POLLUTION STATUS AND CHEMICAL SPECIATION IN SURFACE WATER AND SEDIMENTS OF TWO RIVERS IN AKWA IBOM STATE, NIGERIA

By

Ini Udofia UMOREN
MATRIC NUMBER: 109443
B. Sc. Applied Chemistry (Uyo), M. Sc. Analytical Chemistry (Ibadan)

A DISSERTATION IN THE DEPARTMENT OF CHEMISTRY
SUBMITTED TO THE FACULTY OF SCIENCE IN PARTIAL FULFILMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF PHILOSOPHY
OF THE UNIVERSITY OF IBADAN, IBADAN, NIGERIA

JUNE, 2014

CHAPTER ONE

INTRODUCTION

1.1 ENVIRONMENTAL POLLUTION

The natural environment is clean but due to multifarious activities of man it gets polluted, resulting in environmental pollution. According to Bora (2013), pollution refers to the contamination of the environment by harmful and waste materials, which brings about a significant change in the quality of the surrounding atmosphere. GESAMP (1993) defines aquatic pollution as the introduction by humans, directly or indirectly, of substances or energy into the aquatic environment resulting in such deleterious effects as harm to living resources, hazards to human health, hindrance to aquatic activities including fishing, impairment of quality for use of water, and reduction of amenities. Pollutants can be naturally occurring substances or energies, but are considered contaminants when in excess of natural levels. Different anthropogenic activities such as mining operations and ore processing industry lead to increased metal pollution of surface waters and soils mostly near industrial areas, but their impact can be transported through the surface waters and have adverse effects in larger areas (Salomons, 1995; Banks *et al*., 1997).

The aquatic environment is highly fragile, complex and diverse. It includes several distinct ecosystem types such as freshwater streams, lakes, ponds and rivers, estuaries, and marine coastal and deep ocean waters that encompass many different biotic and abiotic components of unique characteristics. Hence, coastal areas are characterised by highly productive and economically valuable ecosystems as well as intense human activities capable of interfering with the system function and properties (UNEP/WHO, 1996). In order to check the pollution of waters and soils in industrial regions, monitoring studies are usually performed to produce data on total trace metal content.

1.2 TYPES OF ENVIRONMENTAL POLLUTION

There are three major types of environmental pollution, *viz*:

(a) Air pollution – this is the accumulation of substances in the atmosphere in sufficient concentrations that endanger human health or produce other measured effects on living organisms and other materials. Some of the most important air pollutants are sulphur dioxide, nitrogen oxides, carbon monoxide, ozone, hydrocarbons, photochemical oxidants and airborne particulates, with radioactive pollutants probably among the most destructive ones, specifically when produced by nuclear explosions. One of the greatest challenges caused by air pollution is global warming, due to the build-up of certain atmospheric gases such as carbon dioxide. With the heavy use of fossil fuels in the 20th century, atmospheric concentrations of carbon dioxide have risen dramatically (Denman *et al*., 2007).

(b) Soil pollution – Soil pollution is the degradation of the Earth's surface through misuse of the soil by poor agricultural practices, mineral exploitation, industrial waste dumping, and indiscriminate disposal of urban wastes. It includes visible waste and litter as well as pollution of the soil itself. The addition of chemical fertilizers, pesticides, and fungicides to the soil interferes with the natural processes occurring within the soil and destroys useful organisms such as bacteria, fungi, and other microorganisms. Some important soil pollutants include:- hydrocarbons, solvents and heavy metals (Mastrandrea and Schneider, 2007).

(c) Water pollution - Water pollution occurs when the body of water is adversely affected due to the addition of large amounts of deleterious materials to the water. When it is unfit for its intended use, water is considered polluted (Chattwal, 2009). Contamination of drinking-water catchments (e.g. by human or animal faeces), within the distribution system (e.g. through leaking pipes or obsolete infrastructure), or of stored household water as a result of unhygienic handling are responsible for several water-borne disease transmissions (WHO, 2010).

1.3 GLOBAL WATER POLLUTION

A good water quality is of global concern due to the vast importance of water to all categories of life. Water quality is a term used to express the suitability of water to sustain various uses or processes. Any particular use will have certain requirements for the physical, chemical or biological characteristics of water (UNEP/WHO, 1996). Therefore, freshwater is a finite resource, essential for human existence. Sustainable development will not be possible without freshwater of adequate quantity and quality. It has been unequivocally demonstrated that water of good quality is crucial to sustainable socio-economic development.

Water is essential for life, but it can and does transmit disease from countries to countries in all continents – from the poorest to the wealthiest. Millions of people are exposed to unsafe levels of chemical contaminants in their drinking-water. This may be linked to a lack of proper management of urban and industrial wastewater or agricultural run-off water, potentially giving rise to long term exposure to pollutants, which can have a range of serious health implications. It may also be linked to naturally occurring arsenic and fluoride, which cause cancer and tooth/skeletal damage, respectively (WHO, 2010).

Sewage, industrial wastes, and agricultural chemicals such as fertilizers and pesticides are the main causes of water pollution. The effects of human activities on water quality are both widespread and varied in the degree to which they disrupt the ecosystem and/or restrict water use. Pollution of water by human faeces, for example, is attributable to only one source, but the reasons for this type of pollution, its impacts on water quality and the necessary remedial or preventive measures are varied. Therefore, increase of faecal pollution in source water is a serious problem in developing countries (Bezuidenhout *et al.*, 2002) and this problem is further aggravated where there is a lack of good sanitation systems and guidelines, thus posing an increased risk for the outbreak of water borne diseases (Pretorious, 2000). Water-borne diseases kill 50,000 people daily (Herschy, 1999), and about 4 million children under the age of five die in developing countries due to water related problems (USAID, 1990; UNEP/WHO, 1996; Warner, 1998).

In developing nations, more than 95 percent of urban sewage is discharged untreated into rivers and bays, creating a major human health hazard. About 90 percent of wastewater in developing countries is discharged into rivers and streams without any treatment (UNEP and World Resources, 2000-2001). Although wastewater effluents standards regulate discharges of industries into surface water, monitoring to ensure compliance in Nigeria is not effective. Water pollutants include insecticides and herbicides, food processing wastes, pollutants from livestock operations, volatile organic compounds (VOCs), heavy metals, chemical waste and others (UNEP/WHO, 1996).

About three-quarters (approximately 75%) of the Earth's surface is covered with water, yet 98 percent is salt water and not fit for consumption. Less than one percent of all the water on Earth is freshwater available for human consumption. An estimated 2.4 billion people lack adequate sanitation and 1.5 billion people are without access to clean and safe water (WHO/UNICEF, 2000). Freshwater makes up less than three percent (3%) of the earth's water, but it is the source of virtually all drinking water. In 2002, each US household used an average of 94,000 gallons of water per year. About 55 percent of that water comes from reservoirs, rivers, and lakes. According to the survey carried out in the year 2000, published in EPA's National Water Quality Inventory, it was reported that 40 percent of rivers and 45 percent of lakes in United States of America are considered too polluted for fishing, swimming, or aquatic life (Chewonki, 2009).

1.4 SURFACE WATER POLLUTION

Surface water is water that is continually moving around, through, and above the earth. It includes water in streams, rivers, lakes, oceans and so on. Water pollution occurs where there is any change in the physical, chemical or biological properties of water by human activities that impair its use for different purposes (Chhatwal, 2009). The quest for economic growth and development vis-à-vis industrial and urban development leading to the generation of large volume of solid wastes poses major environmental risks because of the difficulty in proper management and disposal of this solid waste, especially in developing countries. Landfills and other solid waste disposal sites are major targets of pollution because rainfall and groundwater leach these highly contaminated substances into rivers, streams, lagoons, lakes and other water bodies which are inadvertently used by people residing in such areas (Asonye *et al.*, 2007).

The effects of human activities on water quality are both widespread and varied in the degree to which they disrupt the ecosystem and/or restrict water use. Pollution of water by human faeces, for example, is attributable to only one source, but the reasons for this type of pollution, its impacts on water quality and the necessary remedial or preventive measures are varied. Therefore, increase of faecal pollution in source water is a serious problem in developing countries (Bezuidenhout *et al.*, 2002) and this problem is further aggravated where there is a lack of good sanitation systems and guidelines, thus posing an increased risk for the outbreak of water borne diseases (Pretorious, 2000). Water-borne diseases kill 50,000 people daily (Herschy, 1999), and about 4 million children under the age of five die in developing countries due to water related problems (USAID, 1990; UNEP/WHO, 1996; Warner, 1998).

1.5. SOURCES OF SURFACE WATER POLLUTION

Water pollution is caused due to the discharge of harmful chemicals and compounds in water, which leaves the water unsuitable for drinking and other purposes. This renders the water useless for humans and also endangers aquatic life (Bora, 2013). The important sources of water pollution are domestic wastes, industrial effluents and agricultural wastes. Other sources include oil spills, atmospheric deposition, marine dumping, radioactive waste, global warming and eutrophication. Among these, domestic waste (domestic sewage) and industrial waste are the most important sources contributing to water pollution. Water pollution sources are generally grouped into two categories based on their origin.

Point source pollution

Point source pollution refers to contaminants that enter a waterway through a discrete conveyance, such as a pipe or ditch. Examples of point source pollution include discharges from sewage treatment plant, a factory, or a city storm drain (Chhatwal, 2009). Any drainage outlet delivering polluted runoff into the river is a point source of pollution because the pollution originates from a single, identifiable source (Harvey, 2008). The different sources and methods of pollution of surface water are presented in Table 1.1.

Table 1.1. Sources and methods of water pollution

Pollutant Type	Sources	Methods of Pollution
Petroleum products	• Manufacture of plastics • Manufacture of lubricants • Refinery products (crude oil, vehicle fuel, bitumen for road surfacing, cooking gas, etc.) • Manufacture of solvents • Manufacture of synthetic fabrics; nylon, terylene	• Accidental spills from ships, tanker trucks, pipelines and leaky underground storage tanks. • Old and faulty machineries in industrial factories which are inefficient • Improper refinery processes with the production of toxic by-products
Synthetic Agricultural Chemicals	• Pesticides • Insecticides • Herbicides • Fungicides	• Accumulation of chemicals in dead plants and animals which after decomposition will spread to water sources during rainfall, increasing toxicity of water source.
Heavy metals	• Mining • Automobile exhaust • Metallurgy • Manufacture of semiconductors • Manufacture of batteries	• Leaking pipelines • Untreated industrial discharges which flows into water sources • Emission of oxides of lead automobiles and power plants which dissolves in water • Automobile tyre wear • Improper storage of heavy metals in storage containers
Hazardous wastes	• Radioactive materials • Corrosive materials • Reactive materials	• Improper treatment of waste which are still toxic upon release
Excess organic matter	• Chemical fertilizers • Sewage sludge • Animal waste	• Stimulate algae growth and during decomposition of algae it consumes oxygen which dissolves in the water, decreasing the level of oxygen in aquatic ecosystem and increase the mortality rate (death rate) of flora and fauna. Decaying materials leads to eutrophication.

Table 1.1. Sources and methods of water pollution (contd.)

Pollutant Type	Sources	Methods of Pollution
Sediments	• Soil erosion and soil particulates washed by storms and floodwaters from croplands, unprotected soils, roads and urban soils	• Accumulation of sediments will turn the water murky • Mass flow of mud into water source system will alter the clarity of water
Air pollutant	• Acid rain • Emissions of greenhouse gases	• Dissolves into rainwater which alters the pH of water • Dissolves into water sources which affects the aquatic ecosystem
Thermal pollutants	• Drawn from rivers and lakes to be used as coolants in factories and power plants	• Discharge of warmer water into rivers and lakes will alter the species makeup of the aquatic ecosystem • Reduced oxygen level, threatening the aquatic ecosystem.

Source: Chhatwal (2009)

Nonpoint sources pollution

Nonpoint source pollution refers to diffuse contamination that does not originate from a single discrete source. Nonpoint source pollution is often a cumulative effect of small amounts of contaminants gathered from a large area. Nutrient runoff in storm water from "sheet flow" over an agricultural field or forest are sometimes cited as examples of nonpoint source pollution. Pollution arising from nonpoint sources accounts for the majority of the contaminants in streams and lakes (UNEP, 2005; Chhatwal, 2009). Nonpoint sources of pollution in urban areas may include parking lots, streets, and roads where storm water picks up oils, grease, metals, dirt, salts, and other toxic materials (Harvey, 2008).

1.5.1 Domestic Sewage

Domestic sewage is wastewater generated from the household activities. It contains organic and inorganic materials such as phosphates and nitrates. Organic materials are food and vegetable waste, whereas inorganic materials come from soaps and detergents. The amount of organic wastes that can be degraded by the water bodies is measured in terms of biological oxygen demand (BOD). Many people are not aware of the fact that soaps and detergents enrich the water bodies with phosphates. Phosphates (from soaps and detergents) often lead to algal bloom and eutrophication, which is most common in stagnant water bodies such as ponds and lakes.

1.5.2 Industrial Effluents

Wastewater from the manufacturing and processing industries causes water pollution. The industrial effluents contain organic pollutants and other toxic chemicals. Some of the pollutants from industrial source include lead, mercury, asbestos, nitrates, phosphates, oils, etc. Wastewater from food and chemical processing industries contribute more to water pollution than the other industries such as distilleries, leather processing industries and thermal power plants. Also, dye industries generate wastewater which changes the water quality especially water colour. Since the water colour is changed, there is an alteration in the light penetration and hence it disturbs the aquatic plants and animals.

1.5.3 Agricultural Wastes

Agricultural wastes include manure, slurries and runoffs. Most of the agricultural farms use chemical fertilizers and pesticides. The runoffs from these agricultural farmlands cause water pollution to the nearby water sources such as rivers, streams and lakes. The seepage of fertilizers and pesticides causes groundwater pollution, which is commonly known as leaching. Although the quantity of agricultural waste is low, the effects are highly significant. It causes nutrient and organic pollution to both water and soil. Nutrient pollution causes an increase in the nitrates and phosphates in the water bodies, which leads to eutrophication (Bora, 2013).

1.5.4 Fossil Fuel

Combustion of fossil fuels produces extremely high levels of *air pollutants* and is widely recognized as one of the most important "target" areas for reduction and control of environmental pollution (Houghton, 2004). Fossil fuels also contribute to soil contamination and water pollution (through acid rain and urban runoff). However, there is no reasonable doubt that fossil fuels are among the most serious sources of environmental pollution. Power-generating plants and transport are probably the biggest sources of fossil fuel pollution (Nwilo and Badejo, 2005). Common sources of fossil fuel pollution include industrial (power-generating plants, petroleum refineries, petrochemical plants, production and distribution of fossil fuels, etc.) and transportation (automobiles, shipping industry and aircrafts). Fossil fuel combustion is a major source of carbon dioxide (CO_2) emissions and perhaps the most important cause of global warming (an increase in Earth's temperature due to the build-up of certain atmospheric gases such as carbon dioxide) (Mastrandrea and Schneider, 2007).

1.5.5 Municipal Wastes

The residential sector, markets, supermarkets and other retail outlets are another significant source of pollution, generating large quantities of solid wastes that may end up in landfills or incinerators leading to soil contamination and air pollution which in turn may be carried away by surface runoff into the surrounding water sources.

1.5.6 Radioactive Substances

Radioactive waste is another source of water pollution. Radioactive substances are used in nuclear power plants, industrial, medical and other scientific processes. They can be found in watches, luminous clocks, television sets and x-ray machinery. There are also naturally occurring radioisotopes from organisms and within the environment. If not properly disposed of, radioactive waste can result in serious water pollution incidents.

1.5.7 Oil Spills

In Nigeria**,** the developments of the petroleum industry release pollutants such as petroleum hydrocarbon into the coastal environment. Oil spills can have devastating effects on the environment. While being toxic to marine life, polycyclic aromatic hydrocarbons (PAHs), the components in crude oil, are very difficult to clean up, and last for years in the sediment and marine environment. In 1970, only one oil spill case of about 150 barrels of crude oil was reported with the number increasing to 14 in 1971 involving 15,110 barrels of crude oil. Between 1974 and 1980 the case of oil spill had increased from 14 to 105 and in 1982 there were about 1,581 oil spills involving two million barrels of oil around the world (Sharma, 2005; UNEP, 2005).

According to the Department of Petroleum Resources (DPR) 1997 Annual Reports, over 6000 spills had been recorded in the 40 years of oil exploration in Nigeria with an average of 150 spills per annum. In the period 1976 – 1996, about 647 incidents occurred resulting in the spillage of 2,369,407.04 barrels of crude oil. With only 549,060.38 barrels recovered, 1,820,410.50 barrels of oil were lost to the ecosystem (as shown in Table 1.2). Oil spill statistics in Nigeria were reported by Shell Petroleum Development Company (SPDC), Nigeria, between 2007 and 2012 (Figure 1.1). From the figure 1.1 shows: (a) shows the number of monthly oil spills incidents in 2012, (b) number of oil spill incidents per year (2007-2012); (c) volume of spills per month; and (d) volume of oil spills per year. In 2006, the Nigeria Federal Ministry of Environment assisted by conservation non-governmental organizations, notably the UK World Wildlife Federation, estimates that oil spilled in the Niger Delta over the past fifty years was in the range of nine million to thirteen million barrels. Nevertheless, the region appears to be an ecological disaster especially in most communities.

Table 1.2. Annual report of oil spills between 1976 and 1996 in Nigeria

Year	Number of spills	Quantity spilled (barrels)	Quantity recovered (barrel)	Net loss to the environment (barrel)
1976	128	26157.00	7135.00	19021.50
1977	104	32879.25	1703.01	31176.75
1978	154	489294.75	391445.00	97849.75
1979	157	64117.13	63481.20	630635.95
1980	241	600511.02	42416.23	558094.19
1981	238	42722.50	5470.20	37252.30
1982	257	42841.00	2171.40	40669.60
1983	173	48351.30	6355.90	41995.40
1984	151	40.209.00	1644.80	38564.20
1985	187	11876.60	1719.30	10157.30
1986	155	12905.00	552.00	12358.00
1987	129	31866.00	6109.00	25358.00
1988	108	9172.00	2153.00	7202.00
1989	118	5956.00	2092.55	3830.00
1990	166	14150.35	2785.96	12057.80
1991	258	108367.07	1476.70	105912.05
1992	378	51187.90	2937.08	49711.20
1993	453	8105.32	2335.93	6632.11
1994	495	35123.71	2335.93	32878.78
1995	417	63677.71	3110.02	60568.15
1996	518	399036.67	11838.07	387198.60

Source: Department of Petroleum Resources, (DPR) (1997)

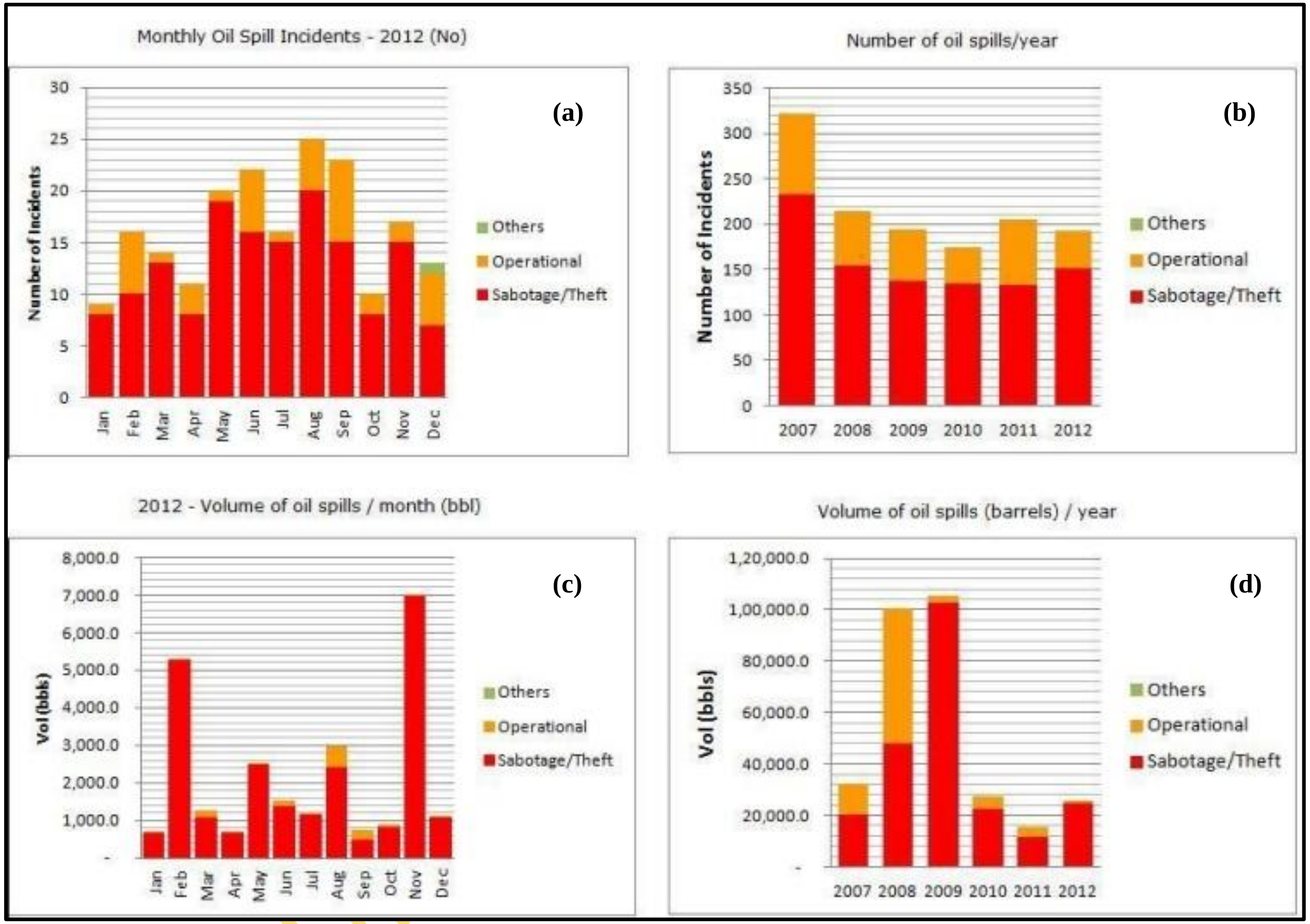

Figure 1.1: Oil spill statistics in Nigeria showing number and volume of spills betwe+en 2007 and 2012 (Source: SPDC Monthly Report, 2012)

1.6 IMPACTS OF WATER POLLUTION

Water is essential for life, but since surface water pollution is trans-boundary in nature, it can and does transmit disease from countries to countries in all continents – from the poorest to the wealthiest. Water pollution occurs when the body of water is adversely affected due to the addition of large amounts of materials to the water. It is established that developed countries suffer from problems of chemical discharge into the water sources mainly groundwater, while developing countries face problems of agricultural run-off in water sources. Polluted water like chemicals in drinking water causes problem to health and leads to water-borne diseases. The impact of water pollution depends on the type and amount of contamination, the period of exposure, and on the characteristics of the waterway itself.

Impacts on human health:

Since humans are at the top of the food chain, they are particularly vulnerable to the effects of non-degradable pollutants. Water contamination is one of the main causes of most health problems in human beings. Water-borne diseases are infectious diseases spread primarily through contaminated water. Though these diseases are spread either directly or through flies or filth, water is the chief medium for the spread of these diseases and hence they are termed as water-borne diseases. Pathogens – which include virus, bacteria, protozoa, and parasitic worms – are disease-producing agents found in the faeces of infected persons. The most predominant waterborne disease, diarrhoea, has an estimated annual incidence of 4.6 billion episodes and causes 2.2 million deaths every year (World Watch; World Health Organization). In the past decade, diarrhoea related to unsafe water has killed more children (under 5 years) than all the people lost to armed conflict since World War II (WSSCC, 2004). In 1997, about 5,853 deaths, due to cholera outbreak, were reported by the World Health Organization in Africa. In Kano, a total of 5,600 cholera cases and 340 cholera deaths were reported between December 1995 and May 1996 (Hutin *et al*., 2003).

In Minamata, Japan, inorganic mercury was used in the industrial production of acetaldehyde which was discharged into the nearby bay as waste water and was ingested by organisms in the bottom sediments. This highly toxic element (Hg) accumulated in the bodies of local fish and eventually in the bodies of people who consumed the fish and suffered from MeHg (methyl mercury) intoxication, later known as the Minamata disease. The disease was first detected in 1956, but the mercury emissions continued until 1968. Even after the emission of mercury stopped, the bottom sediment of the polluted water contained high levels of this mercury. More recently, research has revealed that many chemical pollutants, such as DDT and PCBs, mimic sex hormones and can interfere with the human body's reproductive and developmental functions. These substances are known as endocrine disrupters (*Anon. 2007*).

In most coastal communities, river water is the main source of drinking water and in communities close to the Atlantic Ocean, the intrusion of high salinity (seawater) into the river water makes water unfit for consumption. In such areas, the saying goes: *"Water, water, water everywhere, but none to drink."*

With about 1.2 billion people lacking clean water, waterborne infections account for 80 percent of all infectious diseases. Increased water pollution creates breeding grounds for malaria-carrying mosquitoes, killing 1.2 to 2.7 million people annually, and air pollution kills about 3 million people a year. Non-sanitary living conditions account for more than 5 million deaths each year, of which more than half are children (WHO, 2008).

Water contamination is one of the main causes of most health problems in human beings. About 2.3 billion people are suffering from water-related diseases worldwide (UN-WWAP, 2003). In developing countries, more than 2.2 million people die every year due to drinking of unclean water and inadequate sanitation (WHO/UNICEF, 2000). Water-related infectious and parasitic diseases account for ≈ 60% of infant mortality in the world (Ullah *et al.*, 2009). In Pakistan, contamination of drinking water with industrial wastes and municipal sewage coupled with the lack of water disinfection practices and quality monitoring at treatment plants is the main cause of the prevalence of waterborne diseases (Hashmi *et al.*, 2009a, b; Azizullah *et al.*, 2011).

