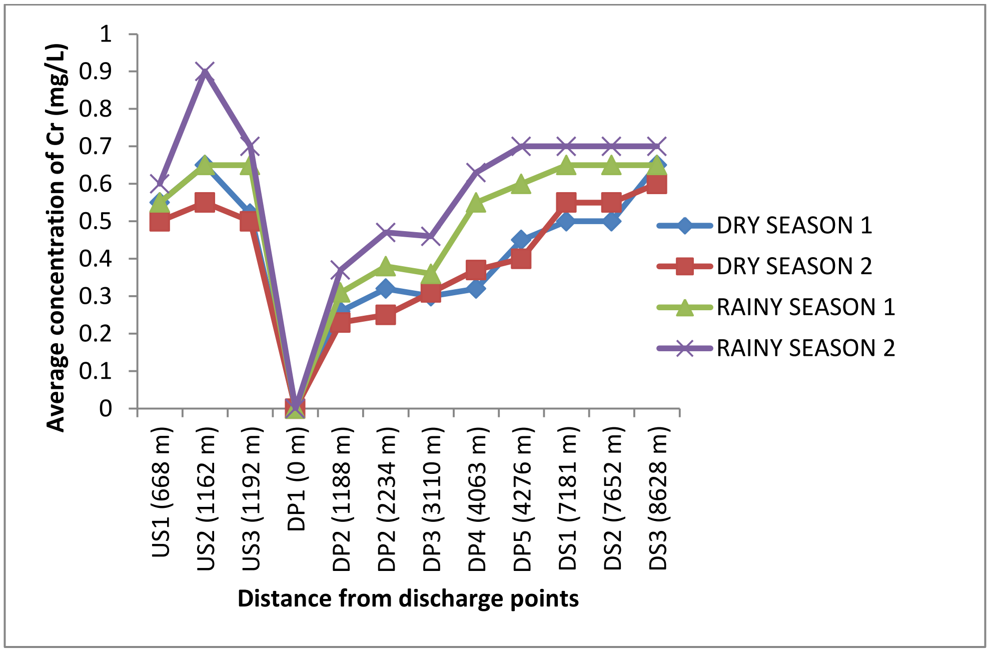

Figure 4.56: Seasonal distribution of Chromium from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream)

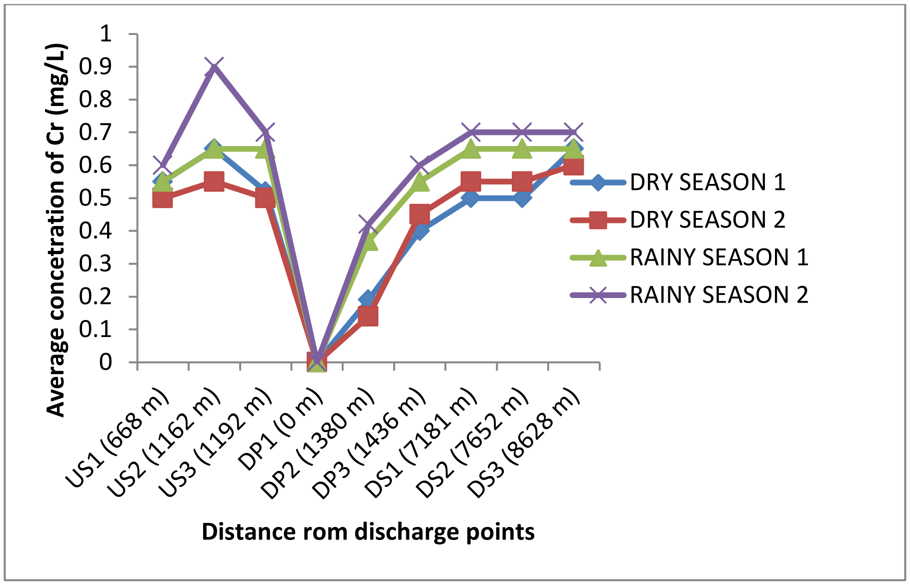

Figure 4.57: Seasonal distribution of Chromium from Battery Company discharge points to Asa River (upstream and downstream)

20. Chloride (Cl)

Variation	SS	Df	MS	F-ratio
Group	14555.605	21	693.124	20.659
Residual	2751.217	82	33.551	
Total	17306.822	103		

F-ratio calculated = 20.659 > the table value F (21, 82) = 3.93 at 5% level, then the effect of distance is significant. That is, the Chloride loading is dependent on distance. Hence, the null hypothesis is rejected. The mean plot affirms that sampling sites KC/SW3, GS/SW3 and KC-GS-TP/SW3 (1188 m, 1856 m and 5255 m) increase in concentration per distance at the discharge points while sites AS4/SW4, AS5/SW5 and AS6/SW6 revealed decrease downstream (Figure 4.58 and 4.59).

The concentrations of cations (Cu^{2+}, Zn^{2+}, Cd, Pb^{2+}, Cr^{3+}, Fe^{2+}, Mg^{2+}, Ca^{2+}, Na^{+}), anions (NO_3^-, PO_4^{3-}, Cl^-, SO_4^{2-}), gases (NH_3), tests for oxygen demands by inorganic and organic substances (DO, COD and BOD), physical analysis (THS, TSS and ALK), analysed showed variations for Asa River surface water samples. Test of significance was carried out using Regression and ANOVA model analysis. No significant difference at 95% probability level for the various samples of surface water obtained on Asa River in Ilorin, Kwara State which was tested.

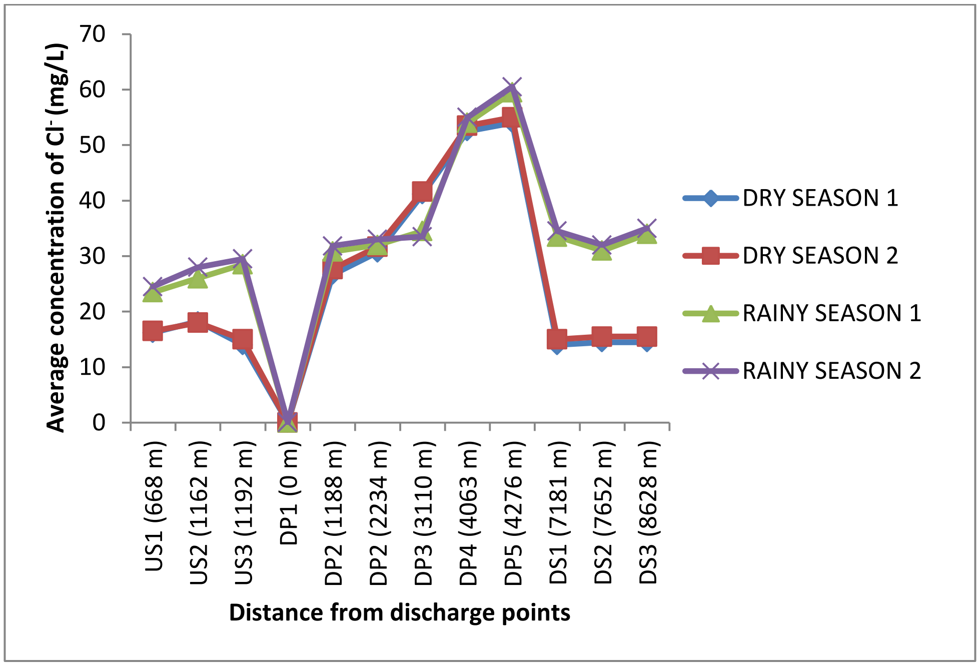

Figure 4.58: Seasonal distribution of Chloride from Detergent, Pharmaceutical Company A and B discharge points to Asa River (upstream and downstream)

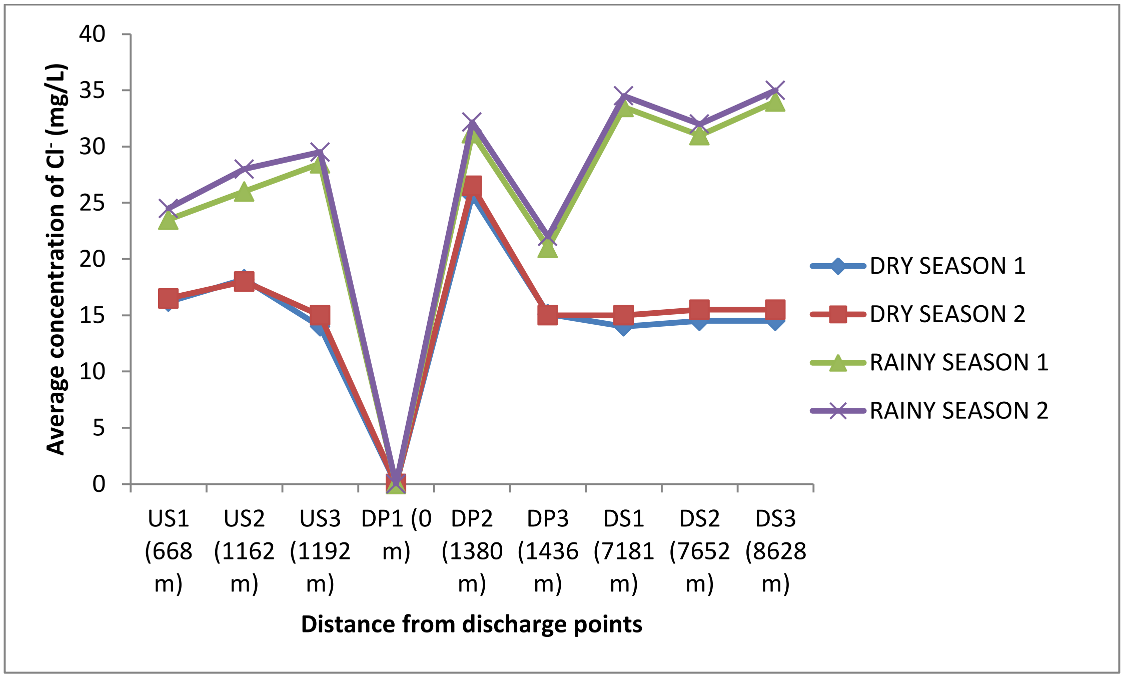

Figure 4.59: Seasonal distribution of Chloride from Battery Company discharge points to Asa River(upstream and downstream)

The effect of DT on ALK, DOX, AMO, NIT, Ca, Zn and Pb were not significant and this was expected because of the following reasons: the nature of materials suspended into the water which the runoff carries away, the amount of microbial activities present in the surface water at a particular period of time, that is the level of consumption of oxygen either high or low, the nature of the underlying soil over which the nature of materials been discharge into the flow are determined were the causes and not dependent on distance.

TS, THS, BOD, COD, SULP, PHO, Mg, Na, Cu, Fe, Cd, Cr and Cl were significant because a lot of poisonous things are being discharged by industries and need to be treated before been discharged into the stream thereby affecting the quality of the surface water by killing the fish. Pollution increases with distance at the discharge points based on agricultural, domestic and industrial discharges. The longer the distance, the heavier is the pollution at the discharge points.

4.9 Socio-economic impact assessment

4.9.1 Stratum features of respondents

The outcomes of the investigations specify in table 4.29 reveals that manly comprised the most rated of respondents (57.8%). This is not uprising taking the fact that most families in the township are man headed due greatly to sub cultural and theological components. Greater than half evaluated are espoused (52.9%). Three-fifths are between lifespan 21-30. Categorically, the bulkiest segments of the defendants (70%) are within these age range. It is not sprucing seeing the case that these age groups are prone to education, industrial attachment from various institutions into industrial companies at Ilorin metropolis. Along awe to the altitude of schooling attained, 2.7% have no schooling while 73.8% have tertiary education (NCE/OND, B.Sc/HND and Postgraduates). Most of the respondents are artisans (51.6%). 74.2% of the respondents use groundwater as source (borehole and well) while only 5.8% of the respondents use tap water.

Table 4.29: Stratum features of respondents

Stratum features		Frequency	Percentage
Gender-specific	Manly	130	57.8
	Womanly	95	42.2
Age	15-20	12	5.3
	21-25	67	29.8
	26-30	93	41.3
	31 and above	53	23.6
Marital Status	Single	106	47.1
	Married	119	52.9
Religion	Christianity	113	50.2
	Muslim	111	49.3
	Traditional	1	0.4
Location	Oke-Oyi Zone	25	11.1
	Unity Zone	25	11.1
	Asa-dam Zone	25	11.1
	New Yidi Zone	25	11.1
	Odota Zone	25	11.1
	Egbejila Zone	25	11.1
	Amilegbe Zone	25	11.1
	Afon Zone	25	11.1
	Ero-omo Zone	25	11.1
Education	No education	6	2.7
	Primary education	20	8.9
	Secondary education	33	14.7
	NCE/OND	94	41.8
	B.Sc/HND	68	30.2
	Postgraduate	4	1.8
Occupation	Artisans	116	51.6
	Skilled workers	109	48.4
Type of water	Well water	79	35.1
	Borehole	88	39.1
	Stream	45	20.0
	Tap water	13	5.8

4.9.2 Research Questions

The facts accessed were analysed as follows to afford the vital erudition specify systematically to direct the inquiry.

Research Question One: Is there effect of domestic purpose component based on location, type of water and occupation?

This question would be answered by using the data in table 4.30 on domestic purpose component. The feedback as pointed out by article 1 shows that 93.9% agrees with the statement that fish and aquatic life are abundant in Asa River while 6.7% disagrees to the statement. It can therefore be said that the assumption is accepted that habitats are present in river water. The other articles 3-7 shows that the river is of good quality for drinking water, point of supply for household aqua for the entire populace, good for crop cultivation; both children and adult swim in the water. The responses as indicated by item 8 revealed that 95.5% respondent disagrees to the statement that the well water been used is smelling and unpleasant for domestic purposes. It can therefore be said that the assumption is rejected that well water have odour.