Increase in algal blooms:

Water pollution can also significantly increase the rate of algal blooms. Urea, animal manure and vegetable peelings are food for algae. Algae grow according to how much waste is in a water body. Bacteria feed off the algae, decreasing the amount of oxygen in the water. The decreased oxygen causes harm to other organisms living in the water.

These blooms create massive fish die-offs as the oxygen in the water gets depleted , and the fish suffocate. Algal bloom and eutrophication lead to the suffocation of fish and other organism in a water body (Skye, 2013).

Effects on marine life:

Chemical water pollution affects marine life in different ways, depending on the nature of the polluting agent. Copper and chrome salts are toxic for algae and marine life. Plankton is strongly affected by numerous pesticides and herbicides. Synthetic detergents are very toxic for marine life, and water pollution with this agent affect the microbial flora. Marine life is easily affected, but the most deaths are due to lack of oxygen in the polluted water, and dumping of pesticides and toxic residue. Water pollution with heavy metals, especially with mercury, also leads to severe problems which accumulate on the food chain. The consequences resulting from the pollution of marine life with mercury, constitutes an alarm signal to the irresponsible behaviour of humankind (Skye, 2013).

Overall ecological risks:

Water pollution also causes negative impacts within the environment to animals and their habitats. The entrance of pollutants into waterways can have a wide range of impacts on the aquatic life. It is possible for the pollutants from industrial effluents discharged into water bodies to raise the temperature of the water enough to force fishes to migrate in search of cooler waters which indeed can create an ecological dead zone (Skye, 2013).

1.7 WATER QUALITY ASSESSMENT

“Water quality” is a term used here to express the suitability of water to sustain various uses or processes. Any particular use will have certain requirements for the physical, chemical or biological characteristics of water; for example limits on the concentrations of toxic substances for drinking water use, or restrictions on temperature and pH ranges for water supporting invertebrate communities. According to Bartram and Helmer (1996), water quality monitoring is the foundation on which water quality management is based. Monitoring provides information that permits rational decisions to be made on the following:

- describing water resources and identifying actual and emerging problems of water pollution,
- formulating plans and setting priorities for water quality management,
- developing and implementing water quality management programmes, and
- evaluating the effectiveness of management actions.

According to Meybeck *et al*. (1996), water quality requirements or objectives can be usefully determined only in terms of suitability for purpose or purposes, or in relation to the control of defined impacts on water quality. For example, water that is to be used for drinking should not contain any chemicals or micro-organisms that could be hazardous to health. Similarly, water for agricultural irrigation should have a low sodium content, while that used for steam generation and related industrial uses should be low in certain other inorganic chemicals (e.g. heavy metals).

The composition of surface and underground waters is dependent on natural factors (geological, topographical, meteorological, hydrological and biological) in the drainage basin and varies with seasonal differences in runoff volumes, weather conditions and water levels. Large natural variations in water quality may, therefore, be observed even where only a single watercourse is involved. Human intervention also has significant effects on water quality. Some of these effects are the result of hydrological changes, such as the building of dams, draining of wetlands and diversion of flow. More obvious are the polluting activities, such as the discharge of domestic, industrial, urban and other wastewaters into the watercourse (whether intentional or accidental) and the spreading of chemicals on agricultural land in the drainage basin.

Water quality is affected by a wide range of natural and human influences. The effects of human activities on water quality are both widespread and varied in the degree to which they disrupt the ecosystem and/or restrict water use. Pollution of water by human faeces, for example, is attributable to only one source, but the reasons for this type of pollution, its impacts on water quality and the necessary remedial or preventive measures are varied. Faecal pollution may occur because there are no community facilities for waste disposal, because collection and treatment facilities are inadequate or improperly operated, or because on-site sanitation facilities (such as latrines) drain directly into aquifers (Meybeck *et al*., 1996).

1.7.1 Water Quality Index

The conditions of a particular water body – river, lake, lagoons, ocean, stream, etc. can fluctuate periodically; therefore, water quality must be measured or examined periodically to look for trends. Water that is said to be safe for one use may be unacceptable for another purpose (Majumder, 2009). Assessment of surface water quality can be a complex process, undertaking multiple parameters capable of causing various stresses on the overall water quality. Different statistical approaches of the individual parameter, multi-stressors water quality indices, etc. have been considered to determine water quality (Bharti and Katyal, 2011).

Several sets of standards, or guidelines for water quality, have been issued from time to time by various agencies and authorities (such as United States Environmental Protection Agency (EPA), World Health Organization (WHO), European Union (EU), Canadian Council of Ministers of Environment (CCME), and other countries) in order to define the maximum acceptable limit of water pollution by various pollutants. Standards for ambient water quality are commonly designated according to the intended use of the water resource (e.g. drinking water, fishing water, irrigation etc.).

Water Quality Index (WQI) is a scale which helps to estimate the overall quality of water based on the values of water quality parameters. The biggest problem of WQI is that the quality of water varies with the source of water collection and the standard range of acceptability which varies between national and international bodies. The index used for estimation of water quality for drinking cannot give a correct estimation of water quality for irrigation, recreational, industrial effluents, etc. The drinking water standards are very high compared to industrial effluents. All over the world, numerous water quality indices, have been proposed which promptly and efficiently assess the overall water quality within a particular area (Majumder, 2009).

There are numerous WQI specific to a particular region or area since several national and international agencies are involved in water quality assessment and pollution control defining water quality criteria for different uses of water considering different indicator parameters. Examples of such WQI used for assessing surface water quality include US National Sanitation Foundation Water Quality Index (NSF-WQI), Canadian Council of Ministers of the Environment Water Quality Index (CCME-WQI), British Columbia Water Quality Index (BC-WQI), and Oregon Water Quality

Index (O-WQI) (Debels *et al*., 2005; Kannel *et al*., 2007; Abbasi, 2002). These indices are based on the comparison of the water quality parameters to regulatory standards and give a single value to the water quality of a source (Khan *et al*., 2003; Abbasi, 2002).

The WQI is one of the most widely used of all existing water quality procedures. The overall results of nine separate tests can be used to determine if a particular stretch of river is healthy. The WQI consists mainly of nine tests including dissolved oxygen (DO), fecal coliform, pH, biochemical oxygen demand (BOD), temperature, total phosphate, nitrates, total solids and turbidity. The results of the nine tests on completion are recorded and transferred to a weighting curve chart where a numerical value was obtained (Majumder, 2009). According to Vanloon and Duffy (2000), guidelines have been established for the physical and chemical properties, complex ions and organic compounds, radiological and microbiological properties. It is obvious that a water body that is polluted for some particular use may be useful for another purpose. Prati *et al*. (1971) considered 13 different parameters of equal weight in their system. Values of these parameters are rated from Class 1 (excellent) to Class 5 (heavy pollution). The Prati Scale (Table 1.3) was used for water classification according to their pollution level.

1.8 CHEMICAL SPECIATION OF METALS IN SEDIMENTS AND SURFACE WATER

Chemical speciation can be defined simply as the identification and quantification of the different species, forms or phases present in a material (Korfali and Jurdi, 2011). The pollution studies of trace metals in surface water and sediments cannot be better understood without the examination of the distribution pattern. Metal speciation in natural waters is of increasing interest and importance because toxicity, bioavailability, environmental mobility, biogeochemical behaviour, and potential risk in general are strongly dependent on the chemical species of metals (Korfali and Jurdi, 2011).

Since metal speciation is dependent on the nature and concentration of chemical species in water, other than the metals themselves, some form of mathematical treatment of analytical data is usually required. More precisely, less labour-intensive means for determining and understanding metal bioavailability are also urgently needed (ANZECC and ARMCANZ, 2000 a,b).

Table 1.3: Parameters used in the classification of water quality (The Prati Scale)

Parameters	Class 1	Class 2	Class 3	Class 4	Class 5
pH	6.5 – 8.0	6.5 – 8.4	5.0 – 9.0	3.9 – 10.1	<3.9 – >10.1
DO	7.8	6.2	6 .0	1.8	< 1.8
BOD	1.5	3.0	6.0	12.1	> 12.1
NH_3-N	0.1	0.3	0.9	2.7	> 2.7
COD	10	20	40	80	>80
Cl^-	50	150	300	620	>620
SS	20	40	100	278	>278

Class 1 = Excellent; Class 2 = acceptable or good; Class 3 = slightly polluted (medium); Class 4 = polluted (fair); Class 5 = heavily polluted (poor).

Source: Prati *et al*. (1971).

Apart from water hardness, metal uptake and toxicity in freshwater organisms can be strongly affected by a range of other important water quality parameters, including pH, water hardness and the concentration of natural dissolved organic matter. Moreover, in freshwaters, water hardness co-varies with pH and dissolved organic matter, as well as other water quality parameters (ANZECC and ARMCANZ, 2000a,b).

Surface waters contain natural organic matter and particles, both of which react with metals to reduce their bioavailability. Often, more than 90% of the metal present in the water is adsorbed to particles or complexed with organic matter. Only a small fraction of the metals found in soils, and natural waters are bioavailable, mainly because a larger fraction is usually bound with reacting chemicals in the environment making less of the metal available for uptake by an organism (Tepavitcharova *et al*., 2011; Rabadjieva *et al*., 2009).

Speciation of metals in water is critical to understand metal behaviour in an aquatic system as that of metal speciation in sediment. The forms of chemical species of toxic metal in the water column, i.e. the organic and inorganic metal complexes and the free solvated metal ion could be used as a predictor of bioavailability to particular aquatic organism. The free ion activity model states that there is a correlation between the toxicity of a metal to an organism and the thermodynamic activity of the free aqua metal ion in solution (Morel and Herring, 1993; Campbell, 1995).

The chemical speciation analyses, although useful, are difficult, very expensive, and not performed regularly. The data on chemical speciation are rarely available, although some of the chemical species are considered to be responsible for the metal toxicity and bioavailability. Thermodynamic modelling is an appropriate approach to the calculation of chemical species distribution because of its facility and rapidity. The accuracy of the calculations depends on the availability and accuracy of analytical data as well as on an appropriate thermodynamic database (Tepavitcharova *et al*., 2010).

The speciation of some metals with inorganic ligands (OH^-, Cl^-, CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} systems) in surface water bodies are made possible using different geochemical models. Dissolved species in water can be described as free hydrated ions or aquo-complexes, or simply complexes. A complex, according to Langmuir (1997), is a dissolved species that exists because of the association of a cation with an anion or neutral molecule. Therefore, the total analytical concentration of a given metal in water is the sum of the concentrations of its free ion and complexes and any metal associated with suspended solids, whether organic or mineral. For example, the total molal concentration of lead, ∑Pb, in natural water might equal:

$$\sum Pb = mPb^{2+} + mPbOH^{+} + mPbCO_3^{o} + mPbHCO_3^{+} + mPbSO_4^{o} + mPb \text{ (suspended solids)}$$

In most natural waters the concentration of free metal ion, mM^{n+}, is less than the sum of the concentrations of its complexes (hydroxyl, carbonate, bicarbonate, and sulphate ions). Severally, only total metal concentrations are determined and reported by most researchers. However, in recent years it has become increasingly apparent that metal toxicity is a function of the concentrations of specific metal species, not of the total metal (Stumm and Morgan, 1996; Langmuir, 1997). In fact, toxicity was often found to be best predicted by the free metal ion activity (Morel and Herring, 1993). In natural waters, metal concentration, or those of other metal species, can sometimes be measured directly, although often with difficulty. Given the appropriate solution analysis and thermodynamic database, the concentrations of individual species can be computed using a geochemical equilibrium modelling program such as MINTEQA2 (U.S. EPA, 1991) or PHREEQC (Parkhurst and Appelo, 1999).

1.9 STATEMENT OF THE PROBLEM AND JUSTIFICATION OF THE STUDY

The Nigeria coastal environment consisting of rich and diverse ecosystems, natural resources and large human population, has been subjected to erosion and other forms of anthropogenic pollution in the past decades. The contamination of soils and natural water bodies by trace metals is of major concern especially in many industrialized cities because of their toxicity, persistence and bioaccumulative nature (Arain *et al.*, 2008, Baig *et al.*, 2009 a & b). The accumulation of trace metals and metalloids in sediments, sludge and soils has posed serious environmental problems concerning possible metal transfer from these sample matrices to aquatic life and thereby affecting the food chain.

Several analytical methods have been employed to estimate water pollution. These include: monitoring total concentration, comparing results with standards, pollution indices (e.g. Prati Scale), geochemical modelling, etc. Pollution monitoring in most cases usually reports the total content of the pollutants and not their chemical species which determines the toxicity and bioavailability of the pollutants (Tepavitcharova *et al*., 2009). The determination of only total metal concentration does not give an accurate account of the likely environmental impact (Tessier *et al*., 1979; Korfali and Jurdi, 2011). The importance of chemical speciation within a coherent framework is increasingly being recognized, and detailed understanding of the bioavailability and toxicity of toxic heavy metals, as well as transport and sedimentation in natural waters, requires full knowledge of their speciation. Therefore, metal speciation studies in water and sediments are crucial to the understanding and prediction of metal behaviour and potential impact in any environmental system (Salomons and Forstner, 1984; Tessier and Turner, 1995).

The Cross River and Qua Iboe River are two major rivers in Akwa Ibom State used for recreation, fishing, irrigation and domestic purposes. They are liable to pollution from diverse sources. Previous studies of water qualities generally determined and reported total metal concentrations and are limited in scope with regard to speciation of metal pollutants which gives accurate information on metal bioavailability and toxicity to aquatic life. However, it has become increasingly apparent that metal toxicity is a function of the concentrations of specific metal species, not of the total metal (Stumm and Morgan, 1996; Langmuir, 1997). The two rivers, Cross and Qua Iboe, have little or no reports on chemical speciation in surface water, although some of these chemical species are considered to be responsible for metal toxicity and bioavailability and on the saturation index which are valuable indices for assessing general pollution status and exposure risks.

This work aimed at determining the physicochemical characteristics and metal speciation in surface water and sediments. The PHREEQCI (pH-Redox-Equilibrium-Computer programming language-Interactive) model, due to its rapidity and facility, will be applied to determine the ionic species and saturation indices in surface water while the European Union Binding Corporate Rules (BCR) reference method will be applied to sediment speciation.

1.10 AIMS OF THE STUDY

The aims of this research, therefore, are to determine the:

- physicochemical characteristics of surface water of Cross River and Qua Iboe River;
- levels of trace metals - Cd, Pb, Cr, Cu, Zn, Ni and Co in surface water and bottom sediment samples;
- speciation of trace metals in sediments using the European Union Binding Corporate Rules (BCR) reference sequential extraction protocol;
- metal speciation in surface water by estimating the activities of various ionic species of the metal ions using PHREEQCI model from the measured ion concentrations; and,
- mineral saturation indices using speciation modelling of PHREEQCI.

CHAPTER TWO

LITERATURE REVIEW

2.1 WATER QUALITY

"Water quality" is a term used to express the suitability of water to sustain various uses or processes. Any particular use will have certain requirements for the physical, chemical or biological characteristics of water; for example, limits on the concentrations of toxic substances for drinking water use, or restrictions on temperature and pH ranges for water supporting invertebrate communities. Consequently, water quality can be defined by a range of variables which limit water use. Although many uses have some common requirements for certain variables, each use will have its own demands and influences on water quality. Water quality is affected by a wide range of natural and human influences. The most important of the natural influences are geological, hydrological and climatic, since these affect the quantity and the quality of water available. Their influence is generally greatest when available water quantities are low and maximum use must be made of the limited resource; for example, high salinity is a frequent problem in arid and coastal areas (UNEP/WHO, 1996).

2.1.1 Some Water Quality Parameters

The major water quality problems are: low dissolved oxygen (DO), high turbidity, organic matter and ammonia contents, severe Cr and Cu pollution and high acute and chronic toxicity. These results in the loss of aquatic life which is inimical since a greater percentage of the coastal population depend largely on natural waters for their daily sustenance and survival. Some water quality parameters include temperature, pH, turbidity, electrical conductivity, salinity, total acidity, total alkalinity, total dissolved solids, hardness, dissolved oxygen, chemical oxygen demand, biochemical oxygen demand, chloride, ammonia nitrogen, nitrates and nitrites nitrogen, sulphates, phosphates and oil and grease (APHA-AWWA-WEF, 2005).

2.2 Surface Water Pollution of Some Nigerian Rivers

Surface water include water in streams, rivers, lakes, oceans. Coastal pollution has been increasingly recognized as a significant and expanding environmental problem in many developing nations. In Nigeria, the marine environment is subjected to contamination by persistent organic pollutants (POPs) and metals largely due to the discharge of untreated domestic and industrial waste waters, agricultural waste water, boat traffic, oil transportation, oil pipeline leakages/spillages and atmospheric fallouts (Odukuma and Okpokwasili, 1997; Otokunefor and Obiukwu, 2005; Rim-Rukeh *et al.*, 2006; Abu and Egenonu, 2008; Nduka *et al.*, 2008; Udotong *et al.*, 2008). Aquatic animals are exposed to chemicals in both the dissolved (ambient water) and dietary (sediment or prey) phases.

Typically, water quality criteria are defined based on the measurements of metal concentrations in seawater. However, given the recent recognition of the quantitative importance of dietary metals as sources for metal accumulation in marine animals (Wang and Fisher, 1999; Wang, 2002), it is desirable to consider metal dietary exposure when developing realistic water quality criteria. Most communities and beaches along the coast are used for recreation by the public while the entire coast is used mainly for commercial fish farming. Fish growth largely depends on the quality of the culture medium. Physicochemical parameters are known to affect the biotic components of any aquatic environment (Ugwumba and Ugwumba, 1993; Owhonda *et al.*, 2007) and some of these parameters like pH, salinity, and dissolved oxygen are fundamental to the basic metabolic activities of the fish and are very vital to its survival most especially in brackish water environment (Francis *et al.*, 2007; Owhonda *et al.*, 2007).

According to Abu and Egenonu (2008), the input of environmental pollutants of all sorts in aquatic systems in Nigeria is a common phenomenon. The degree of pollution in the region and many other parts of Nigeria is attributed to the lack of governmental control regarding anthropogenic inputs into the water ways. The activities of oil exploration including gas flaring, pipeline leakages, crude oil spillages and other nefarious activities has led to the introduction of different forms of contaminants and pollutants to the environmental media especially in the Western Niger Delta environment. Other industrial and municipal discharges such as untreated effluents, indiscriminate dumping of domestic and municipal solid wastes, dumping of metal scraps, the use of agrochemicals by farmers and the washing of agricultural farmland by surface run-off into the surrounding lakes, streams and rivers are also major sources of these contaminants in the environment. Also, lumbering activities, forestry operations, dredging activities and domestic sewage inputs may lead to wide scale contamination of surface water in the area (Odukuma and Okpokwasili, 1997; Krantz and Kifferstein, 1998; Morrison *et al.*, 2001; Alam *et al.*, 2006; Abu and Egenonu, 2008).

In an extensive study on some physicochemical characteristics and heavy metal profiles of some Nigerian rivers, streams and waterways, Asonye *et al.* (2007) reported that 93% of all samples studied had high turbidity values which was higher than WHO and EEC standards, 57% of the entire samples had conductivity values above normal limits and 81% of the entire samples had pH values above WHO and EEC limits.

Olaifa (2006), reported that the total hydrocarbon (THC) and heavy metal contents of surface water, bottom water and sediments (intertidal and waterbed) in coastal areas of Cross River and Akwa Ibom States are affected by a major oil spill. The author attributed higher concentrations of Pb during the dry season than rainy seasons to a reduction in the water levels during the dry season thereby causing greater concentrations of pollutants. Francis *et al.* (2007) investigated monthly variation of the physicochemical parameters of the Andoni River, a tributary of Imo River, between 1999 and 2000 and reported the following ranges of values for some of the physicochemical parameters studied: 26.05–32.1 ^{o}C for temperature, 6.38–8.90 for pH, 12.0–22.0 mgL^{-1} for salinity, and 5.00–12.3 mgL^{-1} for dissolved oxygen.

In Orogodo River, Agbor, Rim-Rukeh *et al.* (2006) reported that the water quality status of some sampling stations corresponds to a polluted stream as values of measured parameters exceeded standard values for drinking water. The authors reported that the water was slightly acidic and exceeded the acceptable levels for drinking water with pH values ranging from 5.10–6.10, due to the formation of humic acid from decayed organic matter. The authors added that low concentration of dissolved oxygen, 2.17 – 6.80 mgL^{-1}, was below the level that could support aquatic life, while relatively high levels of BOD, 21.0–38.2 mgL^{-1}, was reported, which exceeded the WHO limit of 10.0 mgL^{-1} for drinking water. In all the sampling stations, the authors reported the following ranges of values occurred : temperature - 25.7–29.6 ^oC; turbidity, 0.8–29.4 NTU; conductivity, 41.8–8177 $µScm^{-1}$; TSS, 1.72–221mgL^{-1}; TDS, 41.0–2078 mgL^{-1}; NO_3^-, 9.70–28.0 mgL^{-1}; PO_4^{3-}, 5.18–28.67 mgL^{-1} and SO_4^{2-}, 21.7–36.8 mgL^{-1}. In another study, Rim-Rukeh *et al.* (2007) reported levels of some water quality parameters from the Western Niger Delta as follows: pH (5.6–6.9), temperature (26.9–28.6^oC), turbidity (23–63 NTU), electrical conductivity (52–184$µScm^{-1}$), DO (5.4–7.2 mgL^{-1}), BOD (21–57 mgL^{-1}), TDS (6.0–217 mgL^{-1}), PO_4^{3-} (0.19–1.72 mgL^{-1}), SO_4^{2-} (25–36.8 mgL^{-1}), and NO_3^- (20.3–28.0 mgL^{-1}).

The seasonal variation of some physicochemical properties of River Ethiope in Abraka was also investigated by Agbaire and Obi (2009). The results obtained for the two seasons (dry and wet) showed higher values during the dry season except for DO and TSS and were given as (*values for wet season in parenthesis*): pH - 6.82 (6.82), temperature - 29.15 (27.73) ^oC, conductivity - 87.2 (81.7) µS cm^{-1}, TDS - 0.34 (0.26) mgL^{-1}, TSS - 15.21 (16.21) mgL^{-1}, DO - 17.45 (16.80) mgL^{-1}, BOD- 4.38 (4.50) mgL^{-1}, total hardness - 2.42 (2.43) mgL^{-1} and alkalinity - 1.65 (1.45) mgL^{-1}.

According to Abowei (2010), the mean levels of some physicochemical parameters in Nkoro River, a tributary of the Andoni River in the Niger Delta, was reported as follows: pH range of 6.68 to 7.03, which was characteristic of a tidal brackish water environment. The author added that salinity values ranged from 12.8±0.30‰ to 13.30±0.10‰, showing gradual increase in salinity values from the upstream stations to downstream stations along the creek, and dissolved oxygen values ranged from 6.0 to 10.0 mgL^{-1}.

However, Davies *et al.* (2008) reported lower dissolved oxygen values (4.48 mgL^{-1}) in wet season than dry season (5.14 mgL^{-1}) for Woji Creek in Rivers State and attributed it to reduced photo-period and photosynthetic activities of aquatic plants. According to Otokunefor and Obiukwu (2005), the levels of some physicochemical parameters of effluent receiving water body around Port Harcourt refinery had very high concentrations (mgL^{-1}) of phenol (11.06), oil and grease (7.52), ammonia (8.52), COD (91.76), TDS (390.6), sulphate (30.74) and phosphate (6.21) in observation pond wastewater. Also, Udosen (2000) reported the following mean values of physicochemical variables of four different streams in Itu area of Akwa Ibom State: DO (1.99±0.12 mgL^{-1}), BOD (0.40±0.04 mgL^{-1}), TDS (53.00±31.99 mgL^{-1}), TSS (30.00±18.86 mgL^{-1}) and TS (88.00±27.41 mgL^{-1}), temperature (26.04±0.32 ^{o}C) and pH (6.77±1.34).

Ohimain *et al.* (2008) reported that the dredging of an oil well access canal in a tributary of Warri Rivers triggered physicochemical changes of the water body, particularly pH, TDS, conductivity, TSS, turbidity, sulphate, DO, BOD and COD. Consequently, the pH of the dredged canal was decreased from 7.2 to 4.0, dissolved oxygen (DO) decreased considerably from 6.0 mgL^{-1} to 0.4 mgL^{-1}, while BOD increased from 1.0 mgL^{-1} to 18.0 mgL^{-1}. COD, oil and grease, conductivity, TDS and sulphate values similarly increased, while nitrate and alkalinity values decreased after dredging. At the dredged canal, turbidity and TSS increased rapidly after dredging, attaining a value of 11,398 NTU and 8200 mgL^{-1} respectively.

Nubi and Nubi (2010) reported mean values of some physicochemical parameters of some upstream samples of River Ona, a major river in Ibadan, Southwest Nigeria as: DO - 4.9±0.3 mgL^{-1}, COD - 54.5±0.5 mgL^{-1}, PO_4^{3-} - 0.47±0.09 mgL^{-1}, SO_4^{2-}- 20.65±0.85 mgL^{-1}, while the downstream stations recorded mean values for the same parameters respectively as: 3.72±0.37 mgL^{-1}, 211.20±59.6 mgL^{-1}, 1.06±0.20 mgL^{-1} and 23.6±3.2 mgL^{-1}. Results obtained were ascribed to the influence of industrial effluents discharged, and other anthropogenic pollutants, into the river. According to Longe and Omole (2008), the assessment of the pollution status of River Illo in Otta - Ogun State, revealed the following average concentrations of measured parameters: 2.24 mgL^{-1} for DO, 313 mgL^{-1} for BOD, 783 mgL^{-1} for COD, and 621 mgL^{-1} for total solids. The authors asserted that the river was a significant sink for wastes but had limited assimilative capacity.

2.3 SURFACE WATER QUALITY OF SOME OTHER RIVERS AROUND THE WORLD

In Ghana, Fianko *et al.* (2010) investigated the physicochemical status of the Densu River basin and reported the following ranges (mean levels in parenthesis): ammonia - 0.21 - 2.10 mgL^{-1} (1.19±0.02 mgL^{-1}), nitrate - 0.13 - 5.21 mgL^{-1} (2.07±0.01 mgL^{-1}), and PO_4^{3-}–P - 0.54 - 1.04 mgL^{-1} (0.84±0.01 mgL^{-1}). The authors also reported that the river was found to be circum-neutral and fresh with pH ranging between 6.54 and 7.84. The river recorded BOD values ranging from 6.91 to 18.8 mgL^{-1}. They added that the increased concentrations of nutrients and organic pollutants were as a consequence of anthropogenic inputs, particularly from domestic, agricultural and municipal sources.

The pollution parameters and water quality index of Nairobi River was assessed by Dulo (2008), in order to ascertain whether the water meets the surface water quality criteria for water supply. The author observed that anthropogenic activities along the river contributed to the high level of pollution of the river. The author reported the following mean levels pH, 7.04; turbidity, 41.5 NTU; suspended solids, 116 mgL^{-1}; dissolved oxygen, 4.32 mgL^{-1}; BOD, 183 mgL^{-1} and COD, 49.5 mgL^{-1}. The river was classified as being bad, attributable to industrial and municipal sewerage discharges into the river.

In a two-day study of the Bebar River in Malaysia, Gasim *et al.* (2007) asserted that the main sources of pollutants generating both organic and inorganic wastes were found to originate from illegal logging, agricultural activities, un-sustainable development and household activities of indigenous people living along the bank of the river. The following concentration range of some physicochemical properties of the river system was reported: pH - 3.53 to 4.32; electrical conductivity (EC) - 53.0 to 62.15 μScm^{-1}; TDS - 57 to 120 mgL^{-1}; turbidity - 1.5 to 17.15 NTU; and dissolved oxygen - 0.54 to 1.76 mgL^{-1}.

In a baseline study of Ennore Creek, Chennai - India, Jayaprakash *et al.* (2005) reported high values of temperature at the stations near the thermal power plant (34.2–37.4 ^{o}C), high pH values (7.9 – 8.2) attributable to the influence of seawater penetration and the biological activities within the Ennore Creek. Low DO value of 0.54 mgL^{-1} was attributable to the closeness of the stations to the effluent discharge points in the Creek, and to the combined effect of temperature, photosynthetic action and biochemical degradation of wastes entering the Ennore Creek. High salinity values (17.8 – 31.9%), indicating a gradual increase and combined effect of seawater through the Creek were also reported. Sodium and potassium concentrations reveal similarity with salinity concentration, hence, the positive correlation of Na^+ vs. salinity ($r = 0.94$, 0.84) and K^+ vs. salinity ($r = 0.53$, 0.67) indicates that they are strongly interrelated.

In another related study of the physicochemical parameters and quality assessment of Kosi River in Uttarakhand – India, Bhandari and Nayal (2008) reported the following concentration range of values: 0.041-0.05 mgL^{-1} for NO_3^-, 0.12-0.17 mgL^{-1} for Cl^{-1}, 24.3-54.3 mgL^{-1} for TDS, 0.32-0.45 mgL^{-1} for SO_4^{2-}, 0.04-0.063 mgL^{-1} for PO_4^{3-}, 21.33-24.00 mgL^{-1} for COD and 6.56-9.03 mgL^{-1} for BOD. The authors concluded that all the variables studied were within the maximum permissible limit set by WHO except turbidity and BOD values which exceeded the WHO permissible values.

In the Pondicherry mangroves of southeast coast of India, Satheeshkumar and Khan (2009) asserted that the mangrove was polluted due to the discharge of domestic, industrial and agricultural wastes through small tributaries and channels into the Bay of Bengal. The authors reported the following concentrations: salinity - 6.36 – 36.77 ppt; dissolved oxygen - 3.45 – 5.49 mgL^{-1}; pH - 7.11 – 8.52; electrical conductivity - 26.7 – 52.0 mScm^{-1}; sulphide - 2.8 – 47.2 mgL^{-1}; soil parameters (%): sand - 63.7 – 87.3; silt - 9.9 – 29.3; clay - 3.1 – 18.0 and organic matter - 0.94 – 3.94% for Pondicherry mangroves, India. The authors added that the water quality revealed high salinity values in all four stations studied during the summer thereby playing a dominant role in water quality.

2.4 HEAVY METAL POLLUTION OF SURFACE WATER AND SEDIMENTS

Heavy metals have densities greater than 5.0gcm^{-3} and are toxic. These include aluminium, arsenic, beryllium, bismuth, cadmium, chromium, cobalt, copper, lead, mercury, nickel, selenium, strontium, thallium, tin, titanium, and zinc. These metals and their compounds are discharged from industries, agricultural farmlands, municipal urban effluents, etc. into surface waters to cause pollution (Izoafuo *et al*., 2004).

Heavy metals are present in both natural and contaminated environments. In natural environments, they occur at low concentrations. However, at high concentrations, they result in public health impacts. Heavy metals may be released into the environment from metal smelting and refining industries, scrap metal, plastics/rubber industries, and various consumer products and from burning of wastes containing these elements. When released into the air, the element travel long distances and are deposited onto the soil, vegetation and water depending on their density. Once deposited, they are not degraded but persist in the environment for many years, poisoning humans through inhalation, ingestion and skin absorption. Acute exposure leads to nausea, anorexia, vomiting, gastrointestinal abnormalities and dermatitis.

According to Nriagu and Pacyna (1988), the major sources of metal pollution in marine and freshwater systems come from domestic wastewater effluents (especially As, Cr, Cu, Mn and Ni), coal-burning power plants, power plants (As, Hg and Se in particular), non-ferrous metal smelters (Cd, Ni, Pb and Se), iron and steel plants (Cr, Mo, Sb and Zn) and dumping of sewage sludge (As, Mn and Pb). Some metals such as Cd, Co, Cr, Cu, Pb and Zn, however, are known to form discrete solid phases under specific soil conditions, when they occur in elevated concentrations, and due to diagenetic processes or pollution. Several mineral structures such as $Cu_2(OH)_2CO_3$, $Pb_3(PO_4)_2$, $Pb_5(PO_4)_3Cl$, $Zn_3(OH)_6(CO_3)_2$, $Zn_3(PO_4)_2{\bullet}H_2O$, and $ZnSiO_4$ were identified in soils which in turn gets into water bodies (Jenny, 1986).

The major sources of environmental exposure to lead include industrial, vehicular emissions, paints and burning of plastics, papers, etc., while mercury derives its sources from electronics, plastic waste, pesticides, pharmaceutical and dental wastes and cadmium (Cd), electronics, plastics, batteries and contaminated water. Poor waste management poses a great challenge to the well-being of riverine residents, particularly those living near the river banks where all wastes, including human wastes, are dumped into the river. The poor disposal and handling of waste thus lead to environmental degradation, destruction of the ecosystem, and pose great risks to public health. Many of these communities lack solid waste regulations and proper disposal facilities, including harmful wastes. Such wastes may be infectious, toxic or radioactive (UNEP, 2009).

Numerous studies have demonstrated that the concentrations of metals in suspended and bed sediments can be sensitive indicators of contaminants in hydrological systems (Salomons and Forstner, 1980; Luoma, 1990). The presence of trace metals in sediments are affected by particle size and composition of the sediments (Sakai *et al.*, 1986). More than 97% of the mass transport of heavy metals to the oceans is associated with river sediments (Jain and Sharma, 2001).

2.4.1 Heavy Metal Pollution of Some Nigerian Rivers

Essien *et al.* (2009a) examined the burden of Zn, Cu, Ni, Pb, Cr and V in patches of asphyxiated mangrove swamp areas within Qua Iboe Estuary mangrove ecosystem by sediments and surface water analysis in order to ascertain the anthropogenic influences on them. The authors asserted that although heavy metal concentrations in surface water of the asphyxiated swamp were low, their accumulative effect was significant. The authors also added that the concentrations of Cu and Pb in surface water of this ecosystem exceeded the water quality criteria while Ni and Cr were under the maximum concentration for drinking water quality and protection of aquatic life. In a related studies, Oze *et al.* (2006) reported that surface water from Qua Iboe River estuary was polluted with trace metals investigated except for Mn and Zn with the following mean concentrations (n=10): Ni - 0.21±0.01 mgL^{-1}, Cr - 0.53±0.01 mgL^{-1}, Cd - 0.03±0.01 mgL^{-1}, Mn - 0.14±0.09 mgL^{-1} and Pb - 0.3±0.1 mgL^{-1}.

Benson and Etesin (2008) reported mean seasonal concentrations of heavy metals (in mgL^{-1}) in surface water from Iko River - Akwa Ibom State during the dry season (with wet season values in parenthesis) as: Fe - 3.29 (3.60) mgL^{-1}; Pb - 0.004 (0.006) mgL^{-1}; Cu - 0.13 (0.13) mgL^{-1}; Cd - 0.04 (0.02) mgL^{-1}; Zn - 0. 35 (0.51) mgL^{-1}; Mn, 0.11 (0.03) mgL^{-1}; Ni - 0.42 (0.25) mgL^{-1} and V - 0.23 (0.14) mgL^{-1}. The authors concluded that the dry season samples recorded higher concentration of metals compared with the wet season samples, except for Fe and Pb.

The heavy metal pollution profiles of surface water from about nine different river systems in Rivers State (Anieze River, Orashi River, Abuloma River, Iwofe River, Okirika River, Ozubo River, Tombia River, Woji River and Ozubuko–Ama-well stream) was assessed during the dry season and wet season by Nduka and Orisakwe (2010). The authors reported higher concentrations (mgL^{-1}) of heavy metals during the two seasons, dry and wet season (in parenthesis) as: Pb - 0.56±0.02 (0.48±0.01) and Ni - 0.72±0.01 (0.68±0.00) for Tombia River; Cd - 0.16±0.04 (0.13±0.02), Cr - 0.23±0.02 (0.20±0.01), Pb - 0.59±0.03 (0.52±0.02) and Ni - 0.65±0.01 (0.58±0.00) for Okirika River; Cd - 0.17±0.03 (0.14±0.02) and Pb - 0.58±0.04 (0.53±0.02) for Ozubo River and Fe - 9.09±0.00 (8.50±0.01) for Orashi River.

The concentration ranges of heavy metals, according to Rim-Rukeh *et al.* (2007), of some waters used for drinking and domestic purposes in the Niger Delta, Nigeria was reported as (in mgL^{-1}): Fe (6.07 – 15.71), Zn (0.04 – 0.24), Pb (0.01 – 0.17), Ni (0.01 – 0.13), V (0.01 – 0.20) and Hg (0.001 – 0.002). Asonye *et al.* (2007) reported that the heavy metal profile of some Nigerian rivers, streams and waterways showed that Pb, Cd, Cr, Zn and Mn levels in some samples were above the guidelines of WHO and EEC, with about 55% of all the samples exceeding recommended level of 0.20 ppm for Fe, 15% exceeded 0.05 ppm for Cr, 11% exceeded 0.003 ppm for Cd, 7% exceeded 3.0 ppm and 0.10 ppm for Zn and Pb respectively. To this effect, the authors concluded that heavy metal pollution and toxicity might pose serious health risks to communities residing around and using the available surface water for their domestic, commercial and socio-cultural purposes.

Oribhabor and Ogbeibu (2009) reported the minimum and maximum concentrations of some heavy metals in a Niger Delta mangrove (Buguma) Creek as: 7.21-228.5 mgL^{-1} for Ca, 51.18-428.3 mgL^{-1} for Mg, 0.01-6.78 mgL^{-1} for Fe, 0.010-0.43 mgL^{-1} for Zn, 0.01-0.61 for Pb, 0.01-0.11 for Cd, 0.01-1.49 mgL^{-1} for Cr, 0.01-2.73 mgL^{-1} for Ni, while Hg and the total hydrocarbon content was approximately 0.01 mgL^{-1} throughout the study period.

According to Oguzie and Izevbigie (2009), the mean metal concentrations (mg/kg) for the upstream river sediments and the reservoir sediments (in parenthesis) of Ikpoba River in Benin City were as follows: 0.01 (0.01) for Cd, 0.28 (0.21) for Cr, 1.09 (0.92) for Cu, 3.23 (2.75) for Fe, 0.98 (0.01) for Ni, 1.26 (1.19) for Pb, 0.01 (0.03) for V and 2.36 (1.95) for Zn. Also, Aderinola *et al.* (2009) reported levels of heavy metals in surface water from Lagos Lagoon as: As (0.01±0.00) mgL^{-1}, Cu (0.20±0.14) mgL^{-1}, Mn (0.09± 0.04) mgL^{-1} and Zn (0.53± 0.36) mgL^{-1} and asserted that metal levels were generally below the WHO guideline limit for drinking water. The authors added that metal concentrations (mgL^{-1}) of Cd (0.35±0.30), Cr (0.06±0.03), Pb (0.26±0.12) and Ni (0.14±0.08) were above the guideline values of WHO (2004).

2.4.2 Heavy Metals Pollution of Some Rivers around the World

Abdel-Satar *et al.* (2010) reported elevated levels of some heavy metals in majority of surface water samples of Lake Qarun, Egypt as: > 50µgL^{-1} for Zn, 20µgL^{-1} for Cu, 50µgL^{-1}for Pb, 10µgL^{-1}for Cd, and attributable to the anthropogenic sources such as fertilizers and pesticides, other than natural sources of metal input. The concentrations of metals (µgL^{-1}) in Hindon River water, India, was reported by Suthar *et al.* (2009) showing a wide variation as: Cd - 2.40 – 24.1; Cu - BDL – 4373; Cr - 31 –331; Fe - BDL – 1247; Mn - 1.7 – 868; Zn - 0.5 – 836 and Pb - 30 – 902. Higher metal levels were attributed to impact of industrial and urban wastewater discharge to the river.

Violintzis *et al.* (2009) reported higher pollution level of particulate elements in sediment samples from coastal environments of Thermaikos Bay, Greece, with ranges (mean values in parenthesis) as: Cd - 3–95 (37) µgg^{-1}; Pb - 55–348 (153) µgg^{-1}; Cr - 125–440 (339) µgg^{-1}; Co - 45–183 (95) µgg^{-1}; Ni - 71–311 (188) µgg^{-1}; Cu - 47–376 (129) µgg^{-1}; Zn - 147–851 (432) µgg^{-1} and As - 19–86 (53) µgg^{-1}. The authors asserted that most metals had significant contributions from anthropogenic sources particularly at the inner part of the Bay and were found at concentrations that could adversely affect the marine biota.

Seasonal concentrations of heavy metals in coastal waters of Alang-Sosiya, India during the summer, monsoon and winter seasons, according to Srinivasa-Reddy *et al.* (2005) showed that the concentrations of all metals were the highest in the winter season followed by the monsoon and summer. They concluded that, high degree of dispersion of metals into waters at low temperatures and low tides during the winter may be an explanation for the highest concentration of heavy metals.

2.5 SEDIMENT QUALITY: HEAVY METALS AND OTHER PHYSICOCHEMICAL PARAMETERS

Sediment is the loose sand, clay, silt and other soil particles that settle at the bottom of a body of water. Sediments form a natural buffer and filter system in the material cycles of water and is an important habitat as well as the main nutrient source for aquatic organisms (Adeyemo *et al.*, 2008). In estuarine ecosystems, sediments are important sinks for metals and may also serve as an enriched source of metal for benthic organisms (Campbell *et al.*, 1988; Cheggour *et al.*, 2005). River sediments are basic components of our environment, and it also constitutes a major source of persistent, bioaccumulative toxic chemicals which may pose threats to ecological and human health even after contaminants are no longer released from point and nonpoint sources (Lasheen and Ammar, 2009).

Apart from being a sink for pollutants, sediments are potential sources of pollution toxicity to aquatic organisms and are known to sequester hydrophobic chemical pollutants entering water bodies such as estuaries (McCready *et al.*, 2006). It is established that the total concentrations of trace metals in sediments cannot predict their bioavailability and toxicity, in spite of the somewhat convenient measures of metal pollution in sediments (Luoma, 1989; Di Toro *et al.*, 1990).

Heavy metals such as Cd, Hg, Pb, Cu and Zn are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence; toxicity and ability to be incorporated into food chains (Forstner and Wittman, 1983). Nearly all metals in the aquatic environment reside in water sediments while the fractions in the biota are small (Ademoroti, 1996a). The concentrations of harmful and toxic substances are of many orders of magnitude higher in sediments and biological tissues than in water itself. Globally, high concentrations of trace metals and organic pollutants have been found frequently in sediments near industrialized and urbanized harbours and lakes (NRC, 1989; Bryan and Langston, 1992; Simpson *et al.*, 1996).

In a study of Lagos lagoon, Aderinola *et al.* (2009) reported low mean levels of heavy metals in the sediments, with values falling within the acceptable limits of national and international standards (FEPA, 1999; WHO, 2008). The authors reported mean metal (As, Cd, Ni, Cr, Cu, Fe, Pb, Mn and Zn) concentrations (in mgkg^{-1}) as: 0.08±0.04; 1.15±0.09; 0.87±0.08; 0.62±0.19; 0.60±0.27; 19.39±6.65; 0.45±0.60; 2.04±1.05 and 0.73±0.34, respectively.

In another related development, Essien et al. (2009b) examined the burden of Zn, Cu, Ni, Pb, Cr and V in patches of asphyxiated mangrove swamp areas of Qua Iboe estuary and reported their concentrations ranges in sediments as: 36.3 – 179.4, 29.2 – 43.2, 3.6 – 37.4, 39.6 – 93.8, 0.15 – 0.53 and 2.9 – 9.3, respectively.

The determination of physicochemical quality of sediments of the lower reaches of Okpoka Creek, a tributary of the Upper Bonny estuary, gave the following results: pH

- 5.22±0.27; THC - 0.24±0.05 μgg^{-1}; TOM - 3.78±1.56%; TOC - 1.43±0.17%; and conductivity - 5077±848 μScm^{-1} (Davies and Abowei, 2009). However, the authors asserted that TOC and TOM values exceeded the FEPA and US-EPA guideline limits in sediments, which was indicative of organic pollution in the estuary.

In Lake Qarun, Egypt, Abdel-Satar *et al.* (2010) reported elevated levels of heavy metals in lake sediments with highest concentrations (μgg^{-1}) as: 419 for Zn, 195 for Cu, 147 for Pb, and 27 for Cd. The authors attributed high levels of these metals to anthropogenic source such as agricultural fertilizers and pesticides and also from sewage discharges entering the lake through El-Bats and El-Wadi drains.

Muohi *et al.* (2003) reported higher metal concentrations obtained from Makupa Creek and Port Reitz Creek sediments in the Mombasa city of Kenya. Mean values reported for the Makupa Creek was: Cu - 102±46; Zn - 1017±840; Pb - 103±36; Cd - 51.0±14.3 as compared to Port Reitz Creek system whose values were reported as Cu - 21.6±7.1; Zn - 57.1±17.9; Pb - 26.2±11.6; Cd - 1.38±0.70. The authors attributed the higher elemental values particularly at Makupa Creek to industrial activities and nearby municipal dumpsite.

According to Kishe and Machiwa (2003), levels of Cd, Cr, Cu, Pb, Hg and Zn in sediment samples from Mwanza Gulf of Lake Victoria, Tanzania were reported with concentration levels (in ppm) as: Cu - 26.1±4.8, Hg - 0.2±0.05, Pb 30.7±5.6 and Zn - 45.4±13.1. The authors added that heavy metals concentration in the sediment decreased with increasing distance from the shoreline except for Cd and Cr whose highest concentrations were found at approximately 2000m from the shoreline. On the other hand, the authors added that sediment samples collected at the shores within the urban area of Mwanza showed elevated levels of Pb (54.6±11.1 ppm) and Zn (83.7±21.5 ppm) with the highest concentrations of Cd (7.0±2.1 ppm), Cr (12.9±1.0 ppm) and Hg (2.8±0.8 ppm) recorded at sampling stations adjacent to the river mouth.

In another related study, Mostafa *et al.* (2009) reported the concentration ranges (μgg^{-1} DW) of heavy metals in the coastal sediments from Hadhramout (mean in parenthesis) as: 5.4 – 24.2 (12.4) for Ni; 6.0 – 27.5 (12.8) for Co; 23.8 – 242 (72.1) for Mn; 0.3 – 2.6 (1.5) for Cd; 448 – 2915 (1498) for Fe; 3.1 – 51 (20.4) for Cu; 10.6 – 90.6 (55.6) for Zn; 5.7 – 25.3 (10.9) for Cr and 5.3 – 23 (10.3) for Pb. Also, Prieto *et al.* (2008), reported the following concentrations (mgkg^{-1}) ranges of sediment metals in Bilbao estuary: As - 8.3 – 285, Hg - 0.2 – 11.0, Cd - 0.2 – 12, Zn - 145 – 1740 and Sn - 1.6 – 20. The authors attributed high levels of Zn (1740 mgkg^{-1}) and As (285 mgkg^{-1}) in some sites of the study area to the generation and accumulation of metal slag from the steel industry through the 19th and 20th centuries.

Suthar *et al.* (2009) assessed the level of heavy metals (Cd, Cr, Cu, Fe, Mn, Zn and Pb) in water and sediments of Hindon River in industrialized city Ghaziabad, India. From the 6 stations covering the upstream and downstream sites of Hindon selected for this study, the authors reported the ranges of metal concentration (mgkg^{-1}) in river sediments as: Cd - 1.15 – 3.47; Cu - 9.42 – 195.1; Cr - 42.9 – 250.4; Fe 221 – 238; Mn - 61 – 202; Zn - 4.0 – 85.0; and Pb - 5.1 – 59.1 and concluded that industrial and urban (municipal) discharges from the river catchment areas were the major sources of heavy metals in the river.

Jumbe and Nandini (2009) evaluated the degree of heavy metal contamination in lakes and the extent to which the sediment quality of the lakes of Bangalore city, India has deteriorated using lake bed sediments using comparative sediment quality guidelines from various derived criteria. According to the authors, the extent of sediment quality deterioration was more pronounced in Cu (203.50 ppm) and Ni (97.64 ppm) followed by Pb (206.0 ppm) and Cd (8.38 ppm) whereas Cr (96.70 ppm) failed a single sediment quality guideline while Zn (220.0 ppm), Mn (176.0 ppm) and Co (47.7 ppm) remained within the safety levels of sediment quality guidelines prescribed for the study.

In a related study, levels of heavy metals in surficial sediments from 14 locations of the south coast of the Caspian Sea were assessed by Sohrabi *et al.* (2010). The authors reported the concentration ranges (mean in parenthesis) as: 13.1 – 33.5 (23.7) ugg^{-1} for Pb; 18.0– 69.9 (38.6) ugg^{-1} for Ni; 0.62 - 1.5 (0.9) ugg^{-1} for Cd; 30.1– 87.9 (51.5) ugg^{-1} for Zn, 5.9 – 26.4 (14.0) ugg^{-1} for Cu and 1.8 – 4.0 (2.52) % for Fe. The authors added that Cd and Cu showed the least concentrations at most studied locations and asserted that the coastal area of the Caspian Sea was becoming increasingly polluted with massive load of contaminants discharged into the Caspian Sea from various anthropogenic sources.

In an environmental assessment within the Montevideo Harbour in summer and winter, Muniz *et al.* (2004) reported that muddy sediments with high organic matter content dominated the study area and results obtained showed that sediments were highly polluted with Zn (312±102 μgg^{-1}) Pb (85±31 ugg^{-1}), Cu (89±25 ugg^{-1}), Cr (162±62 ugg^{-1}), and Hg (0.63±0.3 ugg^{-1}) and moderately with Ni (30±2 ugg^{-1}) and Ag (1.2±0.4 ugg^{-1}).

The concentrations of heavy metals in the fine fraction (<63 mm) of 19 surficial sediment samples from the border region of Baja California (Mexico) and California (USA) were determined. The concentration ranges (μgg^{-1}) of the metals obtained were: Cu - 4.9 – 23; Zn - 39 – 188; Ni - 16 – 44; Cr - 56 – 802; Pb - 6 – 21; Cd - 0.08 – 0.64; Ag - 0.01 – 0.28; and Mn - 392 – 1506; the intervals (percentage) for Fe and Al were 1.36 – 4.6 and 3.61 – 8.55, respectively (Villaescusa-Celaya *et al.*, 2000).

Cheung *et al.* (2003) reported that anthropogenic activities such as industrialization and urbanization lead to the accumulation of heavy metals in sediments and water of rivers in the Pearl River Delta region, South China. According to the authors, most sediment samples were heavily contaminated with Cd, Pb, and Zn in accordance with the classification by Hong Kong Environmental Protection Department. The authors asserted that although the concentrations of heavy metals in overlying water were low; their accumulations were significant with high levels of nickel (Ni) and zinc (Zn) in water found at certain locations, suggesting the occurrence of some local contamination.

Abdel-Satar *et al.* (2010) reported average concentrations of nutritive salts - nitrite, nitrate and ammonia in lake sediment of Lake Qarum, Egypt as: 0.89, 9.44 and 156.4 μgg^{-1} respectively and attributed it to contamination from accidental release of sewage into the lake from El-bats and El-Wadi drains. The authors noted that ammonia accounted for a major proportion of total soluble inorganic nitrogen, while the low nitrite level was attributable to the rapid conversion of nitrite to nitrate ions by nitrifying bacteria.

Mostafa *et al.* (2009) reported particle size distribution and organic matter of the surface sediments of Hadhramout coastal area, Gulf of Aden in Yemen, as their relative percentages as: 0.3 – 7.3% for silt, 0.3 – 2.4% for clay, 90.3 – 99.4% for sand and 0.1 – 0.4% for organic matter. The coastal sediments were dominated by sand fraction (>92%), while organic matter, clay and silt were generally very low.

Cheung *et al.* (2003) also investigated the effects of anthropogenic activities, industrialization and urbanization on the accumulation of heavy metals and nutrients in sediments and water of the Pearl River Delta region of South China and reported the ranges of total phosphorus and nitrogen concentrations in sediments as: 0.02 to 0.12% and 0.06 to 0.64%, respectively. The authors noted that the concentration of NO_3^--N in surface water was under the maximum contaminant level (10 mgL^{-1}) for portable water.