In summary, it can be reviewed that Asa River is the river that supplies water to the whole populace of Kwara State, which is used for various purpose like drinking water, aquatic life, industrial purpose and even pumping into different homes, which serves as well water, tap water and borehole.

Table 4.30: Domestic purpose component

ARTICLES	FA	%	A	%	D	%	FD	%	MEANS
1	1	0.4	209	92.9	15	6.7	-	-	2.94
2	213	94.7	10	4.4	2	0.9	-	-	3.94
3	200	88.9	21	9.3	4	1.8	-	-	3.87
4	197	87.6	18	8.0	7	3.1	3	1.3	3.82
5	10	4.4	206	91.6	5	2.2	4	1.8	2.99
6	5	2.2	219	97.3	-	-	1	0.4	3.01
7	1	0.4	174	77.3	42	18.7	8	3.6	2.75
8	-	-	10	4.4	205	91.1	10	4.4	2.00

Research Question Two: Is there effect of health impact factor based on location, type of water and occupation?

This question would be answered by using the data in table 4.31 on health impact factor.
Table 4.30 reveals the feedback to articles 10, 11 and 13 that links health impact component. This discovers that health happens to be an important tool to human beings. From the above table, it can be observed that item 10 responses revealed that 92.6% agrees to the statement of skin related problems with people bathing directly on Asa River. It was observed from item 11 that 96% agrees that health problems are rampant within the community as a result of using contaminated well and river water while 4% disagrees with the statement. Item 13 reveals that 90.7% disagrees with the statement that effluent from industrial activities within Ilorin environs have direct impact on people's social well being while 9.3% disagrees to the statement. It can therefore be said that the assumption is accepted that the health impact of the populace is affected by contaminated river water.

In summary, it is noted that people bathing with direct Asa River water especially in streams close to manufacturing companies have skin related disease problems and other health challenge like cholera, dysentery, diarrhea etc.

Table 4.31: Health impact component

ARTICLES	FA	%	A	%	D	%	FD	%	MEANS
9	2	0.9	8	3.6	213	94.7	2	0.9	2.04
10	2	0.9	207	92.0	12	5.3	4	1.8	2.92
11	204	90.7	12	5.3	5	2.2	4	1.8	3.85
12	10	4.4	209	92.9	5	2.2	1	0.4	3.01
13	2	0.9	19	8.4	202	89.8	2	9	2.09
14	1	0.4	209	92.9	11	4.9	4	1.8	2.92
15	9	4.0	215	95.6	-	-	1	0.4	3.03
16	4	1.8	216	96.0	2	0.9	3	1.3	2.98

Research Question Three: Is there effect of environmental impact assessment factor based on location, type of water and occupation?

This question would be answered by using the data in table 4.32 on environmental impact assessment factor. The responses as indicated above by item 19, 20, 23 and 24 observed that 97.8% agrees to the statement that they will prefer to relocate a way from industrial companies to avoid health related problems while 2.2% disagrees. 87.5% agrees to the statement that our environment is not induced by the action of industries while 12.5% disagrees. 92% responded that dumpsites do pose health problems while 8% disagrees with the statement. 97.7% agrees to the statement that both the industries and community are responsible for environmental pollution in the environment but 2.2% disagrees to the statement. It can therefore be said that the assumption is accepted that environmental impact assessment pose a role by both individual, industrial companies and the whole populace.

In summary, it can be observed that industrial companies effluent do have impact on the people and also people living in the locality also contributes to the environmental pollution of the environs through dumping of refuse in improper places like stream side which has cause a lot of havoc in terms of flooding, soil pollution that is wearing away of the top soil. The earlier mentioned issues have contributed to environmental problems.

Table 4.32: Environmental impact assessment component

ARTICLES	FA	%	A	%	D	%	FD	%	MEANS
17	7	3.1	212	94.2	5	2.2	1	0.4	3.00
18	3	1.3	212	94.2	8	3.6	2	0.9	2.96
19	5	2.2	215	95.6	1	0.4	4	1.8	2.98
20	181	80.4	16	7.1	24	10.7	4	1.8	3.66
21	3	1.3	5	2.2	214	95.1	3	1.3	2.04
22	2	0.9	89	39.6	128	56.9	6	2.7	2.39
23	1	0.4	206	91.6	9	4.0	9	4.0	2.88
24	7	3.1	213	94.7	2	0.9	3	1.3	3.00
25	2	0.9	4	1.8	218	96.9	1	0.4	2.03

4.9.3 Research Hypothesis

The ANOVA tables are shown below by comparing general assessment of Asa River, domestic factor, health impact factor and environmental impact factor based on type of water and location while t-test tables were based only on occupation

Hypothesis One: There is no significant difference on general assessment of Asa River (V1-V25) on the basis of location, type of water and occupation.

ANOVA analysis of general assessment of Asa River based on location

VARIATION	SS	DF	MS	F-ratio
Group	572.089	8	71.511	7.831
Residual	1972.560	216	9.132	
Total	2544.649	224		

F-ratio calculated = 7.831 > the table value F (8, 216) = 1.94 at 5% level then the basis of location on general assessment of Asa River is significant. Hence, the null hypothesis can be rejected.

ANOVA analysis of general assessment of Asa River based on type of water

VARIATION	SS	Df	MS	F-ratio
Group	1050.935	3	350.312	51.830
Residual	1493.714	221	6.752	
Total	2544.649	224		

F-ratio calculated = 51.830 > the table F (3, 221) = 2.60 at 5% level then the basis of type of water on general assessment of Asa River is significant. Hence the null hypothesis can be rejected.

A t-test analysis of general assessment of Asa River based on occupation

VARIABLE		N	MEAN	STD.DEV.	DF	t_{cal}	t_{table}
TOT	1	116	73.6293	0.56768	223	2.447	1.962
	2	109	72.5413	4.75420			

T-value calculated (2.447) > the table t-value (1.962), then the null hypothesis is rejected, which implies that the basis of occupation on general assessment of Asa River is significant.

Hypothesis Two: There is no significant difference on domestic purpose factor (V1-V8) of Asa River based of location, type of water and occupation.

ANOVA analysis of domestic purpose factor on the basis of location

VARIATION	SS	Df	MS	F-ratio
Group	116.462	8	14.558	6.665
Residual	471.760	216	2.184	
Total	588.222	224		

F-ratio calculated = 6.665 > the table F (8, 216) = 1.94 at 5% level then the basis of location on domestic purpose is significant. Hence, the null hypothesis is rejected.

ANOVA analysis of domestic purpose factor on the basis of type of water

VARIATION	SS	Df	MS	F-ratio
Group	110.672	3	36.891	17.072
Residual	477.550	221	2.161	
Total	588.222	224		

F-ratio calculated = 17.072 > the table F (3, 221) = 2.60 at 5% level then the basis of type of water on domestic purpose is significant. Hence the null hypothesis is rejected.

A t-test analysis of domestic purpose factor based on occupation

VARIABLE		N	MEAN	STD.DEV.	DF	t_{cal}	t_{table}
DOP	1	116	25.7672	0.63736	223	4.542	1.962
	2	109	24.8257	2.13370			

T-value calculated (4.542) > the table t-value (1.962), then the null hypothesis is rejected, which implies that basis of occupation and domestic purpose is significant.

Hypothesis Three: There is no significant difference in health impact factor (V9-V16) of Asa River based of location, type of water and occupation.

ANOVA analysis of health impact factor on location

VARIATION	SS	DF	MS	F-ratio
Group	47.760	8	5.970	5.597
Residual	230.400	216	1.067	
Total	278.160	224		

F-ratio calculated = 5.597 > the table F (8, 216) = 1.94 at 5% level then the basis of location on health impact is significant. Hence the null hypothesis is rejected.

ANOVA analysis of health impact factor on type of water

VARIATION	SS	DF	MS	F-ratio
Group	89.661	3	29.887	35.040
Residual	188.499	221	0.853	
Total	278.160	224		

F-ratio calculated = 35.040 > the table F (3, 221) = 2.60 at 5% level, then the basis of type of water on health impact is significant. Therefore the null hypothesis is rejected.

A t-test analysis of health impact factor on occupation

VARIABLE		N	MEAN	STD.DEV	DF	t_{cal}	t_{table}
HEI	1	116	22.9655	0.18326	223	1.563	1.962
	2	109	22.7339	1.58490			

T-value calculated (1.563) < the t-value table (1.962), then the null hypothesis is accepted, which implies that basis of occupation on health impact is not significant.

Hypothesis Four: There is no significant difference in environmental impact assessment factor (V17-V25) of Asa River based of location, type of water and occupation.

ANOVA analysis of environmental assessment impact on location

VARIATION	SS	DF	MS	F-ratio
Group	111.449	8	13.931	8.096
Residual	371.680	216	1.721	
Total	483.129	224		

F-ratio calculated = 8.096 > the table F (8, 216) = 1.94 at 5% level, then the basis of location on environmental impact assessment is significant. Hence, the null hypothesis is rejected.

ANOVA analysis of environmental assessment impact on type of water

VARIATION	SS	DF	MS	F-ratio
Group	167.943	3	55.981	39.252
Residual	315.186	221	1.426	
Total	483.129	224		

F-ratio calculated = 39.252 > the table F (3, 221) = 2.60 at 5% level, then the basis of type of water on environmental impact assessment is significant. Hence, the null hypothesis is rejected.

A t-test analysis of environmental assessment impact on occupation

VARIABLE		N	MEAN	STD.DEV	DF	t_{cal}	t_{table}
EVN	1	116	24.8966	0.30586	223	-0.434	1.962
	2	109	24.9817	2.09046			

T-value calculated is (-0.434) < t-value table (1.962), then the null hypothesis is accepted, which implies that the basis of occupation on environmental impact assessment is not significant.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This chapter summarises all the work done in this study for effluent, surface water, sediment, groundwater and organic compounds in surface water and sediment.

5.1.1 Effluent characteristics

The study deduced that volume of effluent discharged into Asa River was already over taxing their capacity for self purification. It has been shown that the discharge of effluent by industries can constitute dense changes in physical status and presence of anions and cations in the receiving water bodies which hampers the quality of water and also affects the aquatic life form. The prevailing practice of unregulated and uncontrolled discharge of effluent into water bodies constitutes serious abuse and portends serious danger to the species diversity and beneficial use to the municipality.

5.1.2 Surface water quality

This study complements previous studies on the impact of industrial, agricultural and domestic discharges on the limnological parameters of aquatic environment. The study however revealed the following: the industries, agricultural fields and domestic usages in the vicinity of Asa River discharges wastes containing high physical, chemical and heavy metal components into the river, thus raising the level of these parameters beyond the recommended levels of WHO and NESREA guidelines. The volume of discharges into Asa River has already over burden the capacity for self-purification and the prevailing practice of unregulated and uncontrolled discharge of such wastes into water bodies constitutes serious abuse to the environment. It is noted in this study that Asa River water was heavily polluted with trace organics and heavy metals using overall pollution index. Therefore, proper treatment is imperative for the river to be appropriate for potable, domestic and industrial purposes.

5.1.3 Sediment

The continuous increase in heavy metal contamination of these water bodies inhabit agent for interest, as these chemical elements keep affecting capacity to bioaccumulate in the netted material of different flora, and may also alter the classification and bulk of benthal life form, in addition the concord and diversification of population within the community. It was noted in this study that the sediments of Asa River were moderately polluted when pollution indices were used. Therefore, unregulated disposal of wastes into the environment should be discouraged with strict vigilance.

5.1.4 Groundwater quality

Underground water is believed to be the purest form of water because of the purification properties of the soil; however, source of contamination could be due to improper design and construction of wells, shallowness and proximity to toilet, refuse duo sites and agricultural farm sites which serve as source of contamination. Thus, proper well and borehole location is essential, good sanitation of environment and control of human and agricultural activities that affect quality of drinking water. Water quality should be controlled in order to minimize acute problem of water related diseases. Domestic treatment of borehole water is also an essential means of improving water quality and regular cleaning of water reservoirs with appropriate cleaning reagents. Constant monitoring of water quality stands as a good means of detecting earlier the deviation of drinking water from the standard. It was observed that the wells were all located within the residential area of the various locations used for these study, traces of agricultural chemical contaminants were seen during the rainy season which most were still within the WHO and NSDWQ limits meanwhile, during the dry season the amount of these parameters reduced. With the current status of groundwater in Ilorin environs observed in this study, it is concluded that the boreholes serve as a good source of drinking water to the community but mini treatment plant can be put in place to make it more perfect.

5.1.5 Organic compounds of surface water and sediment

The effect of organic compounds on humans depends on the specific compound, the level of exposure, the timing of exposure and the individual. In summary, though the organic compounds gave a good recovery due to their concentration being below limit of quantitation, it is evident that the studied area presents a critical situation and offering risks to environmental compartments.

5.1.6 Socio-economic issues

In summary, it can be observed that Asa River water is the River that supplies water to the whole populace of Kwara State which is used for various purposes like drinking, washing, aquatic life, industrial purpose and even pumping into different homes which serves as well water, tap water and borehole. It was also noted that people bathing with direct Asa River water especially in streams close to manufacturing companies have skin related disease problems and other health challenge like cholera, dysentery, diarrhea. This reveals the impact of health factor on humans in that locality. It can be seen from variable seventeen to twenty-five that in some instances industrial effluent do have impact on the people and also people living in the locality also contribute to the environmental pollution of the environment through dumping of refuse in improper places like stream side which has caused a lot of havoc in terms of flooding, soil pollution that is wearing away of the top soil.