In an assessment of metals concentration in surface sediments from Lake Macquarie, New South Wales, Australia, using normalization models to estimate enrichment relative to natural background concentrations and by comparing concentrations with sediment quality guidelines (SQGs) and effects range median quotients (ERMQ) to assess the potential for ecological harm, Roach (2005) reported that industrial activity and catchment development were responsible to significant metal contamination in the lake. According to the author, of all metals examined (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn) only Cd, Pb, Hg, Se, Ag and Zn were enriched in surface sediments throughout the lake with the greatest contamination found in the north of the lake and, for selenium, also in areas adjacent to two power stations. The author added that SQGs possibly overestimated effects for arsenic, which has naturally high concentrations in the lake and underestimated the potential for ecological effects in coarser sediments.

2.6 SPECIATION OF METALS IN SEDIMENTS BY SEQUENTIAL EXTRACTION

The purpose of sequential extraction of metals from environmental samples is to provide relevant information on possible toxicity when they are discharged into the environment. Trace metals are often distributed among many components of sediments and are associated with them in different ways. The nature of this association is often referred to as speciation and it is the chemical species or form of these metals that determines the mobility and bioavailability of the sediment metals to other environmental matrices with a favourable physicochemical conditions. Chemical speciation, therefore, is the identification and quantification of the different species, forms, or phases present in a material. However, the determination of specific chemical forms is difficult and imprecise (Loska and Wiechula, 2002; Gao *et al*., 2008).

The determination of only total metals in sediments does not give an accurate estimate of the likely environmental impacts, since toxicity depends principally on chemical forms (Akcay *et al*., 2003). Fractionation procedures can indicate the propensity for metals to be remobilized and can help distinguish those metals having a lithogenic origin from those with an anthropogenic origin.

Soil and sediment components involved in sorption of trace elements are:

- Oxides (hydrous, amorphic), mainly of iron and manganese and, to a much lesser extent, aluminum and silicon
- Organic matter and biota
- Carbonates, phosphates, sulfides, and basic salts
- Clays

Of all these components, clay minerals, hydrated metal oxides, and organic matter are considered to be the most important group in contributing to and competing for the sorption of trace elements (Kabata-Pendias and Pendias, 2001). Metals of anthropogenic origin (the adsorptive and exchangeable) occur mainly in the early fractions whereas metals having a lithogenic source (the dentrital and primary mineral phases) are found in the residual fraction. The oxidizable fraction (Fe-Mn oxide and organic matter bound) have a scavenging effect and may provide a sink for metals. The release of metals from this matrix will most likely be affected by the redox potential and pH (Singh *et al*., 2005).

Sequential extraction was first designed for the selective removal of trace elements bound to operationally defined soil and sediment fractions (Tessier *et al*., 1979; Salomons and Forstner, 1980). The use of sequential extraction procedures to evaluate the risk in environmental contaminated soils and sediments has increased since some procedures provide comparative information on trace metal mobility with changing environmental conditions such as pH or redox potential. Therefore, this may help to evaluate sources (i.e. particulate/soluble sources) to the mobility (Pueyo *et al*., 2008).

Different protocols have been reported for the study of metal speciation. The theory behind any protocol is that the most mobile metals are removed in the first fraction, and this continues in order of decreasing mobility. Although many different protocols have been reported, the Tessier *et al.* (1979) and the European Union Binding Corporate Rules (BCR) schemes are the most widely adopted (Rao *et al.*, 2008). The principal difference between the two schemes is that the first two steps of the Tessier scheme (the exchangeable and carbonate bound fractions) were replaced by a single step (acid-soluble fraction) in the BCR scheme (Tessier *et al.*, 1979; Ure *et al.*, 1993; Rauret *et al.*, 1999). In addition, larger extractant volume, longer duration of extraction and more concentrated reductants are used in the revised BCR scheme. Furthermore, the optimized BCR procedure has significant advantage in checking the performance of methods and laboratories generally not obtainable for the other procedures, because it is currently the only scheme that is standardized and has certified reference samples available (Rao *et al.*, 2008).

Due to inconsistencies in trace metal extraction using the original BCR protocol (Sahuquillo *et al.*, 1999), the development of the 3-step optimized BCR procedure by Rauret *et al.* (1999) became necessary. The modified BCR procedure is a good option for the analysis of contaminated soils and sediments and results obtained has been used to predict the metal mobility in soils and sediments (Tokalioglu and Kartal, 2005; Tokalioglu *et al.*, 2006; Kartal and Tokalioglu, 2006; Pueyo *et al.*, 2008). The optimized BCR protocol has received wide application to a variety of environmental media including roadside soils and urban river sediments (Sutherland and Tack, 2007). All procedures facilitate fractionation. Tessier *et al.* (1979) named these fraction's exchangeable, carbonate bound, Fe and Mn oxide bound, organic matter bound, and residual.

According to Pueyo *et al.* (2008), sequential extractions are useful in identifying different sources of contamination, and in obtaining additional information on the solubility of secondary minerals formed by pyrite oxidation. Thus, the effectiveness of the BCR procedure has proved to be a useful tool for predicting short- and long-term mobility of trace elements, even in complex environmental matrices.

Table 2.1. Chemical reagents and analytical conditions for the Tessier, optimized and modified BCR sequential extraction procedure

Tessier *et al.* (1979) sequential extraction procedure		**The optimized BCR sequential extraction procedure** (Rauret *et al.* (1999)		**Modified BCR (This study) sequential extraction procedure**	
Operational definition	**Chemical reagents and conditions**	**Operational definition**	**Chemical reagents and conditions**	**Operational definition**	**Chemical reagents and conditions**
Step 1: Exchangeable	1 g is extracted at room temp. for 1 h with 8 ml of 1 M $MgCl_2$ (pH 7) with continuous agitation.	Step 1: Exchangeable (Acid-soluble)	To a 1-g aliquot add 40 ml of 0.11 M HOAc, shake for 16 h at 22±5 ^oC; extractable separate extract from the solid residue by centrifugation at 3000X*g* for 20 min	Step 1: Exchangeable (Acid-soluble)	To a 1-g aliquot add 20 mL 0.11 M CH_3COOH. Shaking at 22 ± 5 ^oC for 16 h , separate extract from the solid residue by centrifugation at 3000X*g* for 20 min
Step 2: Carbonate	To Step 1 residue add 8 ml of 1 M NaOAc adjusted to pH 5 with HOAc, shake for 5 h at room temperature				
Step 3: Reducible	To Step 2 residue add 20 ml of 0.04 M NH_2OH*HCl in 25% HOAc at 96 ^oC for 6 h	Step 2: Reducible	To Step 1 residue add 40 ml of 0.5 M NH_4OH.HCl from a 1- l solution containing 25 ml of 2 M HNO_3 (pH 1.5), shake for 16 h at 22±5 ^oC; centrifuge at 3000X*g* for 20 min	Step 2: Reducible	To Step 1 residue add 20 mL of 0.5 M NH_2OH-HCl (adjusted to pH = 1.5 with HNO_3) Shaking at 22 ± 5 ^oC for 16 h, centrifuge at 3000X*g* for 20 min.
Step 4: Oxidisable	To Step 3 residue add 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (pH 2) and heat to 85 8C for 2 h; add 3 ml of acidified H_2O_2, heat to 85 8C for 3 h; finish with 5 ml of 3.2 M NH_4OAc in 20% HNO_3 and agitate for 0.5 h	Step 3: Oxidisable (organic matter)	To Step 2 residue add 10 ml of H_2O_2 (pH 2–3), 1 h at room temperature; heat to 85±2 ^oC for 1 h; add a further 10 ml of H_2O_2 and heat to 85±2 ^oC for 1 h; add 50 ml of 1 M NH_4OAc (pH 2) and shake for 16 h at 22±5 ^oC; centrifuge at 3000X*g* for 20 min.	Step 3: Oxidisable (organic matter)	To Step 2 residue add 5 mL 8.8 M H_2O_2/another 5 ml 8.8 M H_2O_2. Add 25 mL 1.0 M CH_3COONH_4 (adjusted to pH = 2.0 with HNO_3). Digest at room temp. for 1 h with occasional shaking, heat at 85±2 ^oC for 1 h, then remove the cover and reduce the volume to a few millilitres, cover the tube and heat at 85 ± 2 ^oC for 1 h, and then remove the cover and reduce the volume to near dryness/shaking at 22 ± 5 ^oC for 16 h.
Step 5: Residual	To Step 4 residue add 2 ml of conc. $HClO_4$ and 10 ml of HF, heat to dryness; add 1 ml of $HClO_4$ and 10 ml of HF, heat to near dryness; finish with 1 ml of $HClO_4$, with the residue dissolved in 12 M HCl	Step 4: Residual	To Step 3 residue add 3 ml of distilled H_2O, 7.5 ml of 6 M HCl and 2.5 ml of 14 M HNO_3; leave overnight at 20 ^oC, boil under reflux for 2 h, cool and filter.	Step 4: Residual	To Step 3 residue add 10 ml HNO_3 and $HClO_4$ (HNO_3-$HClO_4$, 4:1 v/v). Hot plate wet digestion

Senol and Tokalioglu (2006) reported the concentration of metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in street sediment samples determined by FAAS using the modified BCR sequential extraction procedure. The authors reported the mobility sequence based on the sum of the BCR sequential extraction stages as: Cd ≈ Zn (90%) > Pb (84%) > Cu (75%) > Mn (70%) > Co (57%) > Ni (43%) > Cr (40%) > Fe (17%). From the results of enrichment factor analysis, the criteria for examining the impact of the anthropogenic emission sources of heavy metals, it was observed that Cd, Pb, and Zn in the dust samples were the highest enriched metals averaging 190, 111, and 20, respectively. The authors, according to result of principal component analysis (PCA), also added that the sampling area was mainly influenced by three pollution sources, namely; traffic, industrial, and natural sources.

Maximum recoveries for heavy metals were observed for all three steps of BCR protocol at 32 h total shaking period by Arain *et al*. (2008). The authors observed that levels of water extractable heavy metals were low compared to those values obtained by acid-soluble fraction of the BCR protocol.

In another related development, Arain *et al*. (2009) applied three extraction methods, ultrasonic assisted extraction (USE), microwave assisted extraction (MSE), and conventional single extraction (CSE), in conjunction with the modified three-stage BCR sequential extraction procedure (SEP) to examine the levels of Cd, Cu, Cr, Ni, Pb and Zn from lake sediment samples, in order to know whether these techniques could reduce extraction time and improve reproducibility. The modified three-stage BCR and the developed alternative single extraction methods were validated by the analysis of certified reference material BCR 601. The authors reported that the recoveries of total extractable metal contents in BCR 601, obtained by three single extractions ranged from 93.3–102%, 88.9–104% and 81.2–96.2% for CSE, USE and MSE, respectively. The precision of a single extraction methods was found in the range of 3.7–9.4% for all metals ($n = 6$).

According to Sutherland and Tack (2003), the standardized sequential extraction procedure (optimized BCR) was applied to two contaminated certified reference soils from Montana, US (SRM 2710 and SRM 2711) for Cu, Pb and Zn. Four operationally defined fractions were isolated, acid extractable, reducible, oxidizable, and residual (by aqua regia). The authors employed the fraction-specific concentrations, percentages and recoveries for Cu, Pb and Zn to explore differences between the optimized BCR procedure and three other sequential extraction schemes with published data for SRM 2710 and 2711 (i.e. Tessier scheme, Geological Survey of Canada scheme and the original BCR scheme). Results obtained showed significant differences between the four schemes, even for schemes that are closely associated (i.e. the original and optimized BCR schemes).

2.7 METAL SPECIATION OF WATER USING GEOCHEMICAL MODEL

Kersten and Forstner (1995) refers to speciation as those aspects of metal chemistry including precipitation-dissolution, adsorption-desorption, and complex formation in relation to pH; redox conditions; and the content of soluble chelating agents. Bodek *et al*. (1988) identified a group of properties or processes that are important for the environmental behaviour of metals, including volatilization, photolysis, sorption, atmospheric deposition, acid/base equilibria, polymerization, complexation, electron-transfer reaction, solubility and precipitation equilibria, microbial transformation, and diffusivity. According to Templeton *et al*. (2000), the recommended IUPAC definition of speciation might be more useful. In that definition, “speciation” refers to the distribution of an element among defined chemical species, which are the specific forms of an element defined as to the isotopic composition, electronic or oxidation state, and/or complex or molecular structure. The oxidation state of the metal is often a significant feature of its speciation due to its impact on other processes. A well-known example is the high mobility of Cr (VI) compared to Cr (III) which demonstrates the significance of oxidation state.

According to Miller (2001), speciation has a direct influence on the environmental availability of chemicals, their behaviour over time, and attenuation under transport conditions. Speciation provides a better quantification of toxicity than use of total metal determinations. It controls the interaction of trace metals with aquatic organisms, the movement of metals in saturated and unsaturated subsurface environments, and the precipitation or dissolution of trace metals in response to different remediation techniques. The primary purpose of speciation modelling is to calculate mineral saturation indices, which are indicators of saturation state of a mineral with respect to a given water composition. The saturation index (**SI**) of a selected mineral phase is the degree of saturation and can be a means of evaluating water quality data to determine if certain minerals have a tendency to dissolve or precipitate out of solution, in order to reach equilibrium (Croxford *et al*., 2004).

Most chemical analytical laboratories generally determine and report total metal concentrations. However, in recent years it has become increasingly apparent that metal toxicity is a function of the concentrations of specific metal species, not of the total metal (Stumm and Morgan, 1996; Langmuir, 1997). In fact, toxicity was often found to be best predicted by the free metal ion activity (Morel and Herring, 1993). In natural waters, its concentration, or those of other metal species, can sometimes be measured directly, although often with difficulty.

Alternatively, given the appropriate solution analysis and thermodynamic database, the concentrations of individual species can be computed using a geochemical equilibrium modelling program such as MINTEQA2 (U.S. EPA, 1991) or PHREEQC (Parkhurst and Appelo, 1999). Errors in the thermodynamic database of the earlier versions of MINTEQA2 (Serkiz et al., 1996) have been corrected in version 4.0 (1999). PHREEQC is a geochemical modelling program designed by the United States Geological Survey (USGS) developed by Parkhurst and Appelo (1999), to perform a wide variety of low temperature aqueous geochemical calculations. PHREEQC is based on an ion-association aqueous model and has capabilities for the following:

(i) speciation and saturation-index calculations;

(ii) batch-reaction and one-dimensional (1D) transport calculations involving reversible reactions, which include aqueous, mineral, gas, solid-solution, surface-complexation, and ion-exchange equilibria, and irreversible reactions, which include specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and temperature changes; and

(iii) inverse modelling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters, within specified compositional uncertainty limits.

In PHREEQCI, input is arranged in keyword data blocks, which can appear in any order. Data fields for a keyword are read in a free format; thus they are not column dependent. For speciation modelling, analytical data for a solution composition (SOLUTION keyword) are needed. Geochemical modelling is often used to understand and predict leaching of toxic contaminants in soils and sediments but more recently, it has also been successfully applied to highly alkaline ($pH > 11$) waste products from industrial processes to understand and control the leaching behaviour of heavy metals (Cornelisa *et al*., 2008).

2.7.1 Theory and Applications of PHREEQCI Model

Geochemical modelling enables the quantitative speciation of elements based on species stability constants. PHREEQCI is a geochemical modelling package capable of describing chemical reactions and transport processes in water. It is based on the equilibrium chemistry of aqueous solutions with other components, such as minerals, gases, solid solutions, and sorbing surfaces. A solid solution forms when compounds containing similar properties, such as size and charge, precipitate to form a homogeneous solid compound (Halim *et al*., 2005).

The PHREEQCI model uses solution ion concentration data to determine saturation indices for the soluble solution ions. The PHREEQCI code simulates chemical reactions and transport processes in water using the observed field data. The model has an inverse modelling capability, which attempts to find sets of mineral and gas mole transfers that account for differences in composition between waters while accounting for specified uncertainties (Parkhurst and Appelo, 1999). Therefore, PHREEQCI is able to determine the potential for any precipitation of secondary mineral and amorphous phases from within the original solution chemistry under any specified environmental conditions. In order to do this, the model has to balance the chemistry between the secondary, aqueous and gaseous phases taking place by using a series of geochemical reactions (Croxford *et al*., 2004).

Ion-association and specific- interaction are the two current approaches to calculate the above mentioned properties. In dilute aqueous solutions, the activity of solute species (a_i) is defined as:

$$a_i = (m_i.\gamma_i)$$

where m_i is the concentration of species i in molal units;

y_i is the activity coefficients.

An alternative means of calculating ion activity coefficients in dilute solutions is provided by the Debye-Huckel theory, which attempts to calculate the effect of electrostatic interactions among ions on their free energies of formation. To evaluate the cumulative effect of attractive and repulsive forces, a charge-weighted function of species concentration known as ionic strength (*I*) is defined as:

$$I = 0.5\sum m_i z_i^2$$

where z_i is the charge on the ion of species *i*.

Therefore, for dilute solutions ($I \leq 10^{-3}$), the activity coefficients (γ) from the *Debye-Huckel equation* is given as:

$$\log_{10} \gamma_i = -Az_i^2\sqrt{I}$$

where A is a constant.

At higher ionic strengths, for example sea water ($10^{-3} < I \leq 0.1$), the Debye-Huckel equation is inadequate because the major ion content is constant and therefore can be modified to take into account the finite size of the hydrated ions of interest, giving the *extended Debye-Huckel equation* (Truesdale-Jones) given as:

$$\log_{10} \gamma_i = -\frac{A z_i^2 (I)^{0.5}}{[1 + B\alpha (I)^{0.5}]} \quad or \quad -\frac{A z_i^2 \sqrt{I}}{[1 + B\alpha \sqrt{I}]}$$

where α is the size parameter for ionic species and *A* and *B* are empirical parameters. *A* and *B* are functions of only pressure and temperature (Satapathy and Panigrahi, 2005). The values of A, B, and α for various ions are listed in Table 2.2 below. Note that the product Bα has a numerical value of about 1. Furthermore, α values for many ions have not been measured experimentally.

These geochemical programmes can be used for mass balance modelling, equilibrium speciation and saturation modelling and equilibrium mass transfer modelling. The development of conceptual geochemical models is enhanced by saturation index calculations that can identify the equilibrium state of minerals. Speciation modelling provides saturation indices that indicate which reaction is thermodynamically possible, which minerals may be dissolving and which may be precipitating in an aquifer system. Speciation models calculate the thermodynamic properties of aqueous solutions, including the molalities and activities of aqueous species and saturation indices of minerals. Molality is used in thermodynamic calculations where a temperature independent unit of concentration is needed.

Table 2.2. Values of constants for use in the Debye-Hückel equation at 1 atmosphere pressure

T (°C)	A	B (×10^8)	Ion	α (×10^{-8})
0	0.4883	0.3241	Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2+}, HCO_3^-, CO_3^{2+}, NH_4^+, Sr^{2+}, Ba^{2+}, Fe^{2+}, Mn^{2+}, Li^+, H^+, Al^{3+}, Fe^{3+}.	5.0
5	0.4921	0.3249		5.5
10	0.4960	0.3258		4.0
15	0.5000	0.3262		3.5
20	0.5042	0.3273		5.0
25	0.5085	0.3281		5.4
30	0.5130	0.3290		2.5
40	0.5221	0.3305		5.0
50	0.5319	0.3321		6.0
60	0.5425	0.3338		9.0

Source: Garrels and Christ (1965)

2.7.2 Distribution of Aqueous Species

Dissolved species in water can be described as free ions or aquo-complexes, or simply complexes. A complex is a dissolved species that exists because of the association of a cation with an anion or neutral molecule (Langmuir, 1997). A ligand is an anion or neutral molecule that can combine with a cation to form a complex. The total analytical concentration of a given metal in water is the sum of the concentrations of its free ion and complexes and any metal associated with suspended solids, whether organic or mineral. For example, the total molal concentration of lead, ∑Pb, in natural water might equal:

$$\sum Pb = mPb^{2+} + mPbOH^{+} + mPbCO_3^{o} + mPbHCO_3^{+} + mPbSO_4^{o} + mPb \text{ (suspended solids)}$$

In most natural waters the concentration of free lead ion, mPb^{2+}, is less than the sum of the concentrations of its complexes, which in this case are lead complexes with hydroxyl, carbonate, bicarbonate, and sulphate ions. Speciation modelling uses ion concentration of water to calculate the distribution of aqueous species by using an ion-association aqueous model (Debye-Huckel equation). It requires only a SOLUTION (or SOLUTION_SPREAD) keyword data block for each water analysis for which saturation indices are to be calculated. Input is arranged in keyword data blocks. The different species or forms of the metals present are adequately distributed with their corresponding concentrations (molalities), activities, log molalities, log activities and log activity coefficients.

According to Tepavitcharova *et al*. (2010), the chemical behaviour of the metals and their species in water systems depends on the anion concentrations (e.g. OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-) and on the metal ability to coordinate predominantly with some of the anions. Therefore, the accuracy of the calculations depends on the availability and accuracy of analytical data as well as on an appropriate thermodynamic database.

2.7.3 The Saturation Index Calculations

The Saturation Index (SI) of a selected mineral phase is the degree of saturation. According to Croxford *et al*. (2004), saturation index can be a means of evaluating water quality data to determine if certain minerals have a tendency to dissolve or precipitate out of solution, in order to reach equilibrium. Thermodynamically, the potential for dissolution or precipitation of solid can be expressed as the computed saturation index (SI):

$$\mathrm{SI} = \log_{10}\left(\frac{\mathrm{IAP}}{\mathrm{K_{SP}}}\right)$$

where, IAP is the empirical ion-activity product for a given mineral in the water of interest and K_{sp} is the equilibrium solubility product constant for the same mineral at the temperature and pressure of the water. The SI of the different mineral phases (e.g. $PbSO_4$) could be calculated and the feasibility of precipitation of the mineral could be evaluated under the modelling solution conditions from the equation:

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{SP}}}\right) = \log\left[\left(C_{Pb^{2+}}\ f_1\right)\left(C_{SO_4^{2-}}\ f_2\right)\right] - \log K_{SP}$$

where $C_{Pb^{2+}}$, $C_{SO_4^{2-}}$ are the concentrations of Pb^{2+}, SO_4^{2-} and f_1, f_2 are the ionic activity coefficient (read from the simulation results). The equation demonstrated that the SI of $PbSO_4$ was correlated with the concentrations of Pb^{2+}, SO_4^{2-} and the coefficient of ionic activity.

The saturation index is typically either negative or positive and rarely 0. If SI > 0, then the solution is super-saturated with respect to the mineral phase, and precipitation will be likely, and this suggests that water may be scale forming. The scale, typically a carbonate residue, could clog or reduce the flow in pipes, cause build-up on hot water heaters, impart an alkali taste to the water, reduce the efficiency of the water heaters, and cause other aesthetic problems. When SI < 0, then the solution is below saturation (undersaturated) of the specified mineral phase, and dissolution of the solid phases will be expected and the water may be more likely to have a greater corrosive potential. If SI = 0, then the solution is in equilibrium with the specified mineral phase, i.e. there is no thermodynamic tendency for net dissolution or net precipitation of the mineral. Thus, saturation index indicates what should happen thermodynamically, however; it does not indicate the rate at which the process will proceed. Concentrations of inorganic elements, pH, alkalinity, temperature of aqueous solutions obtained from this database were used as inputs for geochemical modelling using PHREEQC (Parkhurst and Appelo 1999).

In routine water analysis, the major constituents reported are Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, HCO_3^{-}, SO_4^{2+}, Cl^{-}, NO_3^{-} and dissolved SiO_2, and the minor constituents include Fe^{2+}/Fe^{3+}, Cu^{2+}, F^{-}, etc. In most surface and ground waters, the major ions meet the drinking water standards. In fact, most of the surface and groundwater contamination are caused by constituents in trace amounts (e.g. heavy metals and organic compounds), not the major ions (Miller, 2001). Nevertheless, routine water analyses are necessary to ensure the suitability of the water for human use. A broad spectrum of chemical reactions controls the composition of water in contact with soils, sediments, and rocks. Elements and compounds are leached from the rocks while changing conditions can cause the precipitation of new solids.

Speciation study of metals provides adequate information on the bioavailability and potential toxicity of the metals to the biota under various environmental conditions. In a study of aqueous metal speciation using AQUACHEM software interfaced with PHREEQC geochemical model, Korfali and Jurdi (2011) reported that a high percentage of Pb, Zn and Ni were present as carbonate complex species while the free hydrated ions were low percentages, whereas Cd recorded highest percentage as free hydrated ion followed by carbonate complex species. The authors concluded that the sensitivity attempt of free hydrated ion of Ni, Zn, Pb, and Cd in reservoir water revealed dependence of Zn and Cd on pH and alkalinity, while Ni and Pb were only dependent on pH. The toxicity of any metal is dependent on its speciation which in turn is strongly dependent on pH and solution composition.

During metal transport, trace metals undergo numerous changes in their speciation due to dissolution, precipitation, sorption and complexation phenomena. According to Akcay *et al.* (2003), trace element concentration of river basins does not only depend on anthropogenic inputs - industrial and domestic wastes, but also on the geochemical composition of the area. Thus, the natural and anthropogenic introduction of contaminants into the soil, surface and groundwater would lead to the hydro chemical facies where the underground water quality changes in response to its flow path history which is dependent on pollution status of the overall environment (Awofolu *et al.*, 2007; Olabaniyi and Owoyemi, 2006). The surface water chemistry exchanges matter with the various mineral phases and dissolved gases resulting in a dissolution or precipitation of minerals. Equilibrium is most commonly used to assess whether the surface water is in equilibrium with respect to one or more minerals (Subyani, 2005).

In a related study of surface and ground water of an abandoned mine tailings in Adak, Vasterbotten District - Northern Sweden, using PHREEQC calculations, Bhattacharya *et al*. (2006) reported that almost all the water samples were undersaturated with respect to the investigated minerals due to low pH (3 – 4). Under low pH conditions, water remains undersaturated (as the PHREEQC results indicate), thereby facilitating precipitation of trace elements.

The pollution level of surface natural waters as well as wastewaters in the region of a lead-zinc company in Kardjali city, Bulgaria, were also investigated by Tepavitcharova *et al*. (2010) using PHREEQCI thermodynamic modelling. In natural waters, the authors reported that the studied trace metals especially the hard 'acids' (i.e. Fe^{3+} and Al^{3+}) existed mostly as hydroxy species – $Fe(OH)_2^+$, $AlOH^{2+}$, and $Al(OH)_2^+$, followed by the phosphate species $AlPO_4$ and $Al_2(OH)_2PO_4^+$; while the soft 'acids' (Mn^{2+}, Zn^{2+} and Cd^{2+}) existed mainly as free uncomplexed metal ions (Me^{2+}) with small concentrations of $MeSO_4$, $MeCO_3$ and $MeCl_2$ (Me = Zn, Cd) species; and the Cu^{2+} and Pb^{2+} (another soft 'acids') coordinated with softer CO_3^{2-} ions in water and existed mainly as $MeCO_3$ and $PbHCO_3^+$ followed by free Me^{2+} ions and $MeOH^+$.

According to Tepavitcharova *et al*. (2011), a combined approach consisting of monitoring and thermodynamic modelling was used to calculate the concentration of trace element species in water samples of a broad salinity range (fresh, marine and hyper-saline water) and to explain their chemical behaviour. The authors reported that the predominant species in fresh waters were the free ions of Mn^{2+} (73.6%), Zn^{2+} (58.0%) and Cd^{2+} ions (78.3%) as well as carbonate species $CuCO_3$ (81.8%), $PbCO_3$ (77.2%) and hydroxy species $Fe(OH)_3$ (55.2%) and $Fe(OH)_2^+$ (35.6%); also, an increase in chloride species $MeCl_n^{2-n}$ (n = 1 – 4, Me = Mn, Zn, Cu, Pb and Cd) and of the hydroxy species $Fe(OH)_2^+$ for Fe was calculated for sea and hyper-saline water.

In a related study of thermodynamic modelling of the PHREEQC program for phosphorus removal and recovery by $FePO_4{\cdot}2H_2O$ precipitation, Zhang *et al*. (2010) reported some factors of $FePO_4{\cdot}2H_2O$ precipitation including pH, Fe^{3+}:$PO4^{3-}$ molar ratio (Fe/P), initial PO_4^{3-} concentration, alkalinity, ionic strength, and temperature. According to the authors, increasing the pH from 1.0 to 5.5 leads to a significant increase in SI, and the maximum SI range for $FePO_4 \cdot 2H_2O$ precipitation was observed at the pH of 5.0 – 6.0.

In another related study to determine the water quality in Yola area using PHREEQC speciation model, Obiefuna and Orazulike (2010) reported activities and concentration of some ionic species in surface water of Yola as: Na - 2.2 – 211.0 (73±89,0) mgL^{-1}; K - 1.2 – 9.0 (5.0±2.4) mgL^{-1}; Mg - 12.0 – 84.0 (35.0±19.1) mgL^{-1}; Ca - 8.0 – 37.0 (26.0±9.3) mgL^{-1}; Fe - 0.0 – 0.73 (0.30±0.26) mgL^{-1}; and major anions such as NO_3^- - 9 – 59 (35±19) mgL^{-1}; Cl^- - 28 – 455 (146±138) mgL^{-1}; HCO_3^- - 49 – 273 (137±63) mgL^{-1}; SO_4^{2-} - 2 – 29 (18±8) mgL^{-1}. According to the authors, Fe may occur in solution both as Fe^{+2} or Fe^{+3} oxidation state. The redox conditions in oxygenated waters favour the most oxidized form (Fe^{3+}). Ferrous ions (Fe^{2+}) form complexes with a number of ligands, a strong $FeHCO_3$ and $FeCO_3$ appears likely to be the major form in natural water containing dissolved CO_2. Chemical speciation of Fe in surface water samples indicated that 1.912×10^{-7} m (22.58%) of Fe is in the free ionic form (Fe^{2+}), 5.723×10^{-8} m as $FeHPO_4$, and 4.179×10^{-8} m as $FeHCO_3^+$ (bicarbonates) and 1.704×10^{-8} m as $FeCO_3$, while 4.088×10^{-6} m as $Fe(OH)_3$, 7.852×10^{-7} m as $Fe(OH)_2^+$ and 1.854×10^{-7} m as $Fe(OH)_4$.

CHAPTER THREE

MATERIALS AND METHODS

3.1 DESIGN OF STUDY

The study design included the following components:

(a) Selection of rivers for the study

Two major rivers, Cross River and Qua Iboe River, were selected for the study. In each of these two rivers, six sampling stations located within different riverine communities and cities along the rivers where sites have been adequately impacted owing to different anthopogeinc activities were selected. These stations included:

(i) Cross River

- Okopedi Itu,
- Ayadehe,
- Nwaniba,
- Oron,
- James Town, and
- Ibaka.

(ii) Qua Iboe River

- Iwuokpom 1,
- Iwuokpom 2,
- Iwuoachang,
- Eketai,
- Atabong,and
- Marina.

(b) Study of surface water quality parameters

Location of sampling points: Surface water samples were collected at the selected locations chosen for the study.

Frequency and duration of sampling: Surface water samples were collected monthly at each sampling point for the period of 12 months between June 2009 and May 2010.

Number of samples collected: At each sampling point, one composite sample was collected monthly.

Parameters determined in surface water:

i. Physicochemical parameters included:

   Temperature, pH, alkalinity, turbidity, total dissolved solids (TDS), electrical conductivity (EC), total hardness, dissolved oxygen (DO), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5), chloride (Cl^-), fluoride (F^-), ammonia (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}).

ii. Heavy metals determined were Cd, Pb, Cr, Cu, Ni, Zn, and Co.

(c) Study of bottom sediments

Location of sampling points: Bottom sediment samples were collected from the various locations chosen for the surface water study

Frequency and duration of sampling: Sediment samples were collected bi-monthly at each sampling point for the period of 12 months, between June 2009 and May 2010.

Number of samples collected: At each sampling point, one composite sample of bottom sediments was collected.

Parameters determined in bottom sediments:

i. Physicochemical parameters included:

   Temperature, pH, electrical conductivity (EC), nitrate (NO_3^-), nitrite (NO_2^-), phosphate (PO_4^{3-}), sulphate (SO_4^{2-}), total organic carbon (TOC), total organic matter (TOM), particle size analysis – sand, silt and clay.

ii. Heavy metals determined were Cd, Pb, Cr, Cu, Ni, Zn, and Co.

(d) Modelling for chemical speciation using PHREEQCI

Concentrations of some physicochemical parameters and total metals in surface water determined were fitted into the water-speciation model, PHREEQCI to calculate the concentrations of the different metal complexes and species present in the water, and the saturation states of various minerals in the river.

3.2. DESCRIPTION OF THE STUDY AREA

The study area, Akwa Ibom State, is one of the South-South states of Nigeria, located in the eastern Niger Delta region of Nigeria. The entire coastal South-South Niger Delta is sub-divided into the Western Niger Delta (consisting of Delta and Edo States), Central Niger Delta (consisting of Bayelsa and Rivers States) and the Eastern Niger Delta (consisting of the Atlantic section of Akwa Ibom and Cross River States).

Geographically, Akwa Ibom State, lies between latitudes 4° 32′ and 5° 33′ North and longitudes 7°25′ and 8°25′ East, and is bordered by Abia State on the North, Cross River State on the East, Rivers State and Abia State on the West, and on the South by the Atlantic Ocean. The entire Niger Delta region falls within the tropical rain forest zone with an ecosystem which is diverse and supportive of numerous species of terrestrial and aquatic flora and fauna and human life. There are three major river systems (i.e. Cross, Qua Iboe and Imo Rivers) with many lakes, estuaries and tributaries found within the State, located in the estuary of the Gulf of Guinea (the Atlantic Coast). This research was limited to two major rivers - Cross and Qua Iboe.

(a) Cross River

The Cross River flows from the neighbouring Cameroon Republic through Ikom and Obubra (in Cross River State); Afikpo (in Abia State); Okopedi Itu, Oron to Ibaka-Mbo (Akwa Ibom State) into the Atlantic Ocean, covering about 352 km (Figure 3.1). The river is a major source of water for the highly populated and predominantly rural population of the area.

Geographically, the six sampling stations selected are located within the lower course and major communities along the bank of the river, lying between latitudes 4°30′ and 5°15′ North and 8°00′ and 8°15′ East as shown in Figure 3.1. The stations include Okopedi Itu, Ayadehe, Nwaniba, Oron, James Town and Ibaka; covering a distance of about 95 kilometres (from Okopedi to Ibaka) (Table 3.1).

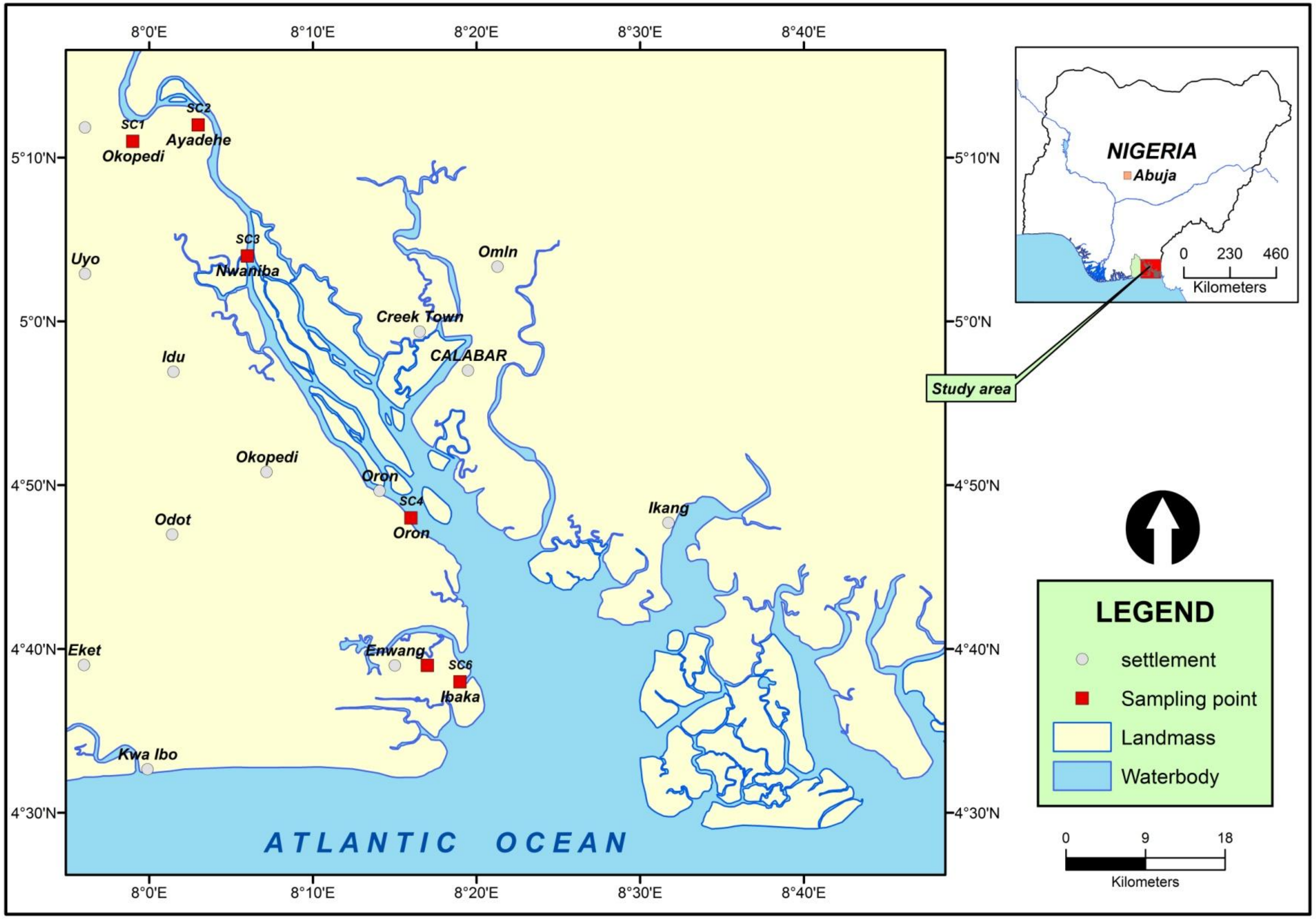

Fig. 3.1. Map of study area showing sampling stations along Cross River

Table 3.1. Sampling stations and human activities near the sampling locations from Cross River system

Sampling Station	Station Code	Latitude	Longitude	Description/anthropogenic activities at stations
1. Okopedi	SC-1	5º 11′ N	7º 59′ E	Markets, agricultural farmlands, garbage dumping, boatyard, faecal pollution.
2. Ayadehe	SC-2	5º 12′ N	8º 03′ E	Agricultural farmland, beach markets, discharges (used engine oil) from heavy duty truck maintenance yards, small scale dredging.
3. Nwaniba	SC-3	5º 04′ N	8º 06′ E	Sawmill industry, wood materials soaked in the estuary, saw dust dumped around the beach, agricultural farmlands, used engine oil/exhaust emissions from machines (dredging and sawmill).
4. Oron	SC-4	4º 48′ N	8º 15′ E	Semi-harbour activities, tourism, recreation, urban discharges through drains, fishing, markets, sea transport, etc.
5. James Town	SC-5	4º 39′ N	8º 17′ E	Fishing, dredging, beach market, fish smoking.
6. Ibaka	SC-6	4º 38′ N	8º 19′ E	Mini-port, tourism, recreation, institutional, discharge of untreated effluents from petrol/diesel stations, open defecation.

(b) Qua Iboe River

The Qua Iboe River is a confluence of rivers from different sources rising from Umuahia in Abia State, and flowing through Eket and Ibeno communities of Akwa Ibom State into the Gulf of Guinea (Atlantic Ocean) (Figures 3.2). The river receives inputs of municipal wastes, municipal/urban runoff, untreated industrial discharges from food processing industries, as well as other solid wastes (garbages, metal scraps, etc.) mainly at Atabong, Marina and Iwuochang stations of the river. The river system serves as a major source of water for the predominantly rural population of the area whose major occupation is commercial fish farming, noting that fish growth depends largely on the quality of the culture medium and other agricultural practices. The Eket/Ibeno community plays host to the multinational oil giant, Exxon-Mobil. The study area lies between latitudes 4°30′ and 4°40′ N and 7°45′ and 8°15′ E. Six (6) stations were selected for the study. These included: Iwuokpom 1, and Iwuokpom 2, Iwuoachang, Eketai, Atabong and Marina (Figure 3.2 and Table 3.2).

3.3 SAMPLING AND SAMPLE PRE-TREATMENT

3.3.1 Collection of Surface Water Samples

(a) Sampling for physicochemical analysis

Surface water samples were collected from the middle axis and the bank of the river in polyethylene bottles from each station for physicochemical analyses. The sampling containers were previously washed with detergent, deionised water, 10 % (v/v) HNO_3, and with deionised water again. The containers were pre-rinsed with the surface water to be collected before samples were taken. The samples were collected just below the surface of water with the bottle pointing downward, filled gradually and then capped under water when full. Fast changing parameters (such as temperature, pH, total dissolved solids and electrical conductivity) were measured *in-situ* using portable pH/EC/TDS/Temperature Meter (HANNA HI 991301 model) while dissolved oxygen, was measured using DO-meter (YSI 550A Model).

For the other parameters such as alkalinity, BOD, COD, chloride, fluoride, nitrate, nitrite, sulphate and phosphorus, samples were preserved in an ice chest without adding any reagent and taken to the laboratory. In the laboratory, samples were stored in a refrigerator maintained at below 4 ^{o}C for between 6 hours to 7 days prior to analysis. All samples were collected in polyethylene containers (for phosphates glass was used).

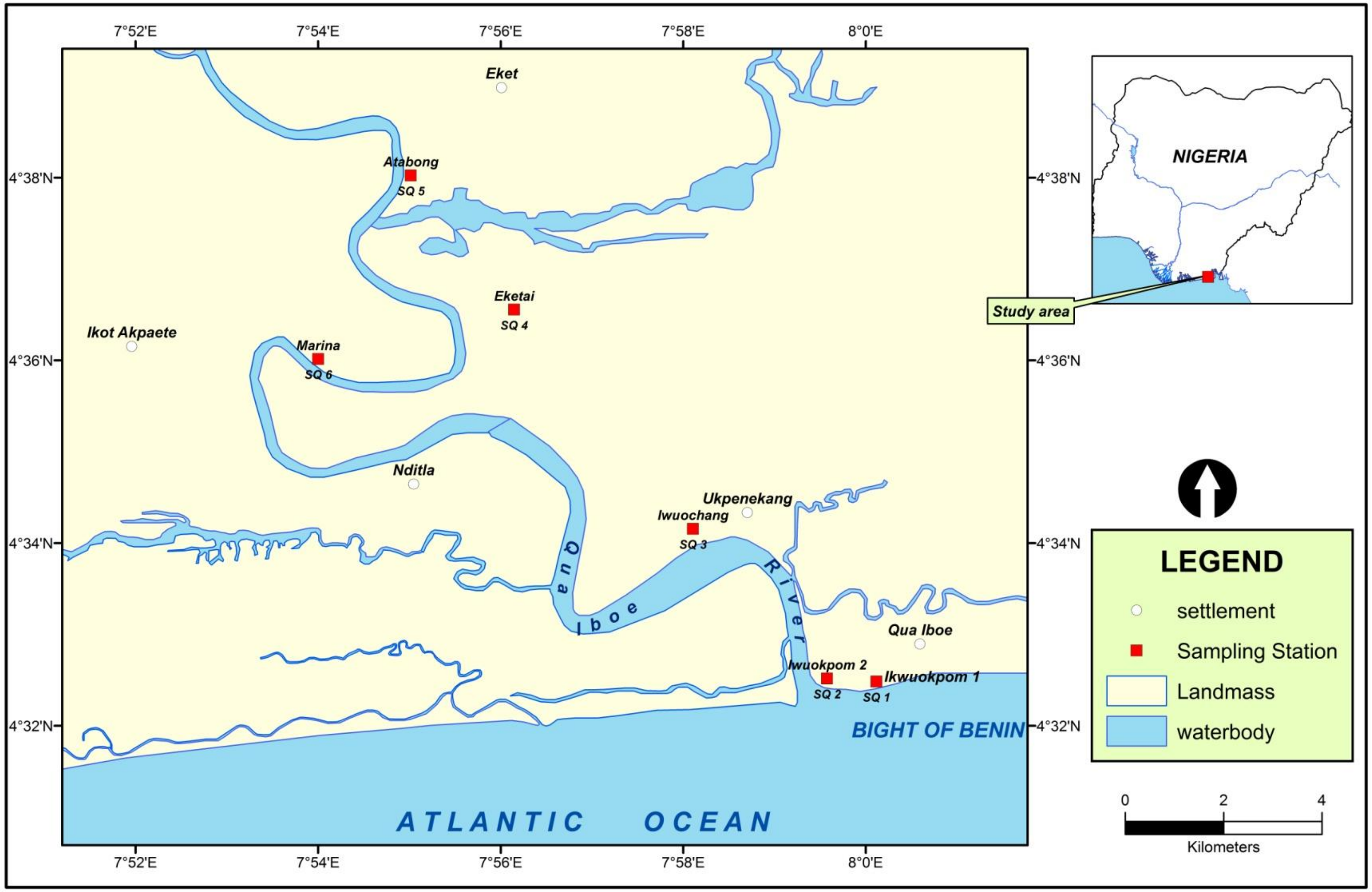

Fig. 3.2. Map of study area showing sampling stations along Qua Iboe River

Table 3.2. Sampling stations and human activities near the sampling stations for Qua Iboe River

Sampling Station	Station Code	Latitude	Longitude	Description/anthropogenic activities at sites
1. Iwuokpom 1	SQ-1	4.54 N	8.00 E	Fishing, wood industry and market wastes.
2. Iwuokpom 2	SQ-2	4.54 N	7.99 E	Fishing, market wastes, boat park, fuel and lubricating oil leakages from boat-engines.
3. Iwuochang	SQ-3	4.57 N	7.97 E	Fishing, market/domestic wastes disposal, boatyard, open defecation.
4. Eketai	SQ-4	4.61 N	7.94 E	Agricultural farmlands, laundry and commercial car wash activities.
5. Atabong	SQ-5	4.63 N	7.92 E	Urban/drainage discharge, abattoir, effluents from fuel stations, auto-mechanic workshop, car-wash activities.
6. Marina	SQ-6	4.60 N	7.90 E	Urban/drainage discharge.

(b) Sampling of surface water for trace metal analysis

Water samples for trace metal analysis were collected into separate 1000 mL polyethylene bottles and acidified *in-situ* with 2.0 mL of conc. HNO_3 (to bring the pH of the sample to 2.0 or less). These were then placed in an ice-chest and taken to the laboratory for analysis. Samples were filtered through Whatman No. 1 filter paper and stored in polyethylene bottles and kept at $<4^oC$ until analysis. All samples were collected as composite samples which served as the true representative of the samples.

3.3.2 Sampling of Bottom Sediment

Bottom sediment samples, at depth of 0 – 5.0 cm, were collected bimonthly during the one-year study period (June 2009 – May 2010) from the twelve (12) sampling stations of Cross River and Qua Iboe River systems. Samples were collected as composites, using a stainless steel hand trowel from each point where water sample was taken. Samples were stored in pre-labelled polythene bags to indicate the code, date and time of collection, kept in an ice-chest and taken to the laboratory. In the laboratory, the samples were air-dried for four days at ambient temperature, coarse materials – small stones, wood, and other large materials were removed by hand picking, and the samples then pulverized using an agate mortar and pestle. The homogenized sediment samples were passed through a 2.0 mm nylon sieve (samples for electrical conductivity were passed through a 0.5 mm sieve) and then stored in clean labelled paper bags until analysis.

3.4 ANALYSIS OF WATER SAMPLES

Water samples were analysed by standard procedures of the American Public Health Association (APHA-AWWA-WEF, 2005).

3.4.1 Determination of Physicochemical Parameters

3.4.1.1 Determination of temperature

Temperature was determined *in-situ* by using a digital temperature meter (HANNA, HI 991301 Model). The instrument calibration was done by inserting the glass electrodes of the instrument into ice-water (ice-blocks) and later into steam to ascertain its accuracy. The thermometer bulb was inserted into a 50 mL capacity beaker containing a portion of the surface water sample, and the temperature was read after about 2 minutes equilibration time.

3.4.1.2 Determination of pH (Electrometric Method)

The pH of the water samples was determined using a digital portable pH meter (HANNA, HI 991301 Model) with a glass electrode.

Instrument calibration: The digital pH meter was initially calibrated using standard buffers 4.0 (potassium hydrogen phthalate) and 7.0 (mixture of potassium di-hydrogen phosphate and disodium hydrogen phosphate).

Procedure: About 40 mL portion of the sample was taken into a 50 mL capacity glass beaker and the pH glass electrode (probe) was inserted into the beaker and the reading was taken at a steady digital display and recorded accordingly. The glass electrode of the pH meter was thoroughly rinsed with deionised water after each determination to prevent cross-contamination.

3.4.1. 3 Determination of total alkalinity (Titration Method)

Principle:

The total alkalinity is usually determined by titration of the sample with standard hydrochloric acid to the end-point of a bromocresol green indicator.

Reagents for alkalinity determination:

Sodium carbonate, 0.025M: 5.0g of primary standard sodium carbonate, Na_2CO_3, was weighed and dried at 250 ^oC for 4h and cooled in a dessicator. 2.5g of the dried Na_2CO_3 was accurately weighed and transferred into a 1000 mL volumetric flask. This was followed by the addition of 500 mL deionised water to dissolve it and the solution was made up to 1000 mL with the deionised water.

Standard hydrochloric acid, 0.100M: 8.4 mL of concentrated HCl was accurately measured out and diluted with deionised water to 1L in a volumetric flask. This was standardized against 0.025M Na_2CO_3 solution, using bromocresol green indicator.

Standard hydrochloric acid, 0.020M: 200 mL of 0.100M standard HCl was measured out and diluted to 1000 mL with deionised water. This was standardized by titrating it against 15 mL 0.025M, Na_2CO_3 using bromocresol green indicator.

Bromocresol green indicator solution, pH 4.5: 100 mg bromocresol green sodium salt was dissolved in 100 mL deionised water.

Sodium thiosulphate solution, 0.050M: This was prepared by dissolving 25g of $Na_2S_2O_3.5H_2O$ in CO_2-free deionised water and diluting to 1000 mL in a volumetric flask.

Procedure:

100 mL of the surface water sample was pipette into a 250 mL conical flask and one drop of 0.05M $Na_2S_2O_3$ was added (to eliminate residual free available chlorine which may bleach the indicator). Three drops of bromocresol green indicator solution were also added. This was titrated with standard 0.02M HCl until the first colour change from blue to faint yellow was observed.

Calculation:

$$\text{Total alkalinity } (\text{mg CaCO}_3\ \text{L}^{-1}) = \frac{\text{vol. of HCl x Molarity of HCl x }100{,}000}{\text{volume of water sample (mL)}}$$

3.4.1.4 Determination of turbidity

Principle:

Turbidity is based on the comparison of the intensity of light scattered by the sample under defined conditions with the intensity of the light scattered by a standard reference suspension under the same conditions.

Reagents:

Hydrazine sulphate: About 1.0g of hydrazine sulphate was accurately weighed and dissolved in turbidity free distilled water. The prepared solution was transferred into a 100 mL standard flask and made up to 100 mL using turbidity free distilled water.

Hexamethylenetetramine: 10 g of hexamethylene tetramine was weighed and dissolved in turbidity free distilled water. The solution was transferred in to a 100 mL standard flask and made up to mark using turbidity free distilled water.

Standard 4000 NTU Solution: Exactly 10 mL of hydrazine sulphate solution and hexamethylenetetramine solution were mixed in a 1:1 ratio in a 100 mL standard flask. The solution mixture was allowed to stand for 24 hours after which the volume was made up to 100 mL using turbidity free distilled water to obtain the standard 4000 NTU solution.