5.2 Recommendations

The under listed are recommended:

- (i) Determination of the coliform count in Asa River water samples and establishment of mathematical relationship, if any, between nitrate concentration and coliform count.
- (ii) Investigation of polycyclic aromatic hydrocarbons in water and sediment samples using solid phase micro extraction.
- (iii) District dwellers must make effort with the government to coordinate the recovery of Asa River posterior sector and its marine life from the present risk-positioning natural complications.
- (iv) It is suggested that regulatory bodies in Kwara State should swing into action to control the practices along the course of this river, which also include industrial companies that directly or indirectly discharge their waste into the water bodies.

5.3 Contribution to knowledge

- (i) A detailed comprehensive data on the assessment of metal contamination (i.e Overall Pollution Index (OPI); Contamination Factor (CF), Geoaccumulation Index (Igeo), modified Hazard Quotient (mHQ) and Ecological Contamination Index (ECI) in Asa River water and sediments have been generated. These data can be used by relevant agencies in planning sustainable environment.

(ii) A surface water model based on channelisation from discharge points to surface water of Asa River downstream to establish pollution status with respect to distance have been done for prediction into the future.

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APPENDIX SPECTRAS

GAS CHROMATOGRAM SPECTRAS FOR OCs

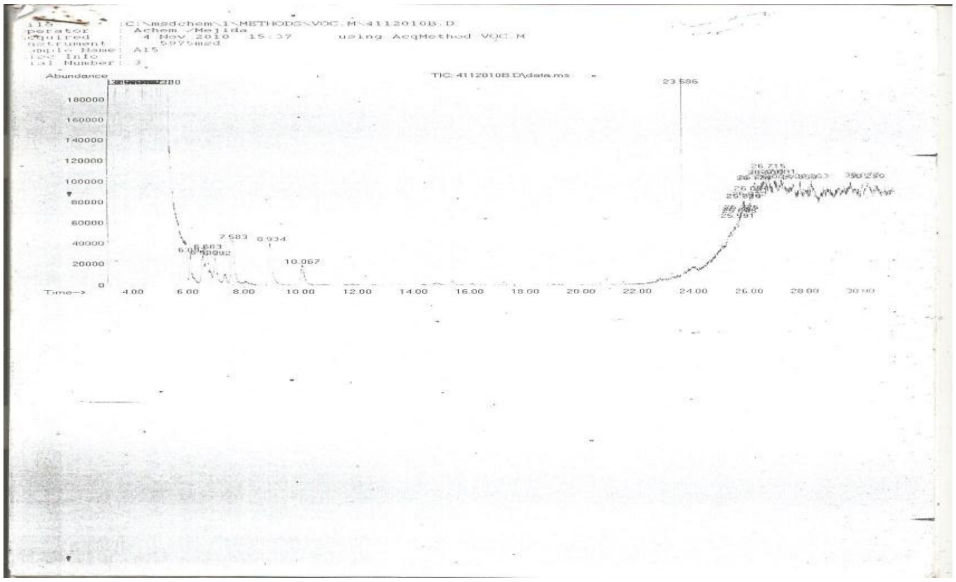

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Figure GC 1: Asa river zone (RW-UN-2)

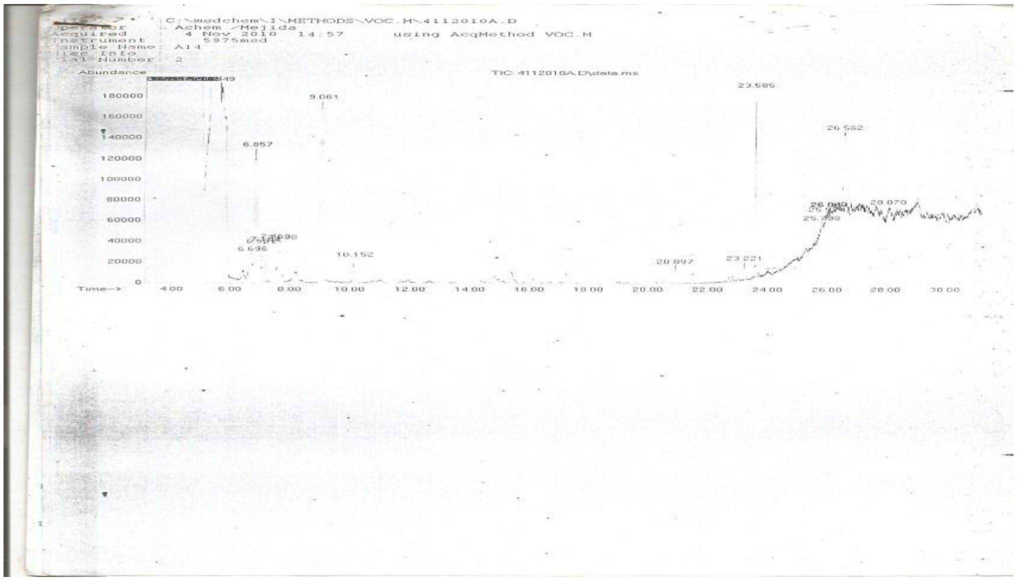

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Figure GC 2: Asa River zone (RW-AM-3)

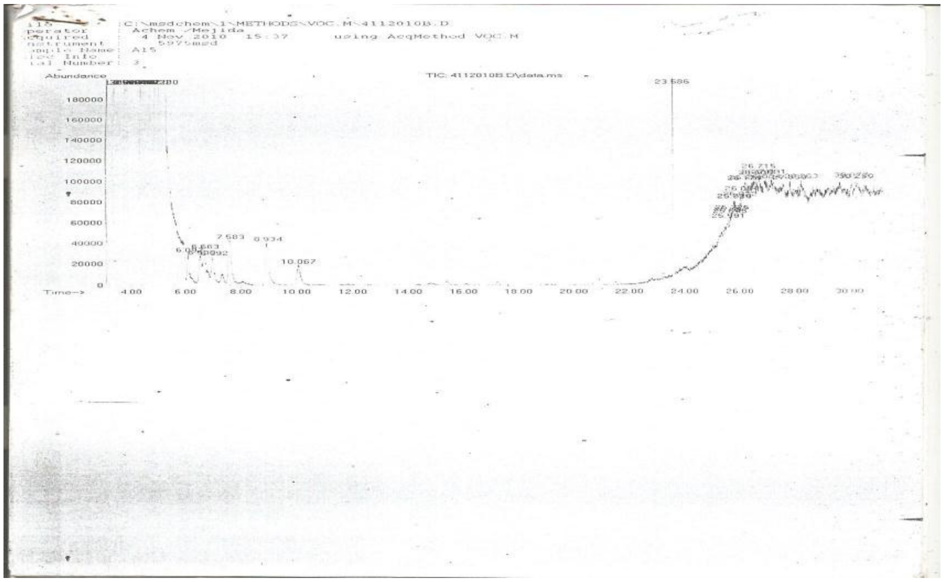

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Figure GC 3: Asa River zone (RW-AS-1)

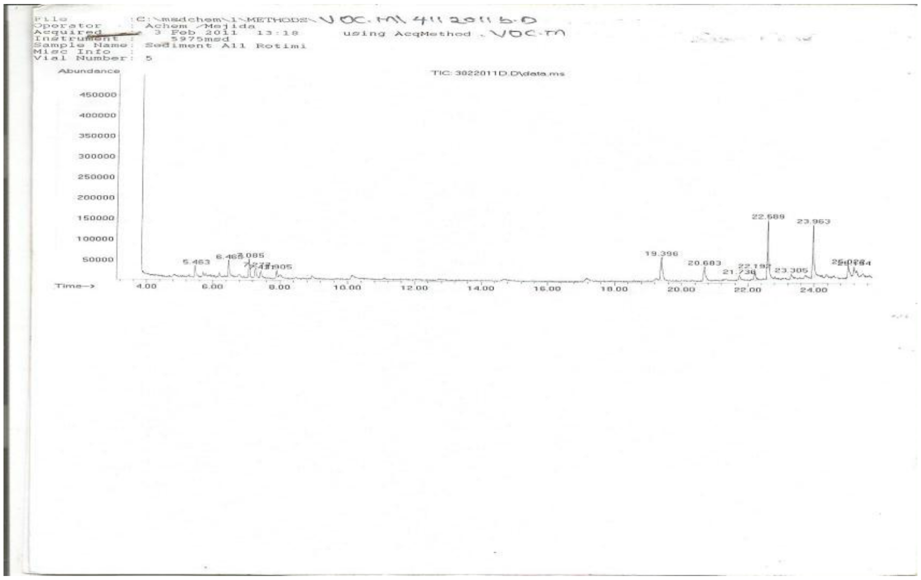

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Figure GC 4: Asa River sediment (SD-UN-2)

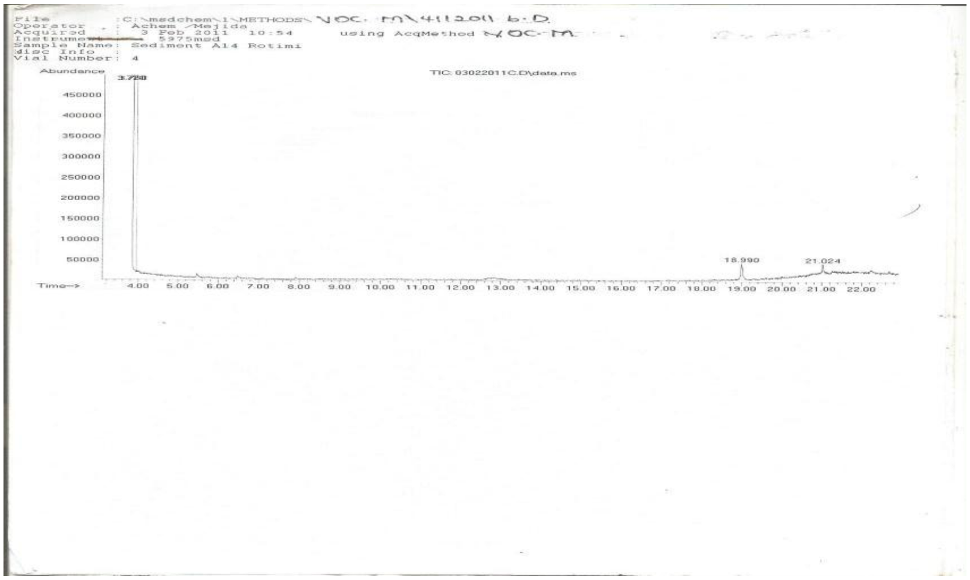

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Figure GC 5: Asa River sediment (SD-AM-3)

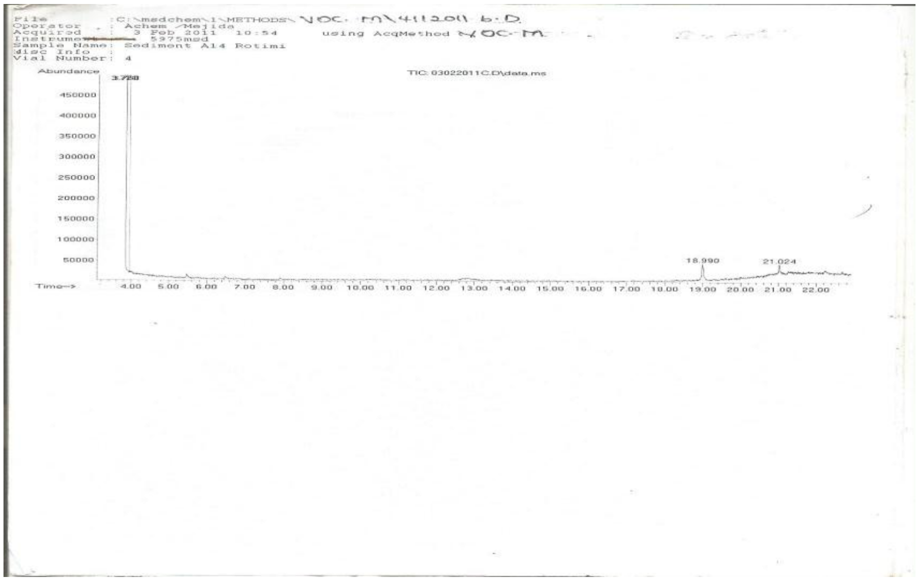

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Figure GC 6: Asa River sediment (SD-AS-1)

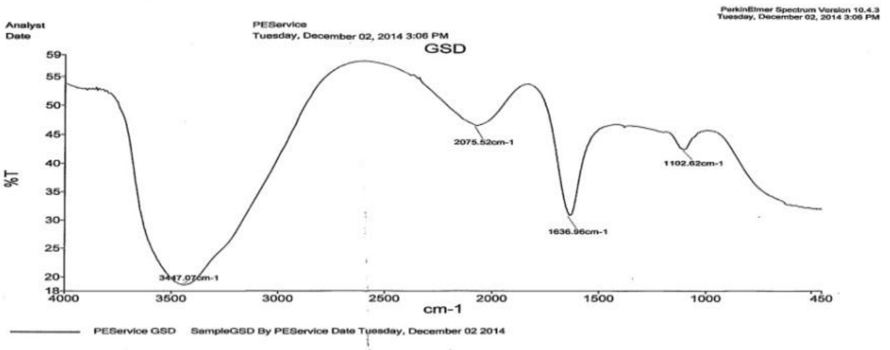


Figure IR 1: EW-GS-1

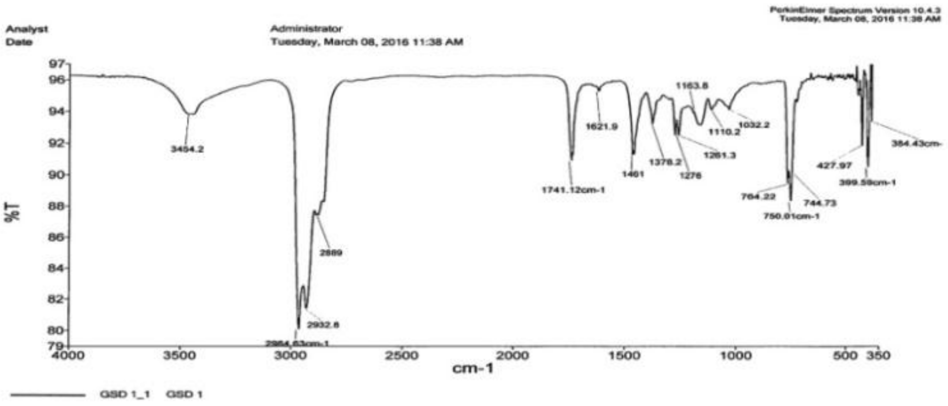


Figure IR 2: GS/SW1

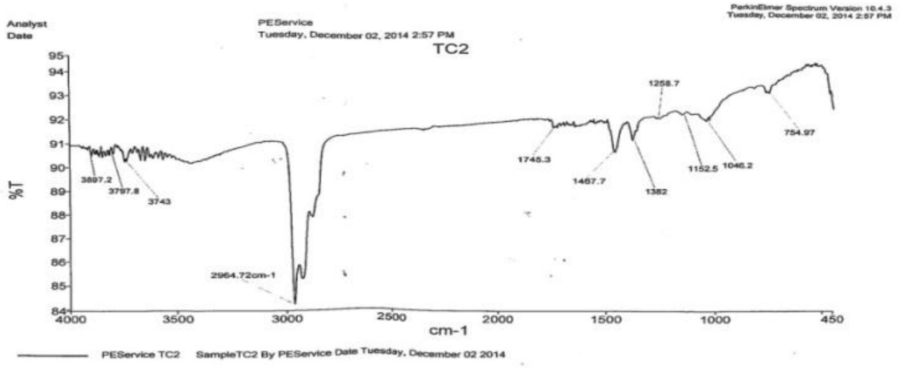


Figure IR 3: EW-TP-2

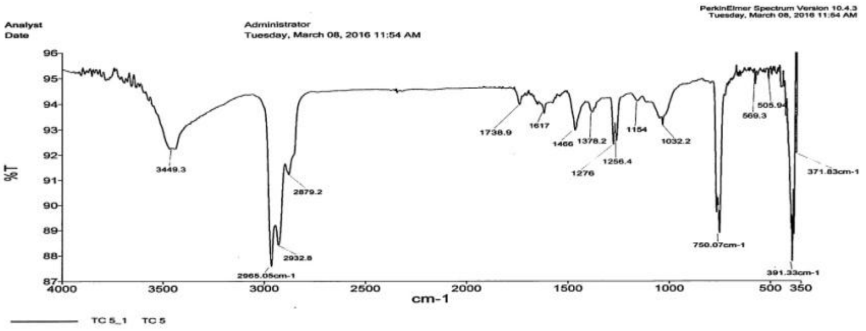


Figure IR 4: KC-GS-TP/SW1

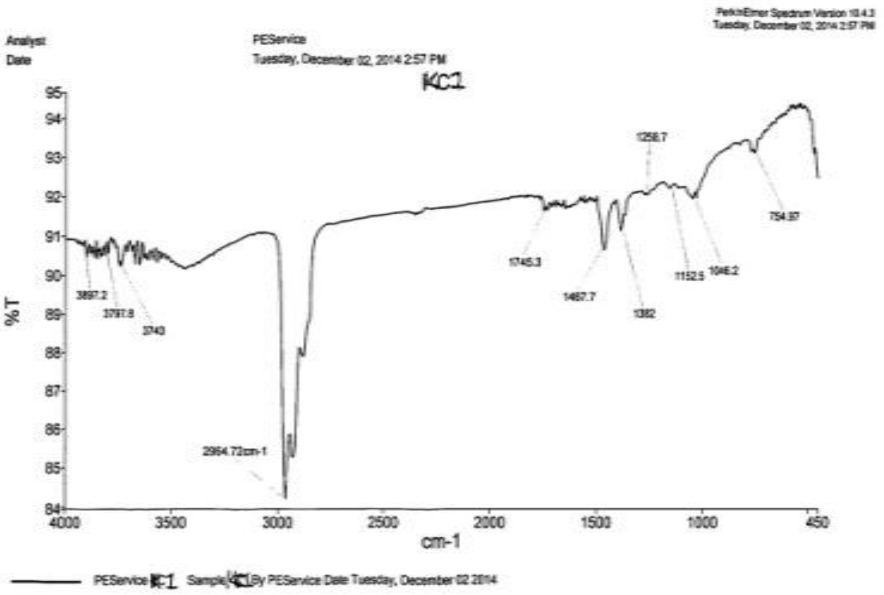


Figure IR 5: EW-KC-3

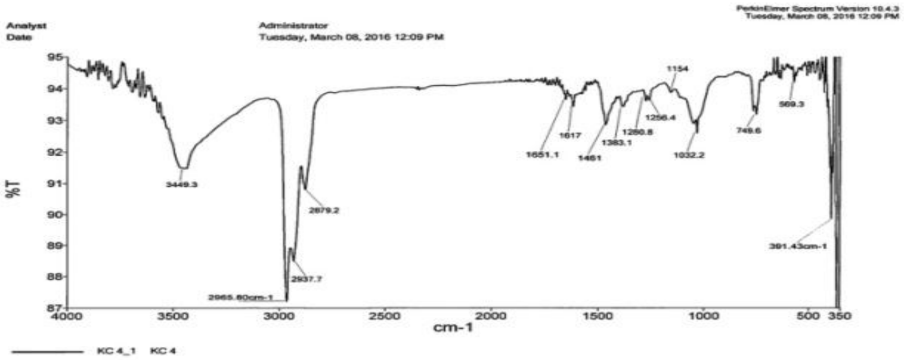


Figure IR 6: KC/SW1

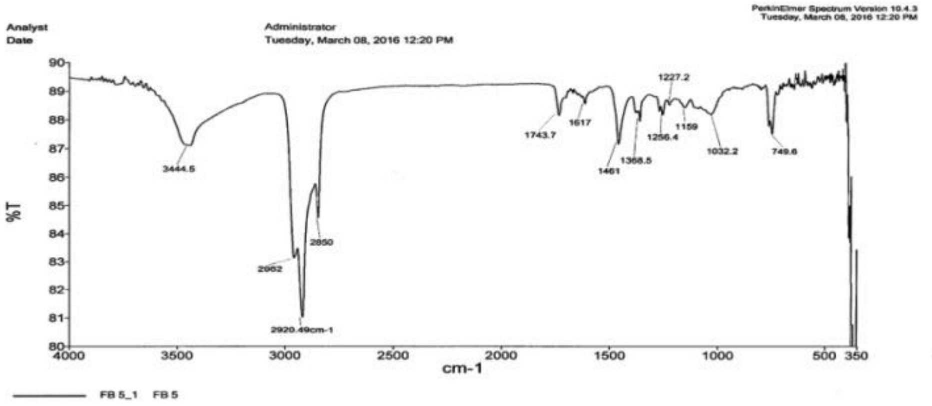


Figure IR 7: EW-FB-4

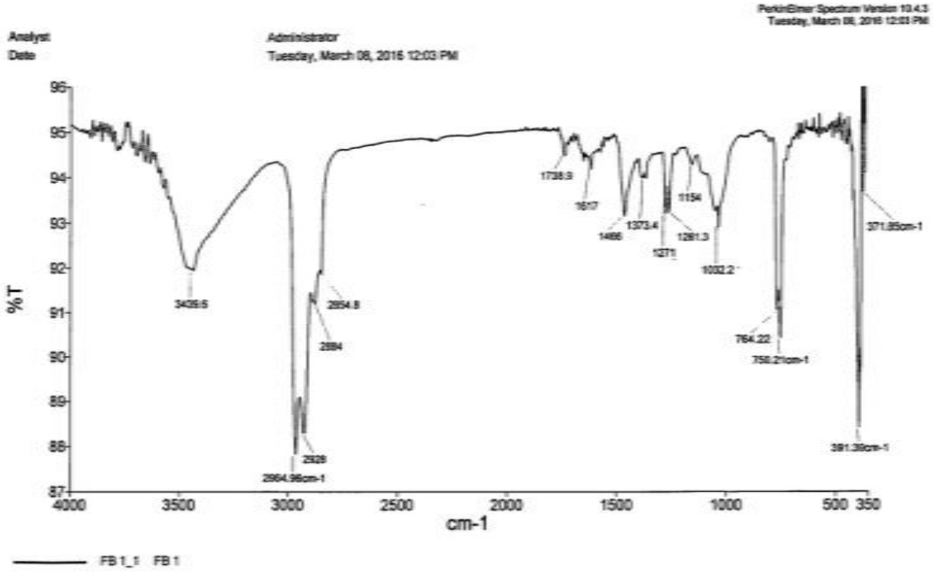
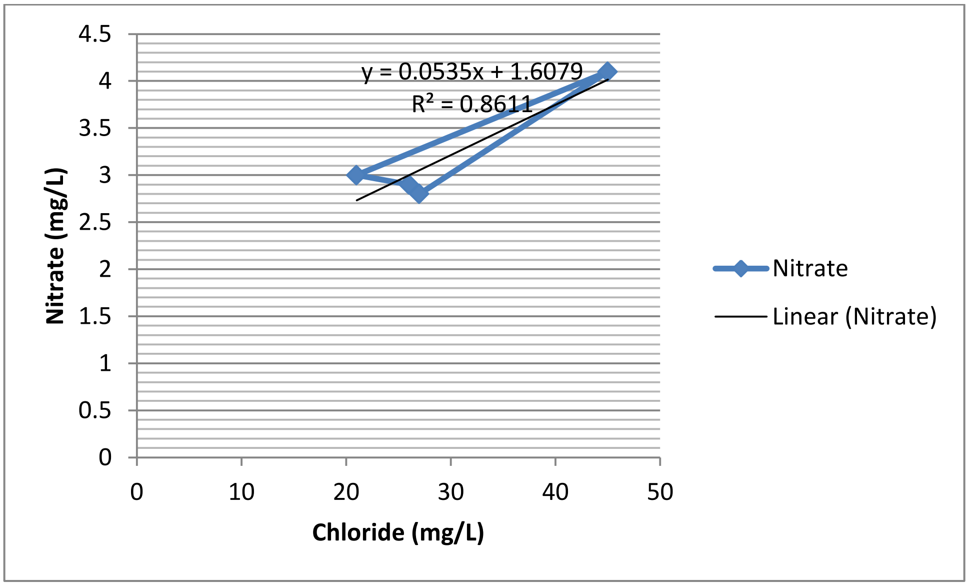


Figure IR 8: FB/SW1

APPENDIX GRAPH



APPENDIX QUESTIONNAIRE

UNIVERSITY OF IBADAN, IBADAN, NIGERIA

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE

GENERAL ASSESSMENT OF ASA RIVER ILORIN, KWARA STATE AND ITS ENVIRONS

Dear Respondents,

This question is designed for research purpose. It seeks to observe the activities going on around Asa River in Ilorin and its environs and how you would react to statements of items below. All information provided would be treated with confidentiality.

Please be honest as much as possible in your responses.

Thank you.

Akiwumi, O.O.

SECTION A (Personal Data)

Please read carefully and supply the information required below. Tick (√) in the box provided in front of your choice/response.

1. Gender-specific: Manly ☐ Womanly ☐
2. Age: 15-20 ☐ 21-25 ☐ 26-30 ☐ 31 and above ☐
3. Marital Status: Single ☐ Married ☐
4. Religion: Christianity ☐ Muslim ☐ Traditional ☐
5. Location: Oke-oyi zone ☐ Unity zone ☐ Asa-dam zone ☐ New Yidi zone ☐ Odota zone ☐ Egbejila zone ☐ Amilegbe zone ☐ Afon zone ☐ Ero-omo zone ☐
6. Education: No education ☐ Primary ☐ Secondary ☐ NCE/OND ☐ B.Sc/HND ☐ Postgraduate ☐
7. Occupation: Fishing ☐ Poultry ☐ Mechanic ☐ Block industry ☐ Hairdressing ☐ Traders’ ☐ Civil servant ☐ Factory worker ☐
8. Type of water: Well water ☐ Borehole ☐ Stream ☐ Tap water ☐

SECTION B

INSTRUCTION: Read the statement below carefully and indicate your response to the following items by putting a tick (√) in the appropriate column.