Procedure:

Sample water was added to the sample cell up to the horizontal mark. The sample cell was gently wiped with soft tissue and placed in the turbidity meter such that the vertical mark in the sample cell coincided with the mark in the turbidity meter. The sample cell was covered and the reading was taken after a stable reading was obtained using a portable Turbidimeter (HACH-Model 2100P).

Calibration:

The instrument was calibrated with a primary standard reference suspension, formazin polymer (as recommended by HACH for calibration following the manufacturers' guides

3.4.1.5 Determination of total dissolved solids (TDS)

Total dissolved solid (TDS) was measured by electrometric method using digital high range TDS meter (HANNA Instruments, HI 991301 model).

3.4.1.6 Determination of electrical conductivity (EC)

The electrical conductivity was measured *in-situ* immediately after the water sample was collected, because conductivity changes with storage time. This was done by electrometric method using a high range Conductivity meter (HANNA Instruments HI 991301 model) and readings recorded accordingly.

3.4.1.7 Determination of total hardness

Principle:

Ethylenediaminetetraacetic acid (EDTA) titrimetric method was used in the determination of total hardness.

Reagents:

The reagents required in testing for total water hardness include:

Sodium Hydroxide, 1.0 N: 40.0g of sodium hydroxide was dissolved in 1000 ml of water.

Standard 0.01 M EDTA solution: Sodium ethylenediaminetetraacetate dihydrate $Na_2H_2EDTA.2H_2O$ was dried at 80^oC for 1.0 h and cooled in a dessicator. 3.723 g was accurately weighed and dissolved in water and diluted to 1000 mL. The solution was standardised against standard zinc sulphate solution. The solution was stored in polyethylene bottle.

Erio T indicator: 0.2 g of the solid indicator was dissolved in 15 mL of triethanolamine and 5 mL of absolute ethanol.

Buffer (pH 10) reagent: 143 ml of concentrated ammonium hydroxide (NH_4OH) was added to 16.9 g of ammonium chloride (NH_4Cl) and diluted to 250 mL with water.

Procedure:

50 mL of surface water sample was placed in a 250-mL conical flask and 2 drops of Erio T indicator was added followed by the addition of 0.50 mL of hardness buffer to hold the pH at around 10. The colour of the mixture turned red if any hardness was present. The 0.01 M EDTA reagent from a burette was added slowly with continuous swirling until the red colour just disappears, giving way to a blue end-point. Blank was run in a similar way as samples.

Calculations:

$$\text{Total hardness } (\text{mgL}^{-1}\ \text{CaCO}_3) = \frac{\text{V x A x 1,000}}{\text{volume of sample (mL)}}$$

V = volume of EDTA titrated (mL)

A = Molarity of EDTA solution (molL^{-1})

3.4.1.8 Determination of dissolved oxygen (by Electrometric method)

Apparatus:

- Battery-powered DO-meter (YSI 550A Model). This is a meter designed specifically for dissolved oxygen measurement.
- Oxygen-sensitive membrane electrode.

Procedure:

The calibration procedure as described in the manufacturer's operational manual was followed. Generally, electrodes were calibrated by reading against air or against a sample of known dissolved oxygen content. This "known" sample was one for which dissolved oxygen concentration had been determined by the Winkler method. The zero end of a calibration curve was determined by reading against a sample containing no dissolved oxygen, prepared by adding excess sodium sulphite, Na_2SO_3, and a trace of cobalt chloride, $CoCl_2$, to the sample. The electrode was rinsed in a portion of the sample which was to be analysed for dissolved oxygen. The electrode was immersed in water, ensuring a continuous flow of water past the membrane to obtain a steady response on the meter.

The manufacturer's instructions provided with the kits were closely followed. The surface water was sampled away from the bank and below the water surface level with much care not to allow any air bubbles in the sample during collection (as this may result in a false high reading). The water was allowed to gently fill the DO sample bottle from bottom to top and the lid was replaced on the bottle while it was still under water. The DO level was immediately determined in-situ using the DO meter. The DO test was repeated three times.

3.4.1.9 Determination of chemical oxygen demand

Principle:

The organic matter present in sample gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) in the presence of sulphuric acid (H_2SO_4), silver sulphate ($AgSO_4$) and mercury sulphate ($HgSO_4$) to produce CO_2 and H_2O. The sample is refluxed with a known amount of $K_2Cr_2O_7$ in the sulphuric acid medium and the excess $K_2Cr_2O_7$ is determined by titration against ferrous ammonium sulphate, using ferroin as an indicator. The dichromate consumed by the sample is equivalent to the amount of O_2 required to oxidize the organic matter.

Reagents:

Sulphuric acid ($d = 1.84$).

Standard potassium dichromate solution, 0.0417 $molL^{-1}$: Dissolve 12.259 g of $K_2Cr_2O_7$ primary standard grade, dried at 103 °C for 2 hours, in distilled water and dilute to 1.0 L.

Dilute standard potassium dichromate ($K_2Cr_2O_7$) solution, 0.0417 $molL^{-1}$: 100 mL of the standard potassium dichromate solution was diluted to 1.0 L.

Standard ferrous ammonium sulphate solution, 0.250 $molL^{-1}$: 98 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ analytical grade crystals was dissolved in deionized water followed by the addition of 20 mL of H_2SO_4 ($d = 1.84$). The solution was left to cool and diluted to 1.0 L. This solution may be standardised against the standard potassium dichromate solution as follows:

10.0 mL of standard 0.0417 $molL^{-1}$ $K_2Cr_2O_7$ solution, was diluted to about 100 mL and 30 mL H_2SO_4 (d = 1.84) was added and allowed to cool. The solution was titrated with the ferrous ammonium titrant, using 2 or 3 drops of ferroin indicator.

Dilute standard ferrous ammonium sulphate solution, 0.025 molL^{-1}. 100 mL of the standard ferrous ammonium sulphate solution was diluted to 1.0 L with deionised water. The solution was standardised daily against the dilute standard potassium dichromate, 0.0417 molL^{-1}.

Silver sulphate, reagent powder. This reagent may be used either directly in powdered form or in saturated solution, or it may be added to the sulphuric acid (about 5 g of Ag_2SO_4 to 1 litre of H_2SO_4; 1-2 days are required for dissolution).

Mercuric sulphate, analytical grade crystals.

Ferroin indicator solution. 0.695g of ferrous sulphate, $FeSO_4.7H_2O$, was dissolved in water, and 1.485 g of 1, 10-phenanthroline monohydrate was added, shaken until dissolved and diluted to 100 mL.

Sulphamic acid, analytical grade (required only if the interference of nitrites is to be eliminated).

Anti-bumping granules that have been previously heated to 600 °C for 1 hour.

Procedure:

If the sample contains more than 100 mgL^{-1} chloride after evaporation or dilution, the following approach was adopted:

To 20.0 mL of sample or aliquot in in a 200 mL conical flask, 0.5 g $HgSO_4$ was added with thorough shaking. This addition was sufficient to complex 40 mg of chloride ion or 2000 mgL^{-1} when 20.0 mL of sample are used. If more chloride is present, more $HgSO_4$ is added to maintain a $HgSO_4$:Cl^- ratio of 10:1. The condenser to the flask was attached and the mixture refluxed for 2 hours and left to cool and then the condenser was washed with distilled water. The mixture was diluted to about 150 mL with distilled water, cooled to room temperature, and the excess dichromate titrated with standard ammonium ferrous sulphate using 2-3 drops of ferroin indicator. The end-point was observed when the colour changed sharply from blue-green to reddish-brown, although the blue-green may reappear within several minutes. In the same manner, a blank sample consisting of 20 mL of distilled water together with the reagents was refluxed and titrated as in with the sample.

Calculation:

$$\text{COD}\ (\text{mgL}^{-1}) = \frac{(A - B)\ x\ C\ x\ 1{,}000}{\text{volume of sample (mL)}}$$

where: A = volume of ferrous ammonium sulphate used for blank (mL)

B = volume of ferrous ammonium sulphate used for sample (mL)

C = molarity of ferrous ammonium sulphate (mol L^{-1})

3.4.1.10 Determination of biochemical oxygen demand

Principle:

The sample is filled in an airtight bottle and incubated at 24 ^{o}C for 5 days. The dissolved oxygen (DO) content of the sample is determined before and after five days of incubation at 24 ^{o}C and the BOD is calculated from the difference between initial and final DO.

Procedure:

The BOD test takes 5 days to complete and is performed using a dissolved oxygen test kit. Two dissolved oxygen bottles (one clear and one black) were filled with sample water, holding them for two to three minutes between the surface and the river bottom.
The initial concentration of dissolved oxygen in one bottle of the mixture of sample and dilution water, and in one of the bottles containing only dilution water were determined immediately using the method described in Section 3.4.1.8. The other bottles were placed in the incubator (those containing the sample, or the mixture of sample and dilution water, and that containing the plain dilution water to act as a blank). The blank dilution water and the diluted samples were incubated for 5 days in the dark at 20 °C. After 5 days, the dissolved oxygen in the diluted samples and the blank were determined using an electrometric method.

Calculation:

$$\text{BOD (mgL}^{-1}\text{)} = \frac{DO_1 - DO_5}{\text{fractional dilution (mL)}}$$

Where,

DO_1 = DO before incubation (mgL^{-1})

DO_5 = DO after 5 days incubation (mgL^{-1})

3.4.1.11 Determination of chloride (Mohr method)

Principle:

The amount of chloride present in water can be easily determined by the titration of a given sample of water with silver nitrate solution. The silver nitrate reacts with chloride ion in a 1:1 ratio. The quantitative precipitation of AgCl is obtained before the red silver chromate is formed from excess $AgNO_3$ which marks the end of titration.

Reagents:

Standard Silver nitrate, $AgNO_3$ (0.0282 N): 4.791 g of $AgNO_3$ was weighed into a 100 mL beaker containing 50 mL deionized water. The solution was transferred into a 100 mL volumetric flask and diluted to volume with deionized water.

Phenolphthalein indicator solution: 0.5 g of phenolphthalein was dissolved in 50 mL of 95 percent ethanol followed by the addition of 50 mL of distilled water. Dilute CO_2-free solution of NaOH (0.02 $molL^{-1}$) was added one drop at a time until the indicator turned faintly pink.

Standard Sodium Chloride solution, NaCl: 1.648 g of NaCl was weighed into a 100 mL beaker containing 50 mL of deionized water. Using a glass rod, the salt was dissolved completely and the solution transferred quantitatively to a 100 mL volumetric flask. The solution was made up to mark with deionized water. The solution was standardized against 0.0282 N NaCl.

Potassium Chromate indicator, K_2CrO_4*:* 25.0 g of potassium chromate was weighed into a 500 mL beaker containing 300 mL deionized water. A few drops of $AgNO_3$ solution was added until slight red precipitate was formed. The solution was left to stand for 12 hours and filtered through a filter paper. The filtrate was transferred into a 1000 mL volumetric flask and made upto mark with deionized water.

Procedure:

50 mL of the water sample was pipette into a 100 mL conical flask and 1.0 mL of potassium chromate indicator was added. Standard silver nitrate solution was then titrated against the sample, a few drops at a time, until the first permanent reddish coloration appeared. A blank titration was also carried out.

Calculation:

$$\text{Conc. of chlorides } (\text{mgL}^{-1}) = \frac{(V_s - V_b) \text{ x Normality x } 35.45 \text{ x } 1000}{\text{volume of sample taken (mL)}}$$

Where, V_s = volume of $AgNO_3$ required by sample (mL)

V_b = volume of $AgNO_3$ required by the blank (mL)

Equivalent weight of chlorine = 35.45

3.4.1.12 Determination of fluoride

Reagent:

1, 2 - cyclohexylene dinitrotetraacetic acid (CDTA) otherwise called TISAB: 28.5 mL of glacial acetic acid, 29 g NaCl, 2 g of disodium EDTA and 250 mL of distilled water were mixed (with stirring) in a 500 mL beaker. The solution was cooled in an ice bath followed by the addition of 3 M NaOH until a pH of 5.0 to 5.5 was reached. The solution was transferred into a 500 mL standard flask and made up to mark with deionized water and stored in a plastic bottle.

Procedure:

500 μgmL^{-1} fluoride standard was prepared by pipetting 5.0 mL of the 1000 μgmL^{-1} fluoride standard solution into a 10-mL volumetric flask and diluted to the mark with the TISAB. 50 mL of water sample, which contains the TISAB at the same concentration as used for the standard calibrations was pipette into a 100 mL plastic beaker and the solution stirred at a constant rate using a magnetic stirrer. The ISE was rinsed with deionized water and blot dry. The electrode probe was inserted into the sample solution and concentration read when stable. 1.0 mL of the 500 μgmL^{-1} F-standard solution was pipetted into the water sample solution and the reading was also recorded when stable.

Calibration of the electrode:

25 mL of the most dilute fluoride standard was pipette into a 50 mL volumetric flask and diluted to the mark with the TISAB. The flask was stoppered and the solution thoroughly mixed. This solution was transferred into a 100-mL plastic beaker and placed on a stirring plate with constant stirring using a magnetic stirrer. The fluoride ISE was connected to a pH meter and the meter set to the mV mode. The electrode was rinsed with deionized water and blot dry with soft tissue. The electrode probe was inserted into the standard solution and mV value recorded when stable. The four steps above were repeated for each of the remaining fluoride standards. The slope (S) was estimated from the difference in the mV readings for each factor of ten increase in the fluoride ion concentration. A graph of the mV reading for the diluted fluoride standards versus the

log of the actual fluoride ion concentration was plotted and the data points with a linear least-squares line were fitted and from the equation for the line, the slope (S) was obtained.

3.4.1.13 Determination of ammonia

Principle:

An intensely blue compound, indophenol, is formed by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium nitroprusside.

Reagents:

Phenol solution: 11.1 mL liquefied phenol ($\geq$89%) was mixed with 95% (v/v) ethyl alcohol to a final volume of 100 mL. (This was prepared weekly).

Sodium nitroprusside, 0.5% w/v: 0.5 g sodium nitroprusside [$Na_2Fe(CN)_5NO.2H_2O$] was dissolved in 100 mL deionised water and stored in amber bottle for up to 1 month.

Alkaline citrate: 200 g tri-sodium citrate ($Na_3C_6H_5O_7.2H_2O$) and 10 g sodium hydroxide was dissolved in deionised water and diluted to 1000 mL.

Sodium hypochlorite (NaOCl), commercial solution, about 5% (v/v): 5.0 mL of NaOCl was mixed with 95 mL of deionized water and made upto 100 mL.

Oxidizing solution: This was prepared by mixing 100 mL alkaline citrate solution with 25 mL sodium hypochlorite (This was freshly prepared daily).

Stock ammonium chloride solution: NH_4Cl crystals were dried for about 1 hour at 100°C. 3.819g of the salt was accurately weighed, dissolved in deionized water and made up to 1.0 litre.

1.00 mL = 1.0 mg N = 1.22 mg NH_3.

Standard ammonium chloride solution: The stock ammonium chloride solution and water was used to prepare a calibration curve ranging between 0.5 – 2.0 mgL^{-1}.

Procedure:

25 mL surface water sample was pipette into a 50 mL conical flask followed by the addition of 1.0 mL phenol solution, 1.0 mL sodium nitroprusside solution, and 2.5 mL oxidizing solution with thorough mixing after each addition. The sample was covered with paraffin wrapper film for colour development at room temperature (24 to 27 °C) in subdued light for at least 1 hour, and was left for colour stability for 24 hours. The absorbance was measured at 640 nm a visible spectrophotometer (HACH-DR 3800 SC). A reagent blank was also prepared but without the sample.

Calculations:

$$\text{Conc. of ammonia } (\text{mgL}^{-1}) = \frac{(\text{Conc. from calibration curve} - \text{blank}) \text{ x } 1000}{\text{Volume of sample (mL)}}$$

3.4.1.14 Determination of nitrate

Principle:

This method is based upon the reaction of the nitrate ion with brucine sulphate in a 13 N H_2SO_4 solution at a temperature of 100°C. The colour of the resulting complex is measured at 410 nm. Temperature control of the colour reaction is extremely critical.

Reagents:

Distilled-deionised water was used in the preparation of all reagents and standards.

Sodium chloride solution (30%): 300g NaCl was dissolved in distilled-deionised water and diluted to 1000 mL in a volumetric flask.

Sulphuric acid solution: 500 mL conc. H_2SO_4 was carefully added to 125 mL distilled-deionised water. The solution was cooled and kept tightly stoppered to prevent absorption of atmospheric moisture.

Brucine-sulphanilic acid reagent: A 1.0g brucine sulphate $[(C_{23}H_{26}N_2O_4)_2\ H_2SO_4.7H_2O]$ and 0.1g sulphanilic acid ($NH_2C_6H_4SO_3H.H_2O$) were dissolved in 70 mL hot distilled-deionised water, followed by the addition of 3.0 mL conc. HCl. The solution was left to cool, mixed and diluted to 100 mL with distilled-deionised water. This was stored in a dark bottle at 5 °C.

Potassium nitrate stock solution, 1.0 mL = 0.1 mg NO_3-N: A 0.7218g anhydrous potassium nitrate (KNO_3) was dissolved in distilled-deionised water and diluted to 1000 mL in a volumetric flask. This was preserved with a 2.0 mL chloroform.

Potassium nitrate standard solution, 1.0 mL = 0.001 mg NO_3-N: Dilute 10.0 mL of the stock solution (6.5) to 1.0 litre in a volumetric flask. This solution was prepared fresh weekly.

Acetic acid (1:3): 100 mL glacial acetic acid (CH_3COOH) was diluted with 300 mL of distilled-deionised water.

Sodium hydroxide (l.0 N): 40.0g of NaOH was dissolved in distilled-deionised water, cooled and diluted to 1000 mL in a standard volumetric flask.

Instrument Calibration: Appropriate volumes (2.0, 4.0, 6.0, 8.0 and 10.0 mL) of nitrate working solution were measured into a series of tubes to cover the range 10 to 50 µg NO_3^-. These contents in the tubes were mixed by swirling in a cold water bath. This was followed by addition of 10.0 mL H_2SO_4 and then 0.5 mL of brucine sulphanilic acid reagent, and heated in a 100 ^{o}C water bath for 25 minutes. The rack of tubes was immersed in the cold water bath and allowed to cool to room temperature. Then, the absorbance of the solution was read at 410 nm using a visible spectrophotometer (HACH DR 3800 SC). Blank determination was done following the same procedure. Deionized water was used in place of nitrate working solution.

Procedure:

The pH of surface water samples were adjusted to approximately 7.0 with acetic acid or sodium hydroxide solution. The solution was then filtered where necessary to remove turbidity. Sample tubes were placed in a rack to handle samples, standards and reagent blank. 10.0 mL of samples was pipette into the tubes. The contents of tubes were mixed by swirling and the rack placed in cold water bath (0 - 10°C). 10.0 mL of sulphuric acid solution was pipette into each tube and mixed by swirling. The tubes were allowed to come to thermal equilibrium in the cold bath. Equilibration of temperatures in all tubes was ensured before continuing. Then, 0.5 mL brucine-sulphanilic acid reagent was added to each tube (and was carefully mixed by swirling and then the rack of tubes was placed in the 100°C water bath for exactly 25 minutes.

The rack of tubes was removed from the hot water bath and immersed again in the cold water bath and allowed to reach thermal equilibrium (20-25°C). Then, the absorbance was read against the reagent blank at 410 nm using a visible spectrophotometer (HACH DR 3800 SC).

Calculation:

$$\text{Conc.of nitrate}\left(\mu\text{gmL}^{-1}\right) = \frac{(\text{Concentration from calibration curve} - \text{blank})}{\text{volume of sample (mL)}}$$

3.4.1.15 Determination of nitrite

Principle:

Nitrite reacts, in strongly acid medium, with sulphanilamide. The resulting diazo compound is coupled with α-(1-naphthyl)-ethylenediamine dihydrochloride to form an intensely red coloured azo-compound. The absorbance of the dye is proportional to the concentration of nitrite present. The method is applicable in the range of 0.01 - 1.0 mgL^{-1} nitrite nitrogen.

Reagents:

Hydrochloric acid, 3.0 molL^{-1}: 1 part concentrated HCl was combined with 3 parts deionized water

Sulphanilic acid reagent: 1.6 g sulphanilic acid was dissolved in 30% acetic acid.

Commercial DPD indicator solution.

Acetic acid, 30% (v/v): 30 mL of acetic acid solution dissolved in 70 mL of deionized water.

Sulphanilamide ($C_6H_8N_2O_2S$) solution: In a 500 mL volumetric flask, 25 mL of HCl was added to 400 mL of deionized water. This was followed by the addition of 2.5 g of sulphanilamide with stirring and the solution was made up to 500 mL volume.

Nitrite and nitrate free distilled water: 1.0 mL of concentrated sulphuric acid and 0.2 mL of manganous sulphate ($MnSO_4$) solution were added to 1.0 L of deionized water. The solution was made pink with 1-3 mL potassium permanganate solution (440 mg $KMnO_4$ in 100 mL deionized water). The solution was redistilled in an all borosilicate glass. The first 50 mL of the distillate was discarded and each subsequent 100 mL fraction of distillate was tested by the addition of DPD indicator, discarding those with a reddish colour that indicated the presence of permanganate.

N-1-naphthylethylenediamine dihydrochloride solution, ($C_{12}H_{14}N_2.2HCl$): 0.25 g of N-1-napthylethylenediamine dihydrochloride was dissolved in approximately 400 mL of deionized water in a 500 mL volumetric flask and the solution was made up to 500 mL volume.

Stock nitrite solution. 0.4926 g of dried anhydrous sodium nitrite, $NaNO_2$ (24 hours in desiccator) was dissolved in deionized water (free of nitrite and nitrate) and diluted to 1000 mL. The solution was preserved with 2 mL chloroform per litre (1.0 mL = 100 µg NO_2^-N).

Working nitrite solution. 10.0 mL of the stock nitrite solution was diluted to 1.0L (1.0 mL = 1.0 µgNO_2^-NL^{-1}) with deionized water free of nitrite and nitrate.

Calibration:

Appropriate volumes (2.0, 4.0, 6.0, 8.0 and 10.0 mL) of working nitrite solution were measured into a series of tubes to cover the range 0.1 to 1.0 µg NO_2^-. These tubes and its contents mixed by swirling in a cold water bath. After cooling at room temperature, the absorbance of the solution was read at 540 nm using a visible spectrophotometer (HACH DR 3800 SC). Blank determination was done following the same procedure using deionized water instead of nitrite working solution. A calibration curve was plotted from the readings.

Procedure:

To 10 mL of each sample in 50 mL volumetric flask, 2 mL of 3.0 M HCl acid was added and the solution obtained diluted to about 30 mL with deionized water. 2 mL sulphanilic acid reagent was added, stirred, and allowed to stand for 5 minutes. This was followed by the addition of 10 mL of N-1-napthylethylenediamine dihydrochloride solution, and the solution was stirred and made up to volume. The absorbance was read against the reagent at 540 nm after 20 minutes with a visible spectrophotometer (HACH DR 3800 SC).

Calculation:

$$\text{Conc. of nitrite (mgL}^{-1}\text{)} = \frac{\text{(conc. of sample} - \text{blank) x 50}}{\text{volume of sample (mL)}}$$

3.4.1.16 Determination of phosphates

Principle:

In a dilute orthophosphate solution, ammonium molybdate reacts under acid conditions to form a hetero-poly acid, vanamolybdophosphoric acid. In the presence of vanadium, yellow vanamolybdophosphoric acid is formed. The intensity of the yellow colour is proportional to the phosphate ion concentration.

Reagents:

Phenolphthalein indicator aqueous solution: 0.5 g of phenolphthalein was dissolved in 50 mL of 95 percent ethanol followed by the addition of 50 mL of distilled water. Dilute CO_2-free solution of NaOH (0.02 $molL^{-1}$) was added one drop at a time until the indicator turned faintly pink.

Sulphuric acid, approximately 2.5 $molL^{-1}$: With thorough mixing, 140 mL of sulphuric acid (*d* = 1.84) was carefully added to water, cooled and made up to 1.0L.

Potassium persulphate, $K_2S_2O_8$ solution: 5.0 g of $K_2S_2O_8$ solid was dissolved in 100 mL deionized water.

1.0 N Sodium hydroxide, NaOH: 4.0g of sodium hydroxide crystal was weighed into a cleaned 50 mL capacity beaker and was quantitatively transferred into a 100 mL capacity standard flask and diluted to mark with deionised water.

Hydrochloric acid, HCl: 50 mL of conc. HCl was added to about 40 mL deionised water in a 100 mL capacity standard flask and diluted to mark with deionised water.

Vanadate-molybdate reagent:

Solution A: This solution was prepared by dissolving 12.5g of ammonium molybdate $(NH_4)_6Mo_7O_{24}.4H_2O$ in 150 mL deionised water.

Solution B: This solution was prepared by dissolving 0.125g of ammonium metavanadate NH_4VO_3 by heating to boiling in 30 mL deionised water. The solution was cooled and 33 mL HCl was added to it. Solution B was cooled to room temperature. Later, Solution A was poured into solution B in 500 mL standard flask. The mixture was thoroughly mixed and diluted to mark.

Standard phosphate solution: 219.5 mg of anhydrous potassium di-hydrogen phosphate KH_2PO_4 was dissolved in deionised water and diluted to 100 mL.

1.0 mL of the solution is equivalent to 50.0µg PO_4^{3-}.

Phosphate working solution: 5 mL of the stock phosphate solution was diluted to 500 mL with deionized water.

1.0 ml = 2.5 µg PO_4^{3-}- P

Procedure:

50 mL of mixed water sample was measured into 250 mL conical flask and a drop of phenolphthalein indicator solution (i.e. 0.05 mL) was added. Then 1.0 mL of sulphuric acid solution was boiled gently on the pre-heated hot plate until a final volume of 10 mL was reached. The sample solution was cooled and diluted to 30 mL with deionised water, and then a drop of phenolphthalein indicator solution was added. The pink colour imparted to the sample solution was neutralized to a faint pink colour by NaOH solution. Finally, the sample solution was made up to 100 mL with deionised water.