Key

FA stands for Firmly Accede

A stands for Accede

D stands for Disaccord

FD stands for Firmly Disaccord

S/N	ITEMS RESPONSES OF SUBJECT TO QUESTION	FA	A	D	FD
1	Fish and aquatic life are abundant in Asa River				
2	Asa River is contaminated on a daily basis by industrial effluent				
3	Well water and borehole is a source of good quality fresh water supply within my community				
4	Asa River is of good quality for drinking				
5	Asa River is point of supply for water systems in my locality				
6	River water is good for crop cultivation				
7	Both children and adults swim and bath in the Asa River				
8	The well water I am using is bad, smelling and unpleasant for domestic purposes				
9	Environmental pollution in Ilorin environs from industries is a disaster waiting to happen				
10	Skin related problems occur with people bathing on the Asa River				
11	Health related problems are rampant within the community as a result of usage of contaminated well and river water				
12	Industrial effluents are destroying our farm lands				
13	Effluents from industrial activities, within Ilorin environs do have direct impact on my social well being				
14	Building structures are affected by wastewaters from the industries				
15	Soil pollution occurs as a result of wastewater discharged from industries				
16	Crops grown on the soil gives poor yield				
17	Preferably the industries should stop the effluent discharge				

18	Company management is concerned about the pollution situation and there is no effort to stop or improve the environment				
19	I will prefer to relocate to avoid health related problems resulting from industrial activity in my area				
20	Our environment is not exempted from the exertion of the industries				
21	Socio-economic life have been destroyed within the areas				
22	My livelihood depends directly on the industries				
23	Dumpsites do not pose health problems				
24	Both the industries and community are responsible for environmental pollution in the estate				
25	Socio-economic life have been destroyed within the area				

APPENDIX TABLES

Appendix table 1: Range and mean concentration of effluent physicochemical parameters

PARAMETERS		EW-GS-1	EW-TP-2	EW-KC-3	EW-FB-4
pH	Range	8.20-8.40	6.50-6.80	6.30-6.80	4.80-6.20
	mean±SD	8.30±0.08	6.70±0.18	6.60±0.18	5.50±0.75
Temp (^{o}C)	Range	23.00-29.00	24.00-28.50	25.00-27.00	23.50-27.50
	mean±SD	25.60±2.87	26.30±2.33	25.90±0.85	25.50±2.04
Turbd (NTU)	Range	10.50-13.50	8.00-10.50	13.00-17.50	6.00-8.60
	mean±SD	12.10±1.38	9.30±1.04	15.30±2.10	7.50±1.25
Colour (Hu)	Range	13.00-15.00	13.00-25.00	10.00-15.00	9.00-14.00
	mean±SD	14.00±0.81	19.50±6.40	12.00±2.45	11.50±2.38
Cond. (µs/cm)	Range	100.67-103.26	89.04-97.17	98.75-106.43	101.76-107.45
	mean±SD	102.21±1.27	93.32±4.94	102.35±4.17	104.95±3.13
TH (mg/L)	Range	52.00-56.00	48.00-54.00	40.00-50.00	48.00-52.00
	mean±SD	54.25±1.71	50.75±2.75	44.75±4.99	50.25±1.71
MgH (mg/L)	Range	20.00-24.00	24.00-24.00	16.00-24.00	16.00-20.00
	mean±SD	21.00±2.00	24.00±0.00	18.50±4.12	18.00±2.31
CaH (mg/L)	Range	30.00-36.00	24.00-30.00	23.00-26.00	28.00-36.00
	mean±SD	33.25±2.75	26.75±2.73	24.25±1.26	32.25±3.86
Alk (mg/L)	Range	130.00-140.00	50.00-60.00	50.00-55.00	40.00-55.00
	mean±SD	135.25±4.27	55.00±4.08	52.50±2.89	46.75±5.35
TS (mg/L)	Range	386.00-402.00	294.00-306.00	326.00-366.00	308.00-326.00
	mean±SD	394.00±8.16	299.75±6.13	345.75±22.20	316.75±9.57
TDS (mg/L)	Range	337.00-344.00	234.00-237.00	256.00-282.00	256.00-266.00
	mean±SD	340.25±3.30	235.50±1.29	269.00±14.40	261.00±4.76
SS (mg/L)	Range	48.00-60.00	60.00-69.00	70.00-85.00	51.00-60.00
	mean±SD	53.75±5.32	64.25±4.92	76.75±7.89	55.75±4.92
DO (mg/L)	Range	4.80-5.00	3.80-5.60	3.40-3.60	7.20-7.20
	mean±SD	4.90±0.11	4.34±0.83	3.45±0.10	7.20±0.00
BOD (mg/L)	Range	3.60-3.80	2.80-3.80	2.80-3.00	3.60-3.80
	mean±SD	3.70±0.11	3.25±0.41	2.85±0.41	3.65±0.10
COD (mg/L)	Range	5.80-6.50	6.20-7.40	5.60-6.50	4.60-6.90
	mean±SD	6.15±0.35	6.80±0.74	6.05±0.47	5.75±1.27

Appendix table 2: Mean and standard deviation of effluent physicochemical parameters for dry and rainy seasons over the sampling period from February 2013-April 2015

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT. 2014]
pH	7.00±0.14	6.50±0.28
Temperature (^{o}C)	27.50±0.71	24.10±0.71
Turbidity (NTU)	11.10±1.41	10.95±1.13
Colour (Hu)	13.00±4.24	15.50±1.41
Conductivity (µs/cm)	101.74±2.70	97.68±0.01
Total hardness (mg/L)	49.00±0.00	51.00±5.66
Magnesium hardness (mg/L)	19.25±1.41	22.50±2.83
Calcium hardness (mg/L)	29.75±1.41	28.50±2.83
Alkalinity (mg/L)	74.88±6.36	69.88±6.36
Total solid (mg/L)	349.00±5.66	329.13±3.54
Total dissolved solid (mg/L)	281.50±0.00	271.40±2.12
Suspended solid (mg/L)	67.50±5.66	57.75±1.41
Dissolved Oxygen (mg/L)	4.88±0.14	5.08±0.99
Biochemical Oxygen demand (mg/L)	3.35±0.00	3.38±0.42
Chemical Oxygen Demand (mg/L)	6.03±0.14	6.35±0.28

Appendix table 3: Range and mean concentrations of effluent nutrient loadings

PARAMETERS		EW-GS-1	EW-TP-2	EW-KC-3	EW-FB-4
Sulphate (mg/L)	Range	23.50-25.00	15.00-23.50	18.50-21.50	38.00-42.00
	mean±SD	24.13±0.63	19.13±4.50	20.00±1.47	39.88±1.93
Nitrate (mg/L)	Range	2.60-3.30	2.70-3.70	3.50-8.50	2.40-2.80
	mean±SD	2.95±0.35	3.20±0.52	5.78±2.6	2.60±0.18
Ammonia(mg/L)	Range	0.00-0.01	0.00-0.01	0.01-0.02	0.00-0.00
	mean±SD	0.01±0.00	0.01±0.00	0.01±0.02	0.00±0.00
Phosphate (mg/L)	Range	0.50-0.70	0.90-1.20	0.25-0.50	0.50-0.70
	mean±SD	0.60±0.08	1.05±0.13	0.36±0.11	0.60±0.01
Chloride (mg/L)	Range	27.50-31.50	28.00-36.00	13.00-19.00	9.00-11.00
	mean±SD	29.50±1.83	32.25±9.83	15.88±3.07	10.30±1.01

Appendix table 4: Mean and standard deviation of effluent nutrient loadings for dry and rainy season over the sampling period

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT. 2014]
Sulphate (mg/L)	25.63±10.43	25.94±7.88
Nitrate (mg/L)	3.15±0.49	4.11±2.38
Ammonia (mg/L)	0.01±0.01	0.01±0.00
Phosphate (mg/L)	0.68±0.30	0.63±0.26
Chloride (mg/L)	22.31±11.9	21.65±7.88

Appendix table 5: Range and mean concentrations of effluent metals and heavy metal loads

PARAMETERS		EW-GS-1	EW-TP-2	EW-KC-3	EW-FB-4
Calcium (mg/L)	Range	12.60-14.40	9.50-11.40	9.50-9.80	11.20-14.40
	mean±SD	13.50±0.93	10.43±1.01	9.63±0.13	12.80±1.79
Magnesium (mg/L)	Range	7.50-7.80	6.80-7.00	5.10-8.60	6.70-7.50
	mean±SD	7.63±0.13	6.88±0.09	6.83±1.94	7.10±0.41
Sodium (mg/L)	Range	2.30-2.60	2.00-2.30	1.80-2.30	2.10-2.60
	mean±SD	2.45±0.13	2.18±0.14	2.05±0.24	2.35±0.24
Iron (mg/L)	Range	2.30-2.70	0.70-1.30	0.50-0.85	2.40-2.70
	mean±SD	2.50±0.18	1.00±0.29	0.68±0.27	2.55±0.13
Copper (mg/L)	Range	0.30-0.60	0.25-0.35	0.20-0.55	0.30-0.70
	mean±SD	0.45±0.13	0.28±0.06	0.38±0.18	0.50±0.18
Zinc (mg/L)	Range	3.70-5.00	2.30-2.90	1.80-2.50	2.70-4.00
	mean±SD	4.13±0.60	2.60±0.25	2.15±0.35	3.13±0.60
Cadmium (mg/L)	Range	0.00-0.00	0.00-0.01	0.01-0.01	0.00-0.00
	mean±SD	0.00±0.00	0.01±0.00	0.01±0.00	0.00±0.00
Lead (mg/L)	Range	0.60-0.80	0.30-0.60	0.01-0.02	1.10-1.80
	mean±SD	0.70±0.08	0.45±0.13	0.02±0.01	1.45±0.35
Chromium (mg/L)	Range	0.32-0.60	0.15-0.25	0.15-0.20	0.22-0.40
	mean±SD	0.44±0.13	0.19±0.04	0.18±0.02	0.31±0.08

Appendix table 6: Mean and standard deviation of effluent metal and heavy metal loadings for dry and rainy season over the sampling period

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT. 2014]
Calcium (mg/L)	11.93±2.53	11.23±1.14
Magnesium (mg/L)	6.58±0.94	7.64±0.62
Sodium (mg/L)	2.25±0.1	2.26±0.33
Iron (mg/L)	1.65±1.07	1.71±0.76
Copper (mg/L)	0.29±0.08	0.51±0.15
Zinc (mg/L)	3.33±0.9	2.68±0.75
Cadmium (mg/L)	0.00±0.00	0.00±0.00
Lead (mg/L)	0.57±0.46	0.74±0.68
Chromium (mg/L)	0.23±0.07	0.33±0.17

Appendix table 7: Range and mean concentrations of surface water for physicochemical parameters

PARAMETERS		GS/SW1	GS/SW2	GS/SW3	KC/SW1	KC/SW2	KC/SW3
pH	Range	7.80-8.10	6.50-6.80	8.10-8.40	6.30-6.60	6.50-6.80	8.10-8.40
	mean±SD	7.95±0.13	6.65±0.13	8.25±0.13	6.45±0.13	6.65±0.13	8.25±0.13
Temp (^oC)	Range	23.00-26.00	22.40-28.00	24.20-29.00	24.00-28.00	22.40-28.50	24.00-27.80
	mean±SD	24.89±1.56	25.23±2.37	25.95±2.42	25.65±1.70	26.10±2.61	25.70±1.77
Colour (Hu)	Range	20.00-24.00	20.00-36.00	20.00-28.00	15.00-19.00	20.00-36.00	20.00-28.00
	mean±SD	22.00±1.63	28.30±8.42	24.30±3.86	17.00±1.83	28.30±8.42	24.30±3.86
Turbidity (NTU)	Range	12.00-17.00	13.00-23.00	12.00-18.50	15.00-20.00	13.00-23.00	12.00-18.50
	mean±SD	14.38±2.50	18.00±5.49	15.10±3.35	17.50±2.38	18.00±5.49	15.10±3.35
Cond. (µs/cm)	Range	95.43-98.02	87.53-92.75	100.60-104.76	101.24-107.40	87.53-92.75	100.60-104.76
	mean±SD	96.97±1.27	90.40±2.75	103.20±2.00	104.33±3.54	90.40±2.75	103.20±2.00
TH (mg/L)	Range	48.00-54.00	48.00-54.00	56.00-58.00	38.00-48.00	48.00-54.00	56.00-58.00
	mean±SD	51.00±2.58	51.00±2.58	57.00±1.15	42.50±4.43	51.00±2.58	57.00±1.15
MgH (mg/L)	Range	20.00-23.00	12.00-17.00	20.00-27.00	16.00-24.00	12.00-17.00	20.00-27.00
	mean±SD	20.75±1.50	15.00±2.16	23.00±3.16	18.50±3.79	15.00±2.16	23.00±3.16
CaH (mg/L)	Range	28.00-32.0 0	35.00-37.00	31.00-37.00	20.00-28.00	35.00-37.00	31.00-37.00
	mean±SD	30.25±1.71	36.00±0.82	34.00±2.94	24.00±3.27	36.00±0.82	34.00±2.94
Alkalinity (mg/L)	Range	125.00-135.00	55.00-60.00	130.00-150.00	45.00-55.00	55.00-60.00	130.00-150.00
	mean±SD	132.50±5.00	57.60±2.75	137.90±9.20	51.25±4.79	57.60±2.75	137.90±9.20
TS (mg/L)	Range	360.00-384.00	365.00-414.00	333.00-354.00	362.00-387.00	365.00-414.00	333.00-354.00
	mean±SD	372.25±13.02	389.30±27.44	343.30±11.30	375.00±13.34	389.30±27.44	343.30±11.30
TDS (mg/L)	Range	302.00-324.00	300.00-338.00	256.00-269.00	275.00-293.00	300.00-338.00	256.00-269.00
	mean±SD	313.25±11.87	319.00±20.82	262.80±6.70	284.00±9.83	319.00±20.82	262.80±6.70
SS (mg/L)	Range	56.00-60.00	64.00-76.00	76.00-85.00	86.00-94.00	64.00-76.00	76.00-85.00
	mean±SD	59.00±2.00	70.30±6.65	80.50±4.65	91.00±3.83	70.30±6.65	80.50±4.65
DO (mg/L)	Range	5.00-6.50	6.50-7.20	6.50-6.70	6.80-7.80	6.50-7.20	6.50-6.70
	mean±SD	5.65±0.72	6.88±0.30	6.60±0.08	7.10±0.48	6.88±0.30	6.60±0.08
BOD (mg/L)	Range	3.30-3.80	2.80-4.30	4.60-5.30	2.80-5.60	2.80-4.30	4.60-5.30
	mean±SD	3.53±0.22	3.60±0.72	5.03±0.34	4.25±1.15	3.60±0.72	5.03±0.34
COD (mg/L)	Range	5.10-6.10	4.80-5.60	5.80-6.90	5.80-7.90	4.80-5.60	5.80-6.90
	mean±SD	5.60±0.52	5.20±0.41	6.35±0.58	6.85±1.16	5.20±0.41	6.35±0.58

Appendix table 8: Range and mean concentrations of surface water for physicochemical parameters

PARAMETERS		KC-GS/SW1	KC-GS/SW2	KC-GS/SW3	KC-GS/SW4
pH	Range	7.80-8.20	7.70-8.10	7.70-7.90	7.50-7.90
	mean±SD	8.05±0.24	7.90±0.18	7.80±0.08	7.70±0.18
Temp (^{o}C)	Range	23.00-27.60	24.50-28.20	24.20-29.20	23.20-26.50
	mean±SD	24.85±2.18	26.28±1.80	26.80±2.05	24.68±1.42
Colour (Hu)	Range	17.00-18.00	16.00-22.00	18.00-19.00	18.00-26.00
	mean±SD	17.50±0.58	19.00±2.94	18.50±0.58	22.30±3.86
Turbidity (NTU)	Range	11.00-15.00	10.00-16.00	10.00-15.00	12.50-16.00
	mean±SD	13.00±1.83	13.80±2.63	13.30±2.22	14.30±1.76
Cond. (µs/cm)	Range	100.00-101.24	99.67-100.07	99.45-100.08	99.78-101.24
	mean±SD	100.40±0.57	99.88±0.22	99.77±0.35	100.26±0.69
TH (mg/L)	Range	56.00-58.00	56.00-58.00	56.00-58.00	56.00-58.00
	mean±SD	57.00±1.15	57.00±1.15	56.80±0.96	56.80±0.96
MgH (mg/L)	Range	20.00-28.00	24.00-28.00	24.00-28.00	24.00-28.00
	mean±SD	24.30±4.35	26.30±2.06	26.00±2.06	26.00±2.06
CaH (mg/L)	Range	28.00-37.00	28.00-33.00	28.00-33.00	28.00-33.00
	mean±SD	32.50±4.65	30.50±2.38	30.80±2.21	30.80±2.21
Alkalinity (mg/L)	Range	80.00-111.00	80.00-111.00	85.00-111.00	80.00-86.00
	mean±SD	95.30±13.30	95.30±13.30	95.30±12.70	84.00±2.71
TS (mg/L)	Range	384.00-407.00	383.00-399.00	380.00-411.00	390.00-414.00
	mean±SD	395.80±12.45	391.00±8.68	395.50±17.33	402.00±12.75
TDS (mg/L)	Range	310.00-325.00	308.00-322.00	306.00-327.00	306.00-335.00
	mean±SD	317.50±8.10	315.00±7.02	316.50±11.56	320.50±16.18
SS (mg/L)	Range	74.00-82.00	73.00-78.00	74.00-84.00	76.00-83.00
	mean±SD	78.30±4.35	76.00±2.16	79.00±5.77	79.00±3.16
DO (mg/L)	Range	4.60-8.80	5.00-5.60	5.00-6.00	5.20-5.60
	mean±SD	6.95±1.81	6.95±0.30	5.40±0.49	5.40±0.23
BOD (mg/L)	Range	3.60-6.20	3.80-4.80	3.40-5.20	4.40-4.80
	mean±SD	5.20±1.19	4.30±0.41	4.35±0.75	4.60±0.16
COD (mg/L)	Range	5.10-6.00	5.20-5.90	5.60-5.90	6.10-6.60
	mean±SD	5.55±0.47	5.55±0.35	5.75±0.13	6.33±0.22

Appendix table 9: Range and mean concentrations of surface water for physicochemical parameters

PARAMETERS		KC-GS-TP/SW1	KC-GS-TP/SW2	KC-GS-TP/SW3	KC-GS-TP-AS/SW
pH	Range	7.30-7.80	7.30-7.80	7.30-7.80	7.30-7.80
	mean±SD	7.53±0.22	7.53±0.22	7.53±0.22	7.53±0.22
Temp (^{o}C)	Range	22.00-27.50	23.20-28.90	25.30-27.50	23.30-27.70
	mean±SD	25.13±2.43	25.73±2.45	26.65±0.95	25.55±8.33
Colour (Hu)	Range	23.00-32.00	25.00-32.00	28.00-32.00	28.00-32.00
	mean±SD	27.30±4.43	28.30±3.30	30.00±1.63	30.00±1.63
Turbidity (NTU)	Range	13.00-21.00	14.00-26.00	16.50-26.00	16.00-30.50
	mean±SD	17.00±4.08	20.00±6.38	21.30±4.94	23.00±8.09
Cond. (µs/cm)	Range	101.23-103.14	102.47-105.26	102.63-105.32	103.16-105.29
	mean±SD	102.20±0.78	103.86±1.19	104.20±1.34	104.23±0.87
TH (mg/L)	Range	60.00-65.00	60.00-65.00	60.00-65.00	60.00-65.00
	mean±SD	62.50±2.89	62.50±2.89	62.50±2.89	62.50±2.89
MgH (mg/L)	Range	24.00-32.00	24.00-32.00	24.00-32.00	24.00-32.00
	mean±SD	27.80±3.30	27.80±3.30	27.80±3.30	27.80±3.30
CaH (mg/L)	Range	32.00-38.00	32.00-38.00	32.00-38.00	32.00-38.00
	mean±SD	34.80±2.75	34.80±2.75	35.50±2.75	34.80±2.75
Alkalinity (mg/L)	Range	55.00-65.00	55.00-65.00	55.00-65.00	60.00-70.00
	mean±SD	60.00±4.08	61.30±4.79	61.30±4.79	65.00±4.08
TS (mg/L)	Range	408.00-422.00	396.00-425.00	418.00-421.00	426.00-452.00
	mean±SD	415.00±7.02	410.50±16.18	419.80±1.26	439.50±15.02
TDS (mg/L)	Range	328.00-338.00	315.00-354.00	331.00-342.00	340.00-362.00
	mean±SD	333.30±4.99	334.30±21.67	336.30±5.56	350.80±11.87
SS (mg/L)	Range	80.00-84.00	71.00-82.00	76.00-90.00	86.00-93.00
	mean±SD	81.80±2.06	76.30±5.56	83.50±6.61	88.80±3.40
DO (mg/L)	Range	4.20-8.60	4.80-5.20	4.80-5.60	4.80-5.00
	mean±SD	6.70±2.00	5.00±0.16	5.00±0.40	4.85±0.10
BOD (mg/L)	Range	3.20-6.60	4.00-4.40	3.80-4.60	3.80-4.20
	mean±SD	5.35±1.56	4.25±0.19	4.10±0.35	4.00±0.23
COD (mg/L)	Range	5.40-6.10	4.80-6.40	5.20-6.70	6.00-6.70
	mean±SD	5.75±0.35	5.63±0.84	5.95±0.81	6.38±0.33

Appendix table 10: Range and mean concentrations of surface water for physicochemical parameters

PARAMETERS		FB/SW1	FB/SW2	FB/SW3	FB-AS/SW
pH	Range	6.50-6.80	6.00-6.30	7.60-8.00	6.70-7.20
	mean±SD	6.65±0.13	6.15±0.13	7.80±0.18	6.90±0.22
Temp (^{o}C)	Range	24.20-29.60	21.00-26.50	22.30-24.50	21.20-27.00
	mean±SD	26.35±2.30	23.33±2.41	23.33±0.93	23.68±2.50
Colour (Hu)	Range	15.0-26.00	15.00-28.00	13.00-25.00	12.00-28.00
	mean±SD	19.50±4.80	21.75±6.70	18.25±5.74	19.40±8.56
Turbidity (NTU)	Range	14.00-21.50	12.50-24.00	11.00-28.50	12.00-22.00
	mean±SD	17.75±3.80	18.13±6.22	19.75±9.54	16.90±5.36
Cond. (µs/cm)	Range	84.26-88.42	94.32-98.04	98.17-99.26	91.64-97.46
	mean±SD	86.35±2.38	96.18±2.14	98.73±0.63	94.80±3.09
TH (mg/L)	Range	42.00-49.00	42.00-49.00	38.0.-49.00	52.00-58.00
	mean±SD	45.75±3.30	45.75±3.30	42.75±4.86	55.00±2.58
MgH (mg/L)	Range	20.00-23.00	20.00-24.00	16.00-21.00	20.00-28.00
	mean±SD	20.75±1.50	21.75±2.06	19.25±2.22	24.00±3.27
CaH (mg/L)	Range	22.00-28.00	18.00-28.00	20.00-28.00	30.00-32.00
	mean±SD	25.00±2.58	24.00±4.32	23.50±3.42	31.00±1.15
Alkalinity (mg/L)	Range	50.00-65.00	30.00-35.00	115.00-125.00	50.00-60.00
	mean±SD	57.50±6.45	32.50±2.89	121.25±4.79	55.00±4.08
TS (mg/L)	Range	260.00-292.00	304.00-330.00	354.00-407.00	364.00-442.00
	mean±SD	276.00±17.36	316.25±13.67	380.50±30.03	402.80±44.18
TDS (mg/L)	Range	218.00-232.00	248.00-260.00	280.00-346.00	290.00-355.00
	mean±SD	224.75±7.27	253.75±6.13	313.75±37.83	322.80±36.67
SS (mg/L)	Range	42.00-60.00	56.00-70.00	60.00-75.00	72.00-87.00
	mean±SD	51.25±10.11	62.50±7.55	66.75±7.89	80.00±7.62
DO (mg/L)	Range	6.00-7.50	6.00-7.20	6.30-7.30	4.80-5.30
	mean±SD	6.48±0.69	6.68±0.54	6.84±0.48	5.03±0.22
BOD (mg/L)	Range	2.80-5.60	3.00-4.20	4.10-4.90	3.80-4.70
	mean±SD	4.40±1.18	3.70±0.53	4.55±0.37	4.23±0.44
COD (mg/L)	Range	5.40-6.30	5.00-5.90	4.40-7.10	5.40-6.80
	mean±SD	5.85±0.47	5.45±0.47	5.75±1.50	6.10±0.75

Appendix table 11: Range and mean concentrations of surface water for physicochemical parameters

PARAMETERS		AS1/SW1	AS2/SW2	AS3/SW3	AS4/SW4	AS5/SW5
pH	Range	6.70-7.20	7.10-7.30	6.80-7.20	6.80-7.20	6.80-7.10
	mean±SD	6.90±0.22	7.18±0.10	7.00±0.18	7.00±0.18	6.98±0.15
Temp (°C)	Range	24.50-27.50	22.00-29.00	23.50-26.00	22.60-28.50	23.40-29.00
	mean±SD	26.05±1.23	26.88±3.29	24.70±1.39	25.90±2.83	26.00±2.73
Colour (Hu)	Range	14.00-28.00	25.00-27.00	16.00-28.00	18.00-32.00	16.00-30.00
	mean±SD	20.40±7.18	25.80±0.96	22.00±6.38	24.80±7.27	22.80±7.27
Turbidity (NTU)	Range	14.00-24.50	15.00-26.00	14.00-26.00	17.00-28.50	15.00-27.00
	mean±SD	19.10±5.65	20.40±5.94	20.00±6.38	22.80±6.09	21.00±6.38
Cond. (µs/cm)	Range	93.12-97.62	97.34-101.64	95.20-101.70	101.34-101.90	99.62-101.72
	mean±SD	95.62±2.34	99.74±0.23	98.45±3.74	101.62±0.32	100.67±1.20
TH (mg/L)	Range	52.00-58.00	56.00-62.00	52.00-58.00	52.00-58.00	52.00-58.00
	mean±SD	55.00±2.58	58.80±2.75	55.30±2.50	55.30±2.50	55.30±2.50
MgH (mg/L)	Range	20.00-26.00	20.00-30.00	20.00-28.00	20.00-28.00	20.00-26.00
	mean±SD	23.50±2.52	25.30±4.57	23.30±3.59	24.30±4.35	22.80±2.75
CaH (mg/L)	Range	30.00-32.00	32.00-36.00	30.00-34.00	28.00-34.00	32.00-34.00
	mean±SD	31.50±1.00	33.50±1.91	32.00±1.63	31.00±2.58	32.50±1.00
Alkalinity (mg/L)	Range	50.00-60.00	60.00-65.00	60.00-65.00	60.00-65.00	60.00-65.00
	mean±SD	53.80±4.79	62.50±3.07	62.50±3.07	62.50±3.07	62.50±3.07
TS (mg/L)	Range	380.00-466.00	412.00-457.00	428.00-452.00	440.00-466.00	431.00-459.00
	mean±SD	423.00±48.51	434.80±25.13	439.80±13.02	452.50±14.46	445.00±15.60
TDS (mg/L)	Range	296.00-372.00	326.00-362.00	344.00-362.00	341.00-372.00	344.00-364.00
	mean±SD	333.80±43.00	343.80±19.94	352.80±9.57	354.30±15.28	353.80±10.72
SS (mg/L)	Range	84.00-96.00	85.00-97.00	84.00-92.00	92.00-99.00	86.00-96.00
	mean±SD	89.30±5.74	91.00±5.48	87.00±3.83	98.30±4.92	90.80±5.50
DO (mg/L)	Range	4.90-6.00	5.90-6.30	4.00-7.20	4.20-5.60	4.40-5.00
	mean±SD	5.33±0.47	6.10±0.18	6.35±1.55	4.80±0.63	4.55±0.30
BOD (mg/L)	Range	4.20-5.10	5.00-5.30	3.40-6.20	3.40-5.00	3.40-4.20
	mean±SD	4.58±0.39	5.15±0.13	5.30±1.29	4.10±0.68	3.75±0.34
COD (mg/L)	Range	5.60-6.80	5.50-6.40	4.80-5.90	5.10-7.30	6.00-7.30
	mean±SD	6.23±0.61	5.93±0.44	5.35±0.58	6.20±1.21	6.65±0.70

Appendix table 12: Range and mean concentrations of surface water for physicochemical parameters