Colour development:

35 mL of digested water sample was measured into a thoroughly cleaned 50 mL volumetric flask; followed by the addition of 10 mL of vanadate-molybdate reagent, and diluted to the mark with deionised water. A blank sample was similarly prepared by

substituting 35 mL of deionised water for the digested water sample. A yellow colour developed after the sample solution was allowed to stay for 15-20 minutes. Standard solutions of 0, 4, 8, 10, 12, 14 and 20 mgL^{-1} concentrations were prepared from the stock standard solution and treated in same way as the samples for colour development. The calibration curve was plotted by reading the absorbance of the standard solutions after colour development using a visible spectrophotometer (HACH DR 3800 SC) at 470nm.

Calculations:

$$\text{Conc.of phosphate (mgL}^{-1}) = \frac{\text{conc. of PO}_4^{\ 3-}\text{ in mg x 1000}}{\text{volume of sample (mL)}}$$

3.4.1.17 Determination of sulphate

Principle:

Sample solution containing sulphate is treated with $BaCl_2$ to form a colloidal suspension of barium sulphate that is dispersed in solution. The absorbance is measured and is proportional to the sulphate concentration in the sample.

Reagents:

Conditioning reagent: This was obtained by placing 30 mL conc. HCl, 300 mL distilled water, 100 mL 95% ethanol and 75 g NaCl in a container followed by the addition of 50 mL glycerol, with thorough mixing and made up to the final volume to 500 mL.

Barium chloride ($BaCl_2$) crystals, to pass through 20 to 30 mesh sieve.

Stock standard sulphate solution (1.0 mL = 1.0 mg SO_4^{2-}): This was prepared by dissolving 147.9 mg of anhydrous sodium sulphate, Na_2SO_4, in deionized water in a 1000 mL volumetric flask, and diluting to the mark with distilled water.

Preparation of calibration standards and blanks: To five 50 mL glass stoppered standard flasks (four for standards and one for the blank), 10, 20, 30 and 40 mL of the standard sulphate solution were added to the four standard flasks and deionized water was added to the fifth standard flask. About 2.0 mL of the conditioning reagent was added to all five standard flasks and final volume made up to the 50 mL mark. A blank sample was similarly prepared by substituting 100 mL of deionised water for the water sample. The absorbances of the different solutions were measured using a visible spectrophotometer (HACH DR 3800 SC) at 420nm.

Procedure for sample determination:

A 100 mL of surface water sample was placed into a 300 mL beaker. Exactly 5.0 mL of the conditioning reagent was added, and the solution mixed with a magnetic stirrer. While the solution was being stirred, about 0.5g of $BaCl_2$ was added and stirring continued. After exactly 1.0 minute, the absorbance of the solution was read at 420 nm in a 1 cm cell using a visible spectrophotometer (HACH DR 3800 SC).

Calculation:

$$\text{Conc. of sulphate } (\text{mgL}^{-1}) = \frac{(\text{conc. of } SO_4^{2-} \text{ in sample - blank}) \text{ x } 1000}{\text{volume of sample taken (mL)}}$$

3.4.1.18 Determination of trace metals in surface water

The method employed involved digestion of water sample with concentrated nitric acid. The metal concentration in the digest was then determined using Flame Atomic Absorption Spectrophotometer (FAAS).

Sample Digestion for Trace Metal Analysis:

200 mL of a well-mixed/filtered water sample was measured into a clean beaker and 3 mL of conc HNO_3 was added. The beaker was heated on a boiling water bath to concentrate the solution to about 15 mL. The solution was allowed to cool and filtered into a 50 mL volumetric flask. The solution was made up to the mark with deionised water and transferred into a polyethylene sample bottle for instrumental analysis. Blank digestion was prepared following the same procedure with deionised water but without the sample.

Reagents:

Stock standard Cd solution (1.0 mL = 1000µg Cd): 1.000 g Cd metal was dissolved in 50 mL (1:1) HNO_3 with heating to effect complete dissolution. The solution was left to cool and diluted to 1000 mL with deionized water.

Stock standard Pb solution (1.0 mL = 1000µg Pb): A 1.5980 g $Pb(NO_3)_2$ was dissolved in 20 ml of (1:1) HNO_3. The solution was diluted to 1000 mL in a volumetric flask with deionised water.

Stock standard Cr solution (1.0 mL = 1000µg Cr): A 1.923 g of CrO_3 was weighed accurately and dissolved in 120 mL (1:5) HNO_3 and left for a while for complete dissolution. The solution was diluted to volume with deionised water in a 1000 mL volumetric flask.

Stock standard Cu solution (1.0 mL = 1000µg Cu): A 1.000 g of Cu metal was dissolved in 50 mL of (1:1) HNO_3 and made up to mark with deionized water in a 1000 mL volumetric flask.

Stock standard zinc solution (1.0 mL = 1000µg Zn): A 1.000 g of Zn metal was dissolved 20 mL of (1:1) HNO_3 and made up to mark with in deionised water in a 1000 mL volumetric flask.

Stock standard nickel solution (1.0 mL = 1000µg Ni): 1.000 g Ni metal was accurately weighed and dissolved in 20 mL hot conc. HNO_3. The solution was left to cool and diluted to mark with deionised water in a 1000 mL volumetric flask.

Stock standard cobalt solution (1.0 mL = 1000µg Cu): A 1.000 g Co metal was accurately weighed and dissolved in 50 mL (1:1) HNO_3. The solution was left to cool and diluted to mark with deionised water in a 1000 mL volumetric flask.

Preparation of calibration curves:

The Atomic Absorption Spectrophotometer was calibrated with all the standard stock solutions of the metals determined. The working standard solutions were prepared by diluting a certain volume of the stock solution of 1000 mgL^{-1} concentration of each metal to an appropriate concentration (see Table 3.3) in a volumetric flask. The working standards were aspirated appropriately into the flame and the standard absorbance determined. A standard curve of absorbance versus concentration (in mgL^{-1}) was plotted automatically by the instrument which was displayed on the readout device. The calibration curve was plotted manually and compared with the plot that was displayed on the readout device. The precision of the instrument was checked from time to time by re-running one or two of the standard solutions used for calibration.

Procedure:

The concentrations of Cd, Pb, Cr, Cu, Zn, Ni and Co were determined, using a flame atomic absorption spectrophotometer (UNICAM 939/59). The operating conditions are listed in Table 3.3 equipped with the appropriate hollow cathode lamps, air-acetylene flame and resonance wavelength of the metals. Each of the samples was aspirated into the instrument successively and the absorbance and concentration of the sample (in ppm) was displayed on the screen. The wavelengths used in this analysis were: 228.8 nm for Cd, 217.0 nm for Pb, 357.9 nm for Cr, 324.8 nm for Cu, 213.9 nm for Zn, 232.0 nm for Ni and 240.7 nm for Co. Calibration standards were prepared from standard stock solutions of each of the metals.

Calculation:

Metal concentration in the sample solution was calculated using the formula:

$$\text{Metal conc. } (\text{mgL}^{-1}) = \frac{A \times B}{Q}$$

Where,

A = conc. of element (instrument reading) in diluted solution (mgL^{-1})

B = final volume of diluted solution (mL)

Q = initial volume of aliquot taken for dilution (mL)

3.4.2 Preparation of Sediment Samples for Physicochemical Analysis

About 5.0 kg of the air-dried sediment samples were pulverized using an agate mortar and pestle, and passed through a 2.0 mm nylon sieve. Samples for electrical conductivity were passed through a 0.5 mm sieve. Samples were then stored in a clean labelled paper bag until time for analysis.

3.4.2.1 Digestion of sediment samples for determination of nutrients (NO_3^--N, NO_2^--N, PO_4^{3-}, and SO_4^{2-})

A 2.0g of the sediment powder was accurately weighed into a previously cleaned 250 mL beaker, 25 mL of conc. HCl was added for pre-oxidation and the content of the beaker covered with a sizeable watch glass and swirled to mix well, placed on a 200°C regulated hot plate in a fume cupboard and heated for 30 minutes. After all the brown fumes were expelled, the beaker was brought down and allowed to cool, followed by the addition of 10 mL $HClO_4$, and the beaker replaced on the hot plate, covered with watch glass and digested for about 90 minutes until all the white fumes had escaped leaving a colourless liquid. The beaker was brought down and allowed to cool followed by the addition of deionised water. The final solution was neutralized with 6.0 M NaOH (added drop wise with litmus paper for neutral test). The solution was filtered through Whatman No. 41 filter paper into a 50 mL volumetric flask and made up to mark with deionised water.

Table 3.3: Operating conditions for the Atomic Absorption Spectrophotometer

Element	Wavelength (nm)	Slit width (nm)	Lamps current (mA)	Flame type	Range of Working Standards (mgL^{-1})
Cd	228.8	0.5	4	Air-C_2H_2	0.02 – 3.0
Co	240.7	0.2	7	Air-C_2H_2	0.05 – 15
Cr	357.9	0.2	7	Air-C_2H_2	0.06 – 15
Cu	324.8	0.5	4	Air-C_2H_2	0.03 – 10
Ni	232.0	0.2	4	Air-C_2H_2	0.1 – 20
Pb	217.0	1.0	5	Air-C_2H_2	0.1 – 30
Zn	213.9	1.0	5	Air-C_2H_2	0.01 – 2.0

.

3.4.2.2 Digestion of bottom sediment samples for trace metal analysis

1.0 g of air-dried sediment sample was weighed into a 200 mL platinum crucible moistened with deionised water and digested with 10.0 mL mixture of concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$) (4:1 v/v). The mixture was swirled gently and the content evaporated to near dryness on a water bath for about 1 hr. On cooling, the dry residue was then dissolved with 5.0 mL of 1.0 M HNO_3 and filtered through Whatman No. 1 filter paper into a 50.0 mL volumetric flask. This was made up to mark with deionised water and stored in acid pre-cleaned polyethylene containers. A reagent blank was also prepared.

3.4.3 Analyses of Bottom Sediment Samples

3.4.3.1 Determination of pH

Procedure:

About 10.0 g of air dried sediment sample was accurately weighed into a 200 mL beaker and 50 mL of double-distilled water was added. The mixture was thoroughly mixed using a glass rod, and allowed to stand for about 15 minutes for the supernatant solution to settle. The electrode of the pH meter was dipped into the supernatant solution and the pH read.

3.4.3.2 Determination of nitrate

After digestion as in section 3.4.2.1, nitrate was determined in the digests, using the procedure described in section 3.4.1.14.

3.4.3.3 Determination of nitrite

After digestion as in section 3.4.2.1, nitrite was determined in the digests, using the procedure described in section 3.4.1.15.

3.4.3.4 Determination of phosphate (PO_4^{3-})

After digestion as in section 3.4.2.1, 25 mL of the filtrate was transferred into another 50 mL volumetric flask, and analysed for phosphate as previously described in Section 3.4.1.16.

Calculation:

$$\text{Conc. of phosphate } (\text{mg kg}^{-1}) = \frac{\text{conc. of } PO_4^{3-} \text{ in mg x } 1000}{\text{mass of sample (kg)}}$$

3.4.3.5 Determination of sulphate

After digestion as in section 3.4.2 (a), 25 mL of the filtrate was transferred into another 50 mL volumetric flask, and analysed for sulphate as previously described in Section 3.4.1.17.

3.4.3.6 Total organic carbon (TOC) and total organic matter (TOM)

The Walkley-Black method measures the amount of degradable organic matter in sediment and soil. Sediment organic carbon is almost completely oxidized with potassium dichromate ($K_2Cr_2O_7$) in the presence of H_2SO_4, leaving the fraction present in inorganic form. The excess dichromate ion is determined by titration with ferrous sulphate (Khwaja *et al.*, 2000).

Reagents:

1.0 N Potassium dichromate, $K_2Cr_2O_7$: 49.04g potassium dichromate (previously dried for 2 hours at 105 ^{o}C) was weighed into a 1.0 L volumetric flask. The salt was dissolved and diluted to volume with deionized water and mixed well.

0.5 N Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 6H_2O$: 20 mL H_2SO_4 was slowly added to a 1.0 L volumetric flask containing 800 mL deionized water. 196.1 g ferrous ammonium sulphate was added to the solution. The solution was mixed and made up to volume with deionized water. (This was prepared daily).

Diphenylamine, $C_6H_5NHC_6H_5$: About 0.5 g of diphenylamine was dissolved in 20 mL deionized water. 100 mL H_2SO_4 was slowly added and the solution was carefully mixed with a glass stirring rod.

Sulphuric acid, H_2SO_4: 500 mL conc. H_2SO_4 was carefully added to 125 mL distilled-deionised water. The solution was cooled and kept tightly stoppered to prevent absorption of atmospheric moisture.

Phosphoric acid, H_3PO_4 solution, conc. (sp.gr. 1.70).

Sodium fluoride, NaF salt.

Procedure:

1.0 g sediment sample was weighed into a 500 mL conical flask. 10 mL of 1.0 N potassium dichromate solution and 20 mL conc. sulphuric acid were added and mixed by gently swirling for 1 min. taking care to avoid throwing soil up onto the sides of the flask. The solution mixture was left to stand for 30 minutes. The solution was diluted to 200 mL with deionized water followed by the addition of 10 mL phosphoric acid, 0.2 g sodium fluoride, and 10 drops diphenylamine indicator. The resultant solution was titrated with 0.5 N ferrous ammonium sulphate solution until the colour changed from dull green to a turbid blue. The titrating solution was added drop wise until the end point was reached when the colour shifts to a brilliant green. A reagent blank was prepared and titrated in the same manner.

3.4.3.7 Particle size analysis of sediment samples

Particle size distribution (i.e. percentage sand, silt and clay) was determined by Bouyoucos hydrometer method (ASTM, 2001)

3.4.3.8 Determination of metals in bottom sediment samples

The concentrations of Cd, Pb, Cr, Cu, Zn, Ni and Co were determined after wet digestion by Atomic Absorption Spectrophotometry as previously described (Section 3.4.1.18).

Calculation:

$$\text{Metal conc. in sediments } (\mu\mu\, g^{-1}) = \frac{(A - B) \times V}{\text{weight of the sample (g)}}$$

where:

A = metal concentration ($\mu g\ mL^{-1}$) in the sample digest (from instrument)

B = metal concentration (μgmL^{-1}) in the blank.

V = final volume of the digest used (mL).

3.5 SPECIATION OF METALS IN SEDIMENTS

Sequential Extraction of Metals from Sediments

Reagents:

Nitric acid, HNO_3 (70%) conc.

Perchloric acid, $HClO_4$ (85.5%), conc.

0.11 M CH_3COOH solution: 1.58 mL of acetic acid was added to 100 mL of deionized water in a 250 mL volumetric flask. The solution was made up to mark with deionized water.

0.5 M hydroxylammonium chloride (NH_2OH-HCl): 5 g of $NH_4OH.HCl$ was dissolved in 150 mL of deionized water in a 500 mL volumetric flask and diluted to 500 mL with anhydrous methanol.

2.5% (v/v) 2.0 M HNO_3: 2.5 mL of 2.0M HNO_3 was measured accurately into 97.5 mL of deionized water.

8.8 M H_2O_2: 150 mL of H_2O_2 solution was added to 100 mL of deionized water in a 500mL volumetric flask. The solution was made up to mark with deionized water

1.0 M CH_3COONH_4 solution: 93.52 g of CH_3COONH_4 was dissolved in about 100 mL of deionized water in a 250 mL volumetric flask and the solution was made upto final volume of 250mL.

2.0 M HNO_3 (sp. gr. 1.42): 63 mL of conc. HNO_3 was added to 200 mL deionized water in a 500 mL volumetric flask. The solution was made up to mark with deionized water.

1.0 M HNO_3 (sp. gr. 1.42): 31.5 mL of conc. HNO_3 was added to 100 mL deionized water in a 500 mL volumetric flask. The solution was made up to mark with deionized water.

Procedure:

The modified BCR protocol was used, and is described below:

Step 1 (Exchangeable - weak acid soluble fraction): 0.5 g sediment sample was weighed into a 50 mL polypropylene centrifuge tube and was extracted with 20 mL of 0.11 M CH_3COOH solution by shaking in a mechanical, end-over-end shaker at 30±10 rpm and 22±5 ^{o}C for 16 h. The extract was separated by centrifugation at 3000-G for 20 min, and the supernatant was decanted and stored in polyethylene bottle at 4 ^{o}C until analysis. The residue was washed by shaking for 15 min with 10 mL of deionised water and then centrifuged, discarding the supernatant and taking care not to discard any solid residue.

Step 2 (Reducible fraction): 20 mL of 0.5 M hydroxylammonium chloride (NH_2OH-HCl) solution was added to the residue from the first step, and the mixture was shaken at 30±10 rpm and 22±5 ^{o}C for 16 h. The reagent was acidified by adding 2.5% (v/v) 2.0 M HNO_3 solutions. The extract was separated and the residue was washed as in step 1.

Step 3 (Oxidizable fraction): 5 mL of 8.8 M H_2O_2 solution was carefully added to the residue from the second step. The mixture was digested for 1 h at 22±5 ^oC (room temperature) and heated to 85±2 ^oC for 1 h in a water bath, and the volume was reduced to <3 mL (uncovered). A second aliquot of 5 mL of H_2O_2 was added, the mixture was digested for 1 h at 85±2 ^oC, and the volume was reduced to about 1 mL. The residue was extracted with 25 mL of 1.0 M CH_3COONH_4 solution, adjusted to pH 2.0, at 30±10 rpm and 22±5 ^oC for 16 h. The extract was separated and the residue was washed as in previous steps.

Step 4 (Residual fraction): The residue from step 3 was digested with 10 mL acid combination of concentrated HNO_3 (65%) and $HClO_4$ (70%) acid mixture (4:1 v/v). The extract was evaporated to near dryness, dissolved with 5 mL of 1.0 M HNO_3 and diluted to 50 mL with deionized water.

Instrumental Analysis of the Extracts:
The extracts from each of the four steps above were analysed for Cd, Pb, Cr, Cu, Zn, Ni and Co using Flame Atomic Absorption Spectrophotometry as described in Section 3.4.1.18.

3.6 SPECIATION OF METAL IONS IN SURFACE WATERS USING PHREEQCI MODEL

3.6.1 Computational Thermodynamic Modelling

The PHREEQCI computer programme version 2.18.0.5134 with Lawrence Livermore National Library (LLNL) thermodynamic database (Parkhurst and Appelo, 1999) was utilized for simulating the soluble inorganic species in the studied river systems. Experimental data on the concentrations of metals - Cd, Pb, Cr, Cu, Zn, Ni and Co and general water quality parameters determined from the two river systems studied were used for the calculations. The model considers the interaction between the metals and the major and minor anions (ligands) as a function of temperature, ionic strength and pH.
The llnl dat. database used in this study is a huge one with thermodynamic constants for so many complexes including Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NO_3^-, NO_2^-, NH_3, PO_4^{3-} etc. The input file uses the SOLUTION or SOLUTION_SPREAD keyword which defines the chemical composition of a solution or multiple solutions in a spread sheet format respectively.

3.6.2 Calculation of Metal Species and Saturation Indices

The llnl.dat database of the PHREEEQCI model distributes aqueous species into different concentrations of various species of the elements and also calculates the different mineral saturation indices indicative of the tendency of a water to dissolve or precipitate a set of minerals by using an ion-association aqueous model. Some thermodynamic data used in the calculation are listed in Table 3.4. The application computes and reports metal speciation in terms of their free hydrated ion, neutral salts and inorganic complexes. The saturation index of a certain mineral, MX, was calculated using the equation below:

$$SI_{MX} = \log\left(\frac{IAP}{K_{SP}}\right) = \log\left[\left(C_{M^{n+}} f_1\right)\left(C_{X^{n-}} f_2\right)\right] - \log K_{SP}$$

where $C_{M^{n+}}$, $C_{X^{n-}}$ are the concentrations of M^{n+}, X^{n-} and f_1, f_2 are the ionic activity coefficient and K_{SP} is the solubility product of the mineral.

3.7 QUALITY CONTROL AND QUALITY ASSURANCE

Quality control/assurance measures were taken to ensure reliability of the results obtained. These measures included:

(i) *Sample collection and handling*. In order to ensure good analytical results, the following quality assurance approaches were taken:

- Sampling tools were thoroughly cleaned before use during sampling.
- During sample collection and on-site preparation, special care was taken not to contaminate or cross-contaminate the samples.
- Clean polythene bags were used for storing sediment samples collected before taking to the laboratory.
- Polyethylene sample bottles used for water samples were washed with detergent, deionised water, 3.0 M HNO_3, and with deionised water before use.
- To ensure sample identity, all samples were labelled accordingly and immediately after collection from site to site with an indelible ink.
- Water samples were carefully collected without disturbing the bottom of the water body when taking a depth sample because this can cause particles to become suspended.

Table 3.4. Some thermodynamic data used for speciation calculations for T = 298.15 K

Compound	Equilibrium reaction	log $K_{SP\ 298K}$	ΔH $kJmol^{-1}$	Formula
Anglesite	$PbSO_4 = Pb^{2+} + SO_4^{2-}$	-7.85	11.26	$PbSO_4$
Atacamite	$Cu_4Cl_2(OH)_6 + 6H^+ = 4Cu^{2+} + 2Cl^- + 6H_2O$	14.28	-132.00	$Cu_4Cl_2(OH)_6$
$Cd(OH)_2$	$Cd(OH)_2 + 2H^+ = Cd^{2+} + 2H_2O$	13.74	-87.02	$Cd(OH)_2$
$CdCr_2O_4$	$CdCr_2O_4 + 8H^+ = Cd^{2+} + 2Cr^{3+} + 4H_2O$	15.00	-255.68	$CdCr_2O_4$
Cerrusite	$PbCO_3 + H^+ = Pb^{2+} + HCO_3^-$	-3.21	13.90	$PbCO_3$
$Co(OH)_2$	$Co(OH)_2 + 2H^+ = Co^{2+} + 2H_2O$	12.30	0	$Co(OH)_2$
Cotunnite	$PbCl_2 = Pb^{2+} + 2Cl^-$	-4.84	26.14	$PbCl_2$
CrO_2	$CrO_2 = ½\ Cr^{2+} + ½\ CrO_4^{2-}$	-19.13	85.98	CrO_2
$CuCr_2O_4$	$CuCr_2O_4 + 8H+ = Cu^{2+} + 2Cr^{+3} + 4H_2O$	16.22	-268.77	$CuCr_2O_4$
Cuprite	$Cu_2O + 2H^+ = 2Cu^+ + H_2O$	-1.90	28.36	Cu_2O
Hydrocerrusite	$Pb_3(OH)_2(CO_3)_2 + 4H^+ = 3Pb^{2+} + 2H_2O + 2HCO_3^-$	1.85	0	$Pb_3(OH)_2(CO_3)_2$
Malachite	$Cu_2CO_3(OH)_2 + 3H^+ = 2Cu^{2+} + 2H_2O + HCO_3^-$	5.94	-76.28	$Cu_2CO_3(OH)_2$
Matlockite	$PbFCl = Pb^{2+} + F^- + Cl^-$	-9.43	0	PbFCl
Nantochite	$CuCl = Cu^+ + Cl^-$	-6.76	41.93	CuCl
$Ni(OH)_2$	$Ni(OH)_2 + 2H^+ = Ni^{2+} + 2H_2O$	12.75	-95.65	$Ni(OH)_2$
$NiCO_3$	$NiCO_3 + H^+ = Ni^{2+} + HCO_3^-$	3.51	0	$NiCO_3$
Otavite	$CdCO_3 + H^+ = Cd^{2+} + HCO_3^-$	-1.77	0	$CdCO_3$
Paralaurionite	$PbOHCl + H^+ = Pb^{2+} + Cl^- + H_2O$	0.20	8.42	PbOHCl
$PbHPO_4$	$PbHPO_4 = Pb^{2+} + HPO_4^{-2}$	-15.73	0	$PbHPO_4$
Phosgenite	$Pb_2(CO_3)Cl_2 + H^+ = 2Pb^{2+} + 2Cl^- + HCO_3^-$	-9.64	49.08	$Pb_2(CO_3)Cl_2$
Pyromorphite	$Pb_5(PO_4)_3Cl + 3H^+ = 5Pb^{2+} + 3HPO_4^{-2} + Cl^-$	-47.90	0	$Pb_5(PO_4)_3Cl$
Smithsonite	$ZnCO_3 + H^+ = Zn^{2+} + HCO_3^-$	0.46	-30.53	$ZnCO_3$
Sphaerocobaltite	$CoCO_3 + H^+ = Co^{2+} + HCO_3^-$	-0.23	-30.70	$CoCO_3$
Tenorite	$CuO + 2H^+ = Cu^{2+} + H_2O$	7.66	-64.50	CuO
Zincite	$ZnO + 2H^+ = Zn^{2+} + H_2O$	11.21	-88.76	ZnO
$ZnCO_3:H_2O$	$ZnCO_3:H_2O + H^+ = Zn^{2+} + HCO_3^- + H_2O$	0.14	0	$ZnCO_3:H_2O$

Thermodynamic data obtained from llnl.database. Source: Parkhurst and Appello (1999).

(ii) Sample preservation/storage.

- The sample bottles used for storage of water samples were thoroughly rinsed with portions of the sample before being filled with samples.
- Samples collected were stored in an ice-chest box (coolers packed with ice cubes) at 4°C and taken to the laboratory.

(iii)Cleaning of glass wares and containers for use in the laboratory.

- All glass wares and containers were washed with detergent solution, rinsed with tap water and then with deionised water.
- *The same* set of glass wares were used throughout the study.
- At the end of each working day, the glasswares were thoroughly washed and dried.

(iv)*Reagent purity*

- All reagents used in this study were of analytical grade obtained from Sigma-Aldrich Laborchemikalian GmbH.

(v) *Calibration.*

- All instruments and glass wares used were duly calibrated to ascertain their accuracy.
- The pH meter was frequently calibrated with buffer 4 and 7 solutions prepared from Analar grade salts.
- Appropriate standard solutions prepared from Analar grade salts, were used to calibrate the Atomic Absorption Spectrophotometer for metals analysis.

(vi) Only deionised and double distilled water was employed during the analysis.

(vii) All reagents and sample bottles were clearly labelled immediately after preparation.