PARAMETERS		AS6/SW6	CONTROL1/SW	CONTROL2/SW
pH	Range	6.60-7.30	6.90-7.10	6.70-7.30
	mean±SD	6.93±0.33	7.00±0.11	7.03±0.28
Temp (^{o}C)	Range	22.80-27.50	22.00-26.00	23.50-25.50
	mean±SD	24.85±1.95	23.80±1.68	24.50±0.82
Colour (Hu)	Range	17.00-28.00	17.00-25.00	9.00-25.00
	mean±SD	22.80±6.08	16.25±10.11	16.60±6.70
Turbidity (NTU)	Range	18.50-27.00	8.00-22.00	10.00-22.00
	mean±SD	22.80±4.37	14.75±7.80	15.80±6.90
Cond. (µs/cm)	Range	98.43-99.94	81.64-87.65	83.55-87.65
	mean±SD	99.19±0.86	84.65±3.46	85.34±1.76
TH (mg/L)	Range	52.00-58.00	35.00-45.00	35.00-45.00
	mean±SD	55.30±2.50	41.00±4.55	41.00±4.55
MgH (mg/L)	Range	20.00-28.00	13.00-16.00	15.00-20.00
	mean±SD	24.00±3.27	15.25±1.5	17.80±2.63
CaH (mg/L)	Range	28.00-35.00	22.00-29.00	20.00-28.00
	mean±SD	31.30±2.99	25.75±3.30	23.30±3.95
Alkalinity (mg/L)	Range	60.00-65.00	50.00-65.00	50.00-65.00
	mean±SD	62.50±3.07	57.50±6.45	57.50±6.45
TS (mg/L)	Range	440.00-470.00	274.00-420.00	274.00-420.00
	mean±SD	454.80±16.48	346.75±83.43	346.80±83.43
TDS (mg/L)	Range	350.00-378.00	236.00-360.00	236.00-360.00
	mean±SD	363.80±15.33	298.25±71.3	298.25±71.30
SS (mg/L	Range	90.00-92.00	38.00-92.00	38.00-92.00
	mean±SD	91.00±1.15	56.50±25.48	56.50±25.48
DO (mg/L)	Range	4.20-4.80	5.20-6.60	5.20-6.60
	mean±SD	4.40±0.28	5.90±0.62	5.90±0.62
BOD (mg/L)	Range	3.20-4.20	4.60-5.40	4.60-5.40
	mean±SD	3.60±0.43	4.85±0.38	4.84±0.38
COD (mg/L)	Range	5.80-6.50	6.00-7.40	6.00-7.40
	mean±SD	6.15±0.35	6.93±0.64	6.93±0.64

Appendix table 13: Mean and standard deviation of surface water physicochemical parameters for dry and rainy season over the sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT 2014]
pH	7.19±0.42	7.39±2.19
Temperature (^{o}C)	24.89±1.65	25.78±1.38
Colour (Hu)	19.45±16.26	26.14±21.21
Turbidity (NTU)	14.25±11.31	22.02±14.85
Conductivity (µs/cm)	98.57±7.03	99.70±2.91
Total hardness (mg/L)	54.68±26.87	54.68±38.18
Magnesium hardness (mg/L)	25.16±30.41	22.39±28.99
Calcium hardness (mg/L)	30.20±27.58	32.30±9.19
Alkalinity (mg/L)	72.20±44.55	76.00±80.61
Total solids (mg/L)	392.41±4.24	405.23±21.21
Total dissolved solid (mg/L)	314.27±2.83	323.91±5.66
Suspended solid (mg/L)	78.09±2.83	81.14±35.36
Dissolved oxygen (mg/L)	5.89±5.66	5.68±0.35
Biochemical Oxygen Demand (mg/L)	4.42±5.23	4.29±1.13
Chemical Oxygen Demand (mg/L)	6.03±0.42	5.84±1.34

Appendix table 14: Range and mean concentration of surface water nutrient loadings

PARAMETERS		GS/SW1	GS/SW2	GS/SW3	KC/SW1	KC/SW2	KC/SW3
Sulphate (mg/L)	Range	21.50-25.00	21.00-30.00	21.00-29.00	22.00-24.00	21.00-30.00	21.00-29.00
	mean±SD	22.63±1.60	25.80±4.43	24.90±1.21	23.00±0.82	25.80±4.43	24.90±1.21
Nitrate (mg/L)	Range	2.80-3.80	3.10-4.80	4.10-4.60	4.20-8.40	3.10-4.80	4.10-4.60
	mean±SD	3.30±0.52	3.95±0.93	4.35±0.24	6.30±2.37	3.95±0.93	4.35±0.24
Ammonia (mg/L)	Range	0.03-0.04	0.04-0.05	0.03-0.04	0.02-0.03	0.04-0.05	0.03-0.04
	mean±SD	0.03±0.00	0.01±0.01	0.03±0.01	0.02±0.00	0.01±0.01	0.03±0.01
Phosphate (mg/L)	Range	0.70-1.00	0.60-2.00	0.70-1.40	0.40-0.75	0.60-2.00	0.70-1.40
	mean±SD	0.85±0.13	1.08±0.64	1.05±0.35	0.58±0.16	1.08±0.64	1.05±0.35
Chloride (mg/L)	Range	23.00-27.00	21.00-37.00	38.00-46.00	14.00-20.50	21.00-37.00	38.00-46.00
	mean±SD	25.00±1.83	28.80±8.42	41.80±4.35	17.25±3.23	28.80±8.42	41.80±4.35

Appendix table 15: Range and mean concentration of surface water nutrient loadings

PARAMETERS		KC-GS/SW1	KC-GS/SW2	KC-GS/SW3	KC-GS/SW4
Sulphate (mg/L)	Range	18.00-24.00	19.40-24.00	20.00-23.00	22.00-26.00
	mean±SD	21.10±3.07	21.60±2.49	21.50±1.29	24.00±1.83
Nitrate (mg/L)	Range	3.90-4.20	3.70-4.10	4.10-4.80	4.30-4.80
	mean±SD	4.05±0.13	3.90±0.18	4.45±0.35	4.55±0.24
Ammonia (mg/L)	Range	0.03-0.03	0.03-0.03	0.03-0.03	0.03-0.04
	mean±SD	0.03±0.00	0.03±0.00	0.03±0.00	0.04±0.00
Phosphate (mg/L)	Range	0.70-1.10	0.65-1.20	0.65-1.00	0.80-0.90
	mean±SD	0.90±0.18	0.91±0.28	0.84±0.19	0.84±0.05
Chloride (mg/L)	Range	35.00-41.50	33.00-39.50	33.00-41.00	33.00-45.00
	mean±SD	38.40±3.35	36.40±3.35	37.00±4.08	39.00±6.38

Appendix table 16: Range and mean concentrations of surface water nutrient loadings

PARAMETERS		KC-GS-TP/SW1	KC-GS-TP/SW2	KC-GS-TP/SW3	KC-GS-TP-AS
Sulphate (mg/L)	Range	24.00-32.00	24.00-34.00	27.00-37.00	26.50-28.00
	mean±SD	27.80±3.86	29.00±5.23	31.60±5.12	32.30±6.36
Nitrate (mg/L)	Range	4.40-5.40	4.20-5.60	4.40-5.60	4.40-6.40
	mean±SD	4.90±0.52	4.90±0.75	5.00±0.64	5.40±1.10
Ammonia (mg/L)	Range	0.04-0.05	0.05-0.06	0.05-0.06	0.05-0.06
	mean±SD	0.04±0.01	0.05±0.01	0.05±0.00	0.05±0.00
Phosphate (mg/L)	Range	0.75-1.10	0.75-1.30	0.85-1.30	0.70-1.35
	mean±SD	0.91±0.17	1.01±0.28	1.05±0.23	1.09±0.25
Chloride (mg/L)	Range	48.00-52.00	52.50-58.00	54.00-58.00	54.00-60.50
	mean±SD	50.00±1.83	55.30±2.66	56.00±1.83	57.30±3.23

Appendix table 17: Range and mean concentration of surface water nutrient loadings

PARAMETERS		FB/SW1	FB/SW2	FB/SW3	FB-AS/SW
Sulphate (mg/L)	Range	19.50-24.00	26.50-29.00	17.50-34.00	13.00-23.50
	mean±SD	21.75±2.10	27.75±1.04	25.50±8.71	18.10±5.65
Nitrate (mg/L)	Range	2.20-3.50	2.40-3.90	2.00-3.60	3.10-4.60
	mean±SD	2.85±0.70	3.15±0.81	2.80±0.87	3.85±0.81
Ammonia (mg/L)	Range	0.02-0.04	0.02-0.03	0.02-0.04	0.03-0.04
	mean±SD	0.03±0.01	0.02±0.01	0.03±0.01	0.03±0.01
Phosphate (mg/L)	Range	0.50-1.00	0.40-1.10	0.30-0.70	0.80-1.40
	mean±SD	0.75±0.24	0.73±0.29	0.48±0.21	1.10±0.29
Chloride (mg/L)	Range	20.50-28.00	31.50-38.50	25.00-30.00	15.00-22.00
	mean±SD	24.25±3.80	34.88±3.64	27.50±2.38	18.30±3.75

Appendix table18: Range and mean concentration of surface water nutrient loadings

PARAMETERS		AS1/SW1	AS2/SW2	AS3/SW3	AS4/SW4	AS5/SW5
Sulphate (mg/L)	Range	15.00-25.00	24.00-28.50	16.00-32.00	16.00-34.50	16.50-32.50
	mean±SD	19.90±5.36	26.10±2.21	23.60±8.56	25.10±10.26	24.50±8.95
Nitrate (mg/L)	Range	3.40-4.90	4.10-5.20	3.40-5.40	3.70-5.60	3.70-5.40
	mean±SD	4.15±0.84	4.65±0.58	4.40±1.10	4.65±1.10	4.55±0.93
Ammonia (mg/L)	Range	0.03-0.04	0.05-0.05	0.04-0.05	0.05-0.06	0.04-0.06
	mean±SD	0.04±0.01	0.05±0.00	0.04±0.00	0.05±0.01	0.05±0.01
Phosphate (mg/L)	Range	0.90-1.60	0.90-1.60	0.80-1.60	1.00-1.60	0.90-1.85
	mean±SD	1.25±0.35	1.25±0.35	1.20±0.41	1.30±0.29	1.38±0.49
Chloride (mg/L)	Range	16.20-24.50	18.00-28.00	14.00-29.50	14.00-34.50	14.50-32.00
	mean±SD	20.20±4.44	22.70±5.20	21.80±8.39	24.30±11.27	23.30±9.54

Appendix table 19: Range and mean concentration of surface water nutrient loadings

PARAMETERS		AS6/SW6	CONTROL 1	CONTROL2
Sulphate (mg/L)	Range	18.50-36.00	14.00-22.00	14.00-22.00
	mean±SD	27.30±9.54	18.00±4.08	18.00±4.08
Nitrate (mg/L)	Range	4.20-5.80	3.80-4.20	3.80-4.20
	mean±SD	5.00±0.87	4.05±0.24	4.05±0.24
Ammonia (mg/L)	Range	0.05-0.07	0.03-0.06	0.03-0.06
	mean±SD	0.06±0.01	0.05±0.01	0.05±0.01
Phosphate (mg/L)	Range	1.00-2.20	0.30-0.70	0.30-0.70
	mean±SD	1.58±0.67	0.50±2.54	0.50±2.54
Chloride (mg/L)	Range	14.50-35.00	18.00-26.00	18.00-26.00
	mean±SD	24.80±11.27	21.75±3.86	21.75±3.86

Appendix table 20: Mean and standard deviation of surface water nutrient loadings for dry and rainy season over the sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT 2014]
Sulphate (mg/L)	20.93±4.38	28.62±16.40
Nitrate (mg/L)	3.77±3.25	4.97±1.56
Ammonia (mg/L)	0.04±0.00	0.04±0.07
Phosphate (mg/L)	0.77±0.35	1.24±2.19
Chloride (mg/L)	30.63±11.67	35.16±10.61

Appendix table 21: Range and mean concentrations of surface water metals and heavy metals loadings

PARAMETERS		GS/SW1	GS/SW2	GS/SW3	KC/SW1	KC/SW2	KC/SW3
Calcium (mg/L)	Range	11.20-12.80	14.20-14.40	12.60-14.40	9.50-9.80	14.20-14.40	12.60-14.40
	mean±SD	12.03±0.84	14.30±0.16	13.50±0.93	9.63±0.13	14.30±0.16	13.50±0.93
Magnesium (mg/L)	Range	7.40-7.80	5.20-6.90	6.40-7.30	5.10-8.40	5.20-6.90	6.40-7.30
	mean±SD	7.60±0.71	6.13±0.85	6.93±0.41	6.73±2.59	6.13±0.85	6.93±0.41
Sodium (mg/L)	Range	2.00-2.50	2.00-2.40	1.90-2.80	2.10-2.80	2.00-2.40	1.90-2.80
	mean±SD	2.25±0.24	2.18±0.21	2.35±0.47	2.45±0.35	2.18±0.21	2.35±0.47
Iron (mg/L)	Range	2.10-2.60	2.40-3.70	1.30-1.80	0.60-0.85	2.40-3.70	1.30-1.80
	mean±SD	2.35±0.24	3.03±0.67	1.55±0.24	0.73±0.10	3.03±0.67	1.55±0.24
Copper (mg/L)	Range	0.40-0.60	0.50-0.90	0.40-0.50	0.25-0.60	0.50-0.90	0.40-0.50
	mean±SD	0.50±0.08	0.71±0.19	0.45±0.06	0.43±2.11	0.71±0.19	0.45±0.06
Zinc (mg/L)	Range	4.60-5.00	5.40-6.50	2.80-3.40	2.20-3.10	5.40-6.50	2.80-3.40
	mean±SD	4.83±0.21	5.95±0.58	3.10±0.29	2.68±0.44	5.95±0.58	3.10±0.29
Lead (mg/L)	Range	0.40-0.50	0.40-0.70	0.40-0.70	0.02-0.03	0.40-0.70	0.40-0.70
	mean±SD	0.45±0.06	0.55±0.13	0.55±0.06	0.03±0.01	0.55±0.13	0.55±0.06
Chromium (mg/L)	Range	0.30-0.50	0.20-0.50	0.25-0.40	0.18-0.23	0.20-0.50	0.25-0.40
	mean±SD	0.40±0.08	0.35±0.13	0.32±0.06	0.21±0.02	0.35±0.13	0.32±0.06
Cadmium (mg/L)	Range	0.00-0.00	0.00-0.01	0.01-0.01	0.01-0.01	0.00-0.01	0.01-0.01
	mean±SD	0.02±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00

Appendix table 22: Range and mean concentrations of surface water metals and heavy metals loadings

PARAMETERS		KC-GS/SW1	KC-GS/SW2	KC-GS/SW3	KC-GS/SW4
Calcium (mg/L)	Range	11.00-14.60	11.00-12.60	11.10-12.80	11.10-12.80
	mean±SD	12.80±1.97	11.90±0.93	11.90±0.90	11.90±0.90
Magnesium (mg/L)	Range	7.00-7.20	7.10-7.60	7.00-7.60	7.10-7.60
	mean±SD	7.13±0.10	7.33±0.22	7.30±0.26	7.33±0.22
Sodium (mg/L)	Range	1.80-2.20	1.80-2.10	2.20-2.40	2.10-2.80
	mean±SD	2.00±0.18	1.95±0.13	2.28±0.10	2.45±0.35
Iron (mg/L)	Range	1.10-1.70	1.00-1.40	1.20-1.40	1.50-1.60
	mean±SD	1.40±0.29	1.20±0.18	1.30±0.08	1.53±0.05
Copper (mg/L)	Range	0.40-0.50	0.30-0.50	0.30-0.50	0.30-0.55
	mean±SD	0.45±0.06	0.40±0.08	0.40±0.11	0.44±0.11
Zinc (mg/L)	Range	3.60-3.80	3.40-3.60	3.50-3.70	3.60-4.20
	mean±SD	3.73±0.10	3.50±0.08	3.60±0.08	3.88±0.28
Lead (mg/L)	Range	0.40-0.60	0.50-0.60	0.50-0.60	0.50-0.70
	mean±SD	0.50±0.08	0.55±0.06	0.55±0.06	0.60±0.80
Chromium (mg/L)	Range	0.30-0.50	0.28-0.40	0.28-0.40	0.32-0.55
	mean±SD	0.38±0.09	0.32±0.05	0.32±0.05	0.42±0.10
Cadmium (mg/L)	Range	0.01-0.01	0.01-0.01	0.01-0.01	0.01-0.01
	mean±SD	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00

Appendix table 23: Range and mean concentrations of surface water metals and heavy metals loadings

PARAMETERS		KC-GS-TP/SW1	KC-GS-TP/SW2	KC-GS-TP/SW3	KC-GS-TP-AS/SW
Calcium (mg/L)	Range	12.60-14.60	12.60-14.60	12.60-14.60	12.60-14.60
	mean±SD	13.60±1.05	13.60±1.05	13.60±1.05	13.60±1.05
Magnesium (mg/L)	Range	7.10-7.80	7.10-7.80	7.10-7.80	7.10-7.80
	mean±SD	7.43±0.33	7.43±0.33	7.43±0.33	7.43±0.33
Sodium (mg/L)	Range	2.70-3.10	2.90-3.20	2.80-3.20	2.80-3.60
	mean±SD	2.90±0.18	3.05±0.13	3.00±0.18	3.20±0.41
Iron (mg/L)	Range	1.65-2.20	1.70-2.40	1.70-2.40	1.70-2.50
	mean±SD	1.93±0.27	2.05±0.35	2.05±0.35	2.10±0.41
Copper (mg/L)	Range	0.50-0.70	0.50-0.70	0.50-0.80	0.55-0.80
	mean±SD	0.60±0.08	0.60±0.08	0.65±0.13	0.68±0.10
Zinc (mg/L)	Range	4.10-4.80	4.20-5.20	3.90-5.20	4.20-5.40
	mean±SD	4.45±0.35	4.70±0.48	4.53±0.67	4.80±0.64
Lead (mg/L)	Range	0.60-0.85	0.55-0.80	0.50-0.80	0.60-0.85
	mean±SD	0.69±0.14	0.66±0.11	0.65±0.15	0.71±0.11
Chromium (mg/L)	Range	0.30-0.65	0.30-0.60	0.35-0.65	0.40-0.70
	mean±SD	0.46±0.17	0.45±0.15	0.49±0.14	0.54±0.14
Cadmium (mg/L)	Range	0.01-0.01	0.01-0.01	0.00-0.01	0.00-0.01
	mean±SD	0.01±0.01	0.01±0.01	0.01±0.00	0.01±0.00

Appendix table 24: Range and mean concentrations of surface water metals and heavy metals loadings

PARAMETERS		FB/SW1	FB/SW2	FB/SW3	FB-AS/SW
Calcium (mg/L)	Range	9.50-11.40	9.50-11.40	8.00-9.80	12.60-12.80
	mean±SD	10.43±1.01	10.43±1.01	8.90±0.93	12.70±0.12
Magnesium (mg/L)	Range	6.80-7.50	6.70-7.60	7.40-7.60	7.60-8.20
	mean±SD	7.15±0.35	7.13±0.44	7.53±0.1 0	7.93±0.28
Sodium (mg/L)	Range	1.60-2.00	1.80-2.20	1.60-3.40	1.60-2.40
	mean±SD	1.80±0.18	2.00±0.18	2.48±0.96	1.98±0.39
Iron (mg/L)	Range	1.80-2.20	2.30-2.60	1.90-2.80	2.60-3.20
	mean±SD	2.00±0.18	2.45±0.13	2.35±0.47	2.90±0.29
Copper (mg/L)	Range	0.50-0.70	0.50-0.60	0.30-0.70	0.50-0.80
	mean±SD	0.60±0.08	0.55±0.06	0.50±0.18	0.52±0.13
Zinc (mg/L)	Range	2.30-3.30	2.70-3.60	2.80-3.30	2.30-2.80
	mean±SD	2.80±0.52	3.15±0.47	3.15±0.22	2.55±0.24
Lead (mg/L)	Range	0.40-0.80	0.90-1.10	0.90-1.45	0.30-0.80
	mean±SD	0.60±0.18	0.98±0.10	1.18±0.27	0.55±0.24
Chromium (mg/L)	Range	0.10-0.40	0.18-0.45	0.15-0.40	0.40-0.60
	mean±SD	0.26±0.14	0.31±0.14	0.27±0.13	0.50±0.09
Cadmium (mg/L)	Range	0.00-0.00	0.00-0.00	0.00-0.00	0.00-0.00
	mean±SD	0.00±0.00	0.00±0.00	0.00±0.00	0.00±0.00

Appendix table 25: Range and mean concentrations of surface water metals and heavy metals loadings

PARAMETERS		AS1/SW1	AS2/SW2	AS3/SW3	AS4/SW4	AS5/SW5
Calcium (mg/L)	Range	12.60-12.80	12.60-14.40	12.60-13.00	11.00-12.80	12.40-12.80
	mean±SD	12.70±0.12	13.50±0.89	12.80±0.16	11.95±0.98	12.70±0.20
Magnesium (mg/L)	Range	7.60-8.20	7.60-9.40	7.80-8.30	7.80-9.40	7.80-8.20
	mean±SD	7.93±0.28	8.50±0.93	8.03±0.21	8.60±0.82	8.00±0.16
Sodium (mg/L)	Range	1.80-2.50	2.50-2.60	1.50-3.20	1.50-3.40	1.75-3.20
	mean±SD	2.13±0.33	2.55±0.06	2.60±0.78	2.75±0.87	2.81±0.71
Iron (mg/L)	Range	3.00-3.40	2.50-2.90	3.20-3.60	3.40-3.90	3.40-3.60
	mean±SD	3.23±0.17	2.70±0.18	3.40±0.18	3.65±0.24	3.58±0.08
Copper (mg/L)	Range	0.50-0.85	0.80-1.00	0.50-1.00	0.60-1.00	0.60-1.00
	mean±SD	0.68±0.16	0.86±0.11	0.74±0.25	0.79±0.19	0.79±0.19
Zinc (mg/L)	Range	2.60-2.90	3.60-3.90	3.10-3.70	3.50-3.70	3.20-3.80
	mean±SD	2.75±0.13	3.75±0.13	3.40±0.29	3.60±0.08	3.40±0.28
Lead (mg/L)	Range	0.40-1.00	0.60-1.20	0.40-1.30	0.40-1.40	0.50-1.20
	mean±SD	0.69±0.31	0.89±0.31	0.80±0.42	0.83±0.46	0.80±0.36
Chromium (mg/L)	Range	0.50-0.60	0.55-0.70	0.50-0.70	0.50-0.70	0.50-0.70
	mean±SD	0.55±0.04	0.64±0.06	0.59±0.11	0.60±0.09	0.60±0.07
Cadmium (mg/L)	Range	0.00-0.01	0.00-0.01	0.00-0.01	0.00-0.00	0.00-0.01
	mean±SD	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00	0.01±0.00

Appendix table 26: Range and mean concentrations of surface water metals and heavy metals loadings

PARAMETERS		AS6/SW6	CONTROL 1	CONTROL2
Calcium (mg/L)	Range	11.20-12.80	9.50-11.40	9.50-11.40
	mean±SD	11.90±0.82	10.43±1.01	10.43±1.01
Magnesium (mg/L)	Range	8.00-8.40	7.10-7.40	7.10-7.40
	mean±SD	8.20±0.16	7.23±2.78	7.23±2.78
Sodium (mg/L)	Range	3.10-3.40	0.80-1.60	0.80-1.60
	mean±SD	2.95±0.58	1.20±0.41	1.20±0.41
Iron (mg/L)	Range	3.60-4.10	0.70-1.40	0.70-1.40
	mean±SD	3.88±0.22	1.03±0.33	1.03±0.33
Copper (mg/L)	Range	0.70-1.20	0.20-0.30	0.20-0.30
	mean±SD	0.91±0.03	0.26±0.05	0.26±0.05
Zinc (mg/L)	Range	3.60-4.00	0.60-1.60	0.60-1.60
	mean±SD	3.78±0.17	1.10±0.52	1.10±0.52
Lead (mg/L)	Range	0.60-1.20	0.10-0.25	0.10-0.25
	mean±SD	0.90±0.32	0.20±0.07	0.20±0.07
Chromium (mg/L)	Range	0.60-0.70	0.60-0.80	0.60-0.80
	mean±SD	0.65±0.04	0.75±0.13	0.75±0.13
Cadmium (mg/L)	Range	0.01-0.01	0.00-0.00	0.00-0.00
	mean±SD	0.01±0.00	0.00±0.00	0.00±0.00

Appendix table 27: Mean and standard deviation of surface water metal and heavy metal loadings for dry and rainy season over sampling period (February 2013-April 2015)

PARAMETERS	DRY SEASON [FEB 2013-APR 2013;] [NOV.2014-APR. 2015]	RAINY SEASON [MAY 2013- OCT 2013;] [JUNE 2014 – OCT 2014]
Calcium (mg/L)	11.77±2.69	12.81±0.28
Magnesium (mg/L)	7.37±2.40	7.64±0.71
Sodium (mg/L)	2.38±1.13	2.46±6.97
Iron (mg/L)	2.15±0.35	2.51±1.63
Copper (mg/L)	0.56±0.49	0.65±1.45
Zinc (mg/L)	3.58±0.42	3.88±2.05
Cadmium (mg/L)	0.01±0.01	0.01±0.01
Lead (mg/L)	0.53±0.06	0.81±1.56
Chromium (mg/L)	0.36±0.18	0.51±1.07

Appendix table 28: STANDARDS FOR DRINKING WATER TYPES

PARAMETERS	MAXIMUM PERMISSIBLE LIMITS IN WATER						
	NAFDAC 2007	SON 2007	FEPA 1991	NSDWQ 2007	WHO 2007	EU 1998	USEPA 1974
pH	6.5-8.5	6.5-8.5	6.0-9.0	6.5-8.5	6.8	6.5-9.5	6.5-8.5
Temperature	-	-	26	-	40	-	-
Conductivity	1000	1000	70	1000	-	-	500
TDS	500	500	500	500	1000	-	500
TA	100	100	-	-	100	-	-
DO	-	-	≥4	-	≥6	-	-
TH	100	100	-	150	100	-	-
Nitrate	10	10	20	-	40	50	10
Turbidity	-	-	-	5	5	-	-
Sulphate	-	-	-	400	500	-	-
Chloride	-	-	-	NS	250	-	-
Calcium	-	-	-	NS	250	-	-
Chromium	-	-	-	0.05	-	-	-
Magnesium	-	-	-	0.02	0.05	-	-
Sodium	-	-	-	200	-	-	-
Zinc	-	-	-	3	5	-	-
Copper	-	-	-	1	1.3	-	-
Iron	-	-	-	0.3	0.3	-	-
Cadmium	-	-	-	0.003	0.005	-	-
Lead	-	-	-	0.01	-	-	-
Colour	-	-	-	-	15	-	-

●Oketola et al, 2006

APPENDIX PLATES

Plate 1: A detergent company effluent section [EW-GS-1]

Plate 2. A pharmaceutical company Effluent Section [EW-KC-3]

Plate 3: New Yidi Zone surface water

Plate 4. Cocacola road mixing point [FB/SW3]

Plate 5: Adjoining stream after [FB/SW2]

Plate 6: Unity Bridge, ASA RIVER [AS4/SW4]

Plate 7: Emir bridge, ASA RIVER [AS5/SW5]

Plate8: Adjoining stream before [FB/SW1]

Plate 9: Amilegbe bridge, ASA RIVER[AS6/SW6]

Plate 10: Osere stream [GS/SW1]

Plate 11: Asa dam, Water Corporation [control]