(viii) *Recovery studies of metal determination in samples*.

Recovery studies for trace metals were carried out for selected bottom sediments samples. 2.0 g each of eight sediment samples (four samples each from Cross River and Qua Iboe River) which had been previously analysed were selected for the recovery study of the determination of Cd, Pb, Cu and Zn. Standard solutions of different concentrations of the metals were prepared by diluting the prepared stock solutions of the metals (as in Section 3.4.1.18) to the desired concentrations. A known volume of the standard solution containing the desired concentration of the metals which is expected to double the original concentration was taken using a 5.0 mL pipette and transferred into the sediment sample drop by drop. The crucibles with contents were kept in the oven maintained at 80 ^{o}C for 2 h until they became dry. After drying, the samples were left to cool in a desiccator for 20 minutes. All samples were thoroughly homogenized using a glass rod. 1.0 g of the spiked sample was accurately weighed into a 200 mL platinum crucible and digested with 10.0 mL acid mixture of concentrated nitric acid (HNO_3) and perchloric acid ($HClO_4$) (4:1 v/v) following the procedure in Section 3.4.2.2. The digests were then analysed for the selected metals as previously described.

Calculation:

$$\% \text{Recovery} = \frac{(\text{metal conc. from reanalysis} - \text{original metal concentration})}{\text{Concentration increase achieved by spiking}} \, x \, 100$$

Comment on the Recovery:

The results obtained for Cd, Pb, Cu and Zn for Cross River (CR) and Qua Iboe River (QIR) are presented in Tables 3.4, 3.5, 3.6, and 3.7 respectively. From the results of analysis, the average recoveries (%) for Cd, Pb, Cu and Zn for Cross River were 96.9±6.7, 94.8±2.2, 97.4±3.1 and 95.2±2.6 respectively; while in Qua Iboe River, the respective average recoveries (%) were 97.0±0.9, 96.1±4.1, 96.0±1.3 and 96.7±1.7. These ranges of recovery values are good and indicative of good accuracies for the determination of the metals.

Table 3.5. Results of recovery study of Cd in sediment samples

Sample	Original sample conc. (μgg^{-1})	Weight of sample spiked (g)	Conc. of std. soln. spiked (μgmL^{-1})	Vol. of std soln. spiked (mL)	Conc. increase achieved (μgg^{-1})	Total conc. expected by analysis (μgg^{-1})	Results of re-analysis (μgg^{-1})	% Recovery
Cross River								
Okopedi (SC-1)	0.80	2.0	0.80	5.0	0.80	1.60	1.54	92.5
Nwaniba (SC-3)	0.59	2.0	0.59	5.0	0.59	1.18	1.22	106.8
Oron (SC-4)	0.42	2.0	0.42	5.0	0.42	0.84	0.81	92.9
Ibaka (SC-6)	0.87	2.0	0.87	5.0	0.87	1.74	1.70	95.4
								96.9±6.7
Qua Iboe River								
Iwuokpom 1 (SQ-1)	2.10	2.0	2.10	5.0	2.10	4.20	4.12	96.2
Iwuochang (SQ-3)	2.66	2.0	2.66	5.0	2.66	5.32	5.25	97.4
Eketai (SQ-4)	1.34	2.0	1.34	5.0	1.34	2.68	2.63	96.3
Atabong (SQ-5)	3.56	2.0	3.56	5.0	3.56	7.12	7.05	98.0
								97.0±0.9

Table 3.6. Results of recovery study of Pb in sediment samples

Sample	Original sample conc. (µgg^{-1})	Weight of sample spiked (g)	Conc. of std. soln. spiked (µgmL^{-1})	Vol. of std soln. spiked (mL)	Conc. increase achieved (µgg^{-1})	Total conc. expected by analysis (µgg^{-1})	Results of re-analysis (µgg^{-1})	% Recovery
Cross River								
Okopedi (SC-1)	66.1	2.0	66.1	5.0	66.1	132.2	129.5	95.9
Nwaniba (SC-3)	71.8	2.0	71.8	5.0	71.8	143.6	141.6	97.2
Oron (SC-4)	72.6	2.0	72.6	5.0	72.6	145.2	139.6	92.3
Ibaka (SC-6)	84.3	2.0	84.3	5.0	84.3	168.6	163.5	94.0
								94.8±2.2
Qua Iboe River								
Iwuokpom 1 (SQ-1)	12.4	2.0	12.4	5.0	12.4	24.8	23.8	91.6
Iwuochang (SQ-3)	11.3	2.0	11.3	5.0	11.3	22.6	22.3	97.2
Eketai (SQ-4)	16.3	2.0	16.3	5.0	16.3	32.6	32.8	101.2
Atabong (SQ-5)	14.5	2.0	14.5	5.0	14.5	29.0	28.2	94.2
								96.1±4.1

Table 3.7. Results of recovery study of Cu in sediment samples

Sample	Original sample conc. (μgg^{-1})	Weight of sample spiked (g)	Conc. of std. soln. spiked (μgmL^{-1})	Vol. of std soln. spiked (mL)	Conc. increase achieved (μgg^{-1})	Total conc. expected by analysis (μgg^{-1})	Results of re-analysis (μgg^{-1})	% Recovery
Cross River								
Okopedi (SC-1)	84.1	2.0	84.1	5.0	84.1	168.2	165.4	96.7
Nwaniba (SC-3)	74.8	2.0	74.8	5.0	74.8	149.6	150.7	101.4
Oron (SC-4)	93.4	2.0	93.4	5.0	93.4	186.8	181.0	93.8
Ibaka (SC-6)	102.5	2.0	102.5	5.0	102.5	205.0	202.4	97.5
								97.4±3.1
Qua Iboe River								
Iwuokpom 1 (SQ-1)	34.3	2.0	34.3	5.0	34.3	68.6	66.8	94.5
Iwuochang (SQ-3)	37.0	2.0	37.0	5.0	37.0	74.0	72.3	95.4
Eketai (SQ-4)	42.1	2.0	42.1	5.0	42.1	84.2	83.1	97.3
Atabong (SQ-5)	55.4	2.0	55.4	5.0	55.4	110.9	109.1	96.8
Mean±SD								**96.0±1.3**

Table 3.8. Results of recovery study of Zn in sediment samples

Sample	Original sample conc. (µgg^{-1})	Weight of sample spiked (g)	Conc. of std. soln. spiked (µgmL^{-1})	Vol. of std soln. spiked (mL)	Conc. increase achieved (µgg^{-1})	Total conc. expected by analysis (µgg^{-1})	Results of re-analysis (µgg^{-1})	% Recovery
Cross River								
Okopedi (SC-1)	130.0	2.0	130.0	5.0	130.0	260.0	251.7	93.6
Nwaniba (SC-3)	130.1	2.0	130.1	5.0	130.1	260.2	258.3	98.5
Oron (SC-4)	134.9	2.0	134.9	5.0	134.9	269.8	264.1	95.8
Ibaka (SC-6)	155.2	2.0	155.2	5.0	155.2	310.4	299.1	92.7
								95.2±2.6
Qua Iboe River								
Iwuokpom 1 (SQ-1)	121.7	2.0	121.7	5.0	121.7	243.4	236.7	94.5
Iwuochang (SQ-3)	108.1	2.0	108.1	5.0	108.1	216.2	214.6	98.5
Eketai (SQ-4)	98.9	2.0	98.9	5.0	98.9	197.8	195.2	97.4
Atabong (SQ-5)	127.4	2.0	127.4	5.0	127.4	254.8	250.3	96.5
Mean±SD								**96.7±1.7**

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 SURFACE WATER QUALITY CHARACTERISTICS OF CROSS RIVER SYSTEM

The results of physicochemical characteristics and trace metal concentrations in surface water samples obtained from Cross River (CR) were used to assess the water quality in order to determine the pollution status of the river.

4.1.1 Temperature

The mean temperature obtained in this study was 29.5^{o}C. Results obtained from different sampling stations were as follows: Okopedi (SC-1) – 29.1±2.4 ^{o}C, Ayadehe (SC-2) – 29.2±2.5 ^{o}C; Nwaniba (SC-3) - 29.3±2.4 ^{o}C; Oron (SC-4) - 29.4±2.4 ^{o}C; James Town (SC-5) - 29.5±2.6 ^{o}C and lbaka (SC-6) - 29.4±2.7 ^{o}C (Table 4.1). Results obtained revealed that the temperature of the water body was a reflection of the ambient temperature of the environment, as no industrial activity that releases effluents into the river was envisaged. The results showed that dry season samples recorded higher temperature values equal to ambient temperatures ascribed to climate change effects within the coastal region. Results obtained did not exceed the permissible criteria of national and international regulatory bodies (FEPA, 1991; WHO, 2008).

4.1.2 pH

The pH ranged from 5.78 to 7.22. The slightly acidic pH (5.78) obtained from Nwaniba station (SC-3) may have resulted from humic acid formed from decayed organic matter and tree barks dumped into the river from the saw-mill factory (lumberyard) located at the beach. Minimum pH values were obtained during the dry season. Results obtained compared favourably with values reported by Rim-Rukeh *et al.* (2006) for Orogodo River (5.1 – 6.1 pH unit), but lower than values reported for Osun River (6.84 – 8.90 pH unit) in the Southwest Nigeria by Olajire and lmeokparia (2000). The slight acidity obtained during the dry season as observed for samples from Nwaniba and Oron stations may be attributed to high carbon dioxide concentration

Table 4.1. Physicochemical properties of surface water samples from Cross River

Parameters*	Sampling stations/Code						Mean±SD	Range
	Okopedi (SC-1)	Ayadehe (SC-2)	Nwaniba (SC-3)	Oron (SC-4)	James Town (SC-5)	Ibaka (SC-6)		
Temperature^a	29.1±2.4	29.2 ±2.5	29.3±2.4	29.4±2.4	29.5±2.6	29.4±2.7	29.5±2.5	26.3–34.8
pH	6.48-6.88	6.24-6.89	5.78-7.22	6.21-7.14	6.06-6.89	6.24-6.98	6.62±0.31	5.78–7.22
Alkalinity	28.2±15	23.4±17	30.7±20	58.8±14	24.3±4.9	50.9±8.8	36.1±19.2	11.6–82.8
Turbidity^b	19.1±8.3	37.5±6.6	53.3±19	32.5±11	19.6±14	43.1±19	34.2±18.1	8.3–78.2
TDS	162±36	184±69	331±201	319±67	228±38	422±83	275±130	105–628
E. Conductivity^c	272±45	338±47	606±170	594±200	598±170	912±340	550±280	198–1424
Total Hardness	40±9	36±9	294±100	248±95	61±34	427±100	180±160	23–582
Dissolved Oxygen	8.2±0.7	8.6±1.0	6.5±0.4	7.1±1.5	8.2±0.9	7.1±0.9	7.6±1.2	5.2–10.6
COD	33.2±5.2	27.5±4.5	28.3±3.3	21.8±4.9	27.1±3.1	28.4±5.0	27.7±5.4	17.6–42.6
BOD_5	1.73±0.47	1.89±0.51	1.51±0.54	2.05±1.10	2.18±0.96	2.31±0.60	1.94±0.78	0.89–4.10
Chloride	595±94	161±49	1170±220	1330±110	490±160	1540±180	880±520	120–1830
Fluoride	0.19±0.16	0.08±0.17	0.53±0.29	0.38±0.19	0.39±0.32	0.29±0.34	0.31±0.28	0.002–0.99
Ammonia	0.16±0.13	0.21±0.15	0.60±0.39	0.37±0.27	0.46±0.33	0.45±0.27	0.38±0.30	0.01–1.06
Nitrate	3.2±0.7	5.0±0.9	28.7±9.3	7.7±1.9	14.1±4.5	14.8±3.4	12.3±9.6	2.1–40.4
Nitrite	0.02±0.01	0.02±0.01	0.33±0.25	0.04±0.03	0.07±0.04	0.06±0.03	0.09±0.15	0.01–0.69
Phosphate	0.07±0.02	0.06±0.01	0.12±0.14	0.09±0.16	0.03±0.02	0.05±0.01	0.07±0.09	0.01–0.58
Sulphate	27.4±9.7	26.4±10.0	31.5±6.6	30.5±7.6	27.2±2.8	42.1±6.3	30.9±9.0	10.6–55.8

*All units are expressed in mgL^{-1} unless otherwise stated, ^{a} Temperature in ^{o}C, ^{b} Turbidity in NTU, ^{c} Electrical conductivity as µScm^{-1}

due to organic decomposition as previously reported by Satheeshkumah and Khan (2009) for Pondicherry mangrove, India. The fluctuation in water pH indicates the buffering capacity of total alkalinity. Results fell within the WHO guideline value of 6.5 – 8.5 for drinking water (WHO, 2008).

4.1.3 Total Alkalinity

Mean total alkalinity of 36.1±19.2 (range – 11.6 to 82.8) mgL^{-1} was obtained. The highest concentration (58.8±14 mgL^{-1}) was obtained from Oron station (SC-4), with high alkalinity value of 62 mgL^{-1} obtained during the dry season (Appendix 2). The mean alkalinity obtained in this study is lower than the value reported for Elechi Creek, Port Harcourt (47.1-226.0 mgL^{-1}) by Obire *et al.* (2003), but higher than values (13.9±3.8 mgL^{-1}) reported for Esi River, Warri (Akporido, 2010), Ethiope River, Abraka (1.65 mgL^{-1}) by Agbaire and Obi (2009) all in the Niger Delta and Ogunpa River, Ibadan (1.76-28.0 mgL^{-1}) by Onianwa *et al.* (2001). Lower values occurred during the wet season which may be ascribed to increased dilution (APHA, 2005). However, results obtained were found to be within the permissible criteria (200 mgL^{-1}) of national and international guidelines (FEPA. 1991; WHO, 2008).

4.1.4 Turbidity

The turbidity ranged between 8.3 and 78.2 FTU, with an average of 34.2 FTU (Table 4.1). Results revealed that turbidity level was grossly affected by heavy rains leading to the discharge of flood and run-off water into the river, except for Nwaniba (SC-3) station, which may be attributable to the dredging activity at the beach and the sawmill located in the area that continuously add wood debris into the water.

The turbidity values were comparable to those of other rivers in Niger Delta: Orogodo River, Agbor - 21.0-29.4 NTU (Rim-Rukeh *et al.*, 2006), Western Niger Delta, Delta State - 33.3 mgL^{-1} (Omo-Irabor *et al.*, 2008). Turbidity values obtained from all stations exceeded the 2.5 NTU limit for drinking water (WHO, 2008). Turbidity is an important operational parameter in process control and can indicate problems with treatment processes, particularly coagulation/sedimentation and filtration. At some stations, high turbidity values were attributed to suspended sediments which are indicators of both natural and man-made erosions as in Nwaniba (SC-3) and Oron (SC-4) stations.

4.1.5 Total Dissolved Solids (TDS)

TDS levels ranged from 105 mgL^{-1} to 628 mgL^{-1} (average of 275±130 mgL^{-1}). The highest value (628 mgL^{-1}), from Nwaniba station is attributable to the combined effects of the brackish nature of the estuary, the timber materials continuously dumped and soaked in the river and surface runoff from agricultural farmlands containing high salts used in fertilizer formulation.

Large amount of total solids makes the river more turbid and increases electrical conductivity (Tabata *et al.*, 2007). The palatability of water with a TDS level of < 500 $mgL^{–1}$ (ADWG, 2004) and < 600 $mgL^{–1}$ (WHO, 2008) is generally considered to be good, and becomes significantly and increasingly unpalatable at TDS levels greater than about 1000 $mgL^{–1}$.

4.1.6 Electrical Conductivity (EC)

Conductivity ranged from 198 μScm^{-1} to 1424 μScm^{-1} (Table 4.1). The highest mean level (912±340 μScm^{-1}) was obtained from Ibaka station while the least (272±45 μScm^{-1}) was obtained from Okopedi station. Higher conductivity values were obtained during the dry season. Electrical conductivities have a direct relation with total solids. Therefore, a high conductivity value at Ibaka station was attributable to the intrusion of sea water from Atlantic Ocean whose salinity and dissolved salt level was remarkably high during the dry season. Results obtained are comparable with those of Biga stream –Turkey, with mean value of 869.9 μScm^{-1} (Hacioglu and Dulger, 2009). Conductivity values are statistically higher during the dry season. However, the conductivity level is below the WHO recommended maximum permissible limit for potable water quality (WHO, 2008).

4.1.7 Total Hardness

Total hardness ranged from 23 mgL^{-1} to 582 mgL^{-1} (Table 4.1). Average values in all the stations fell within the WHO recommended guideline limit (500 mgL^{-1}) for drinking water (WHO, 2008). The carbonate system provides acid buffering through two alkaline compounds of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). These compounds are usually found with two hardness ions: Ca^{2+} and Mg^{2+}. Total hardness is affected by the type of minerals in the soil and watershed bedrock and the amount of ocean water coming into contact with these minerals especially during high tide. High hardness levels were obtained during the dry season with Ibaka station recording the highest value of 488±100 mgL^{-1} (Appendix 2).

4.1.8 Dissolved Oxygen (DO)

Dissolved oxygen is a crucial parameter for the survival of aquatic organism and is also used to evaluate the degree of freshness of a river (Wakama *et al.*, 2008). The dissolved oxygen values ranged from 5.2 to10.6 (7.6±1.2) mgL^{-1} (Table 4.1), indicating clearly the presence of adequate dissolved oxygen to maintain aquatic life. The highest DO value, 8.6±1.0 mgL^{-1}, was obtained from Ayadehe station. In all stations, the DO level obtained exceeded 5.0 mgL^{-1}, thereby making the water suitable for aquatic life support. The lowest mean DO value, 6.5±0.4 mgL^{-1}, was obtained from Nwaniba station. Higher values occurred during the dry season than wet season.

Tepe and Mutlu (2005) linked significant increase in dissolved oxygen during the rainy season to high runoff due to low temperature and increased mixing of water. Values in this study were higher than those reported for other rivers in the zone - Elechi Creek (4.16-6.62 mgL^{-1}) by Obire *et al.* (2003); Western Niger Delta River (5.31 mgL^{-1}) by Omo-Irabor *et al.* (2008); Orogodo River Agbor (2.17-3.19 mgL^{-1}) by Rim-Rukeh *et al.* (2006) and Ona River, Ibadan (4.9 mgL^{-1}) by Nubi and Nubi (2010) all located in Nigeria.

4.1.9 Chemical Oxygen Demand (COD)

COD values ranged from 17.6 mgL^{-1} to 42.6 mgL^{-1}, with mean of 27.7±5.4 mgL^{-1} (Table 4.1). The highest concentration, 33.2±5.2 mgL^{-1}, was obtained from Okopedi station while Oron station recorded the lowest COD value of 21.8±4.9 mgL^{-1}. Higher values were obtained during the dry season (Appendix 2). Results obtained in this study are comparable with values, 11.9-22.4 mgL^{-1}, reported by Onianwa *et al.* (2001) for Ogunpa River and 27.75 mgL^{-1} reported by Omo-Irabor *et al.* (2008) for Western Niger Delta rivers. However, results obtained are lower than the maximum value of 50 mgL^{-1} recommended for the natural water courses (WHO, 2008).

4.1.10 Biochemical Oxygen Demand (BOD)

The aim of BOD test was to determine the amount of biochemically oxidisable carbonaceous matter. The BOD values ranged from 0.89 mgL^{-1} to 4.10 mgL^{-1}, with Ibaka and James Town stations having the highest BOD level of 2.30±0.61 mgL^{-1} and 2.18±0.96 mgL^{-1} respectively, while Nwaniba station, recorded the least BOD value of 1.51±0.54 mgL^{-1} (Table 4.1). The BOD values reported were generally lower than the maximum permissible limit of 10 mgL^{-1} recommended by FEPA (1991) and fell within the 6 mgL^{-1} limit for drinking water quality (WHO, 2008). Like dissolved oxygen, BOD also indicates the presence of organic pollution which could be attributed to nonpoint sources (Kumar and Bahadur, 2009). Mean values obtained at different stations are lower than values reported for different polluted rivers in Agbor (21.0 - 38.2 mgL^{-1}) by Rim-Rukeh *et al.* (2006). They are comparable with values from New Calabar River, Port Harcourt (Odukuma and Okpokwasili, 1997), Ethiope River, Ethiope (Agbaire and Obi, 2009) and Elechi Creek, Port Harcourt (Obire *et al.*, 2003).

Sources of BOD includes leaves and woody debris, dead plants and animals, animal manure, effluents from pulp and paper mills, wastewater treatment plants, feedlots, and food-processing plants, failing septic systems and urban storm water runoff. Natural waters with BOD values ≤ 4.0 mg L^{-1} are considered to be polluted with organic matter but safe for drinking (Armah *et al.*, 1999). The low BOD might be due to high input of organic matter from domestic and municipal wastes which consumes the oxygen in the water as it decays. A municipal refuse dump at the banks of the river may have contributed to the increased level of BOD in the river although not significant.

4.1.11 Chloride

The levels of chloride (Cl^-) in surface water samples obtained are presented in Table 4.1. Results ranged from 120 mgL^{-1} to 1830 mgL^{-1}, with a mean of 880±520 mgL^{-1}. The highest chloride level was obtained from Ibaka station with a mean value of 1540±180 mgL^{-1} attributed to marine intrusion, while James Town recorded the lowest level of 490±160 mgL^{-1}. Chloride levels for most stations were mostly above the WHO guideline limit (250 mgL^{-1}) for drinking water quality (WHO, 2008). Chloride levels obtained were far higher than those reported from Esi River, Warri (1.45±0.92 mgL^{-1}) by Akporido (2010) and Ogunpa River, Ibadan (70.5 - 688.0 mgL^{-1}) by Onianwa *et al.*

(2001). According to Kumar and Bahadur (2009), chloride is the most common inorganic anion present in water.

4.1.12 Fluoride

Fluoride concentrations obtained ranged from 0.002 $mgL^{-1}$to 0.99 mgL^{-1}, with highest mean level of 0.53±0.29 mgL^{-1}, obtained from Nwaniba station, followed by 0.39±0.32 mgL^{-1} and 0.38±0.19 mgL^{-1} for James Town and Oron stations respectively (Table 4.1). The mean (0.31±0.28 mgL^{-1}) fluoride obtained did not exceed the permissible level for drinking water and fish production (HACH, 2003).

4.1.13 Ammonia

Concentration of ammonia (NH_4^+) was 0.38±0.30 mgL^{-1} (Table 4.1). The maximum and minimum values of 0.60±0.39 mgL^{-1} and 0.16±0.13 mgL^{-1} were obtained from Nwaniba and Okopedi stations respectively. From all the sampling stations, the average results showed that the wet season recorded higher levels of NH_4^+ than the dry season (Appendix 2). Ammonia is toxic to aquatic life, especially fish even at very low concentration. Also, ammonia can cause odour and taste problems at concentrations above 1.5 and 35 mgL^{-1}, respectively (WHO, 1996).

4.1.14 Nitrate

Nitrate (NO_3^-) levels ranged from 2.1 mgL^{-1} to 40.4 mgL^{-1}. The maximum value of 28.7±9.3 mgL^{-1} was obtained from Nwaniba station while the minimum value of 3.1±0.5 mgL^{-1} was obtained from Okopedi Itu (Table 4.1). Higher nitrate levels were obtained during the dry season. Results obtained in this study are higher than values reported for asphyxiated mangrove swamp of Qua Iboe River estuary (Essien *et al.*, 2009b), but show equivalent values with the reports for Western Niger Delta River (5.83 mgL^{-1}) (Omo-Irabor *et al.*, 2008) and Densu River (0.13-5.21 mgL^{-1}) (Fianko *et al.*, 2010). Nitrate levels obtained fell below the WHO maximum permissible limit of 50 mgL^{-1}. According to WHO (2008), high nitrate values leads to eutrophication which gives rise to unpleasant taste and odour, colours the water, and affects the dissolution of other gases, most especially dissolved oxygen as a result of algal bloom (Mustapha, 2008).

4.1.15 Nitrite

Nitrite concentrations ranged from 0.01 to 0.69 mgL^{-1} (Table 4.1). Nwaniba station recorded the highest mean value (0.33±0.25 mgL^{-1}). The highest value (0.69 mgL^{-1}) was obtained during the dry season (Appendix 2). According to Hasan *et al.* (2009), the different forms of nitrogen are relatively stable in most rivers with ammonia transforming into nitrite, and nitrite slowly transforming into nitrate in well oxygenated rivers. Decomposing organic matter releases ammonia, which is converted to nitrate if oxygen is present (Boyd and Turker, 1998). All inorganic forms of nitrogen (NO_3^-, NO_2^- and NH_4^+) can be used by aquatic plants and algae. However, if this exceeds 0.3 mgL^{-1} (as N) in wet season, it will imply that there is sufficient nitrogen to support dry season algae blooms (Tepe *et al.*, 2005).

4.1.16 Phosphate

Phosphate levels ranged from 0.01 mgL^{-1} to 0.58 mgL^{-1} (Table 4.1), with Nwaniba station recording the highest value of 0.12±0.14 mgL^{-1}. High phosphate levels recorded was attributed to the use of phosphate detergents in nearby streams and phosphate fertilizers in nearby agricultural farmlands which enter the river through surface runoff as previously reported by Adeyemo *et al.* (2008). Results obtained in this study are low compared with reports from other rivers in the Niger Delta (Rim-Rukeh *et al.*, 2006; Nduka *et al.*, 2008) and in Kano (Wakawa *et al.*, 2008; Mustapha, 2008). Phosphate concentration obtained is below the tolerable limits of 2.0 mgL^{-1} (WHO, 2008), but far exceeded natural background phosphate level in riverine waters, usually ranging between 0.005 and 0.05 mgL^{-1} (Koukal *et al.*, 2004). High phosphate and nitrate level can lead to eutrophication, which increases algal growth and ultimately reduces dissolved oxygen levels in the water (Murdoch *et al.*, 2001; De Wit *et al.* 2002; Karikari and Bosque-Hamilton, 2004; Karikari *et al.*, 2006).

4.1.17 Sulphate

Average sulphate level obtained was 30.9±9.0 mgL^{-1} (Table 4.1). The highest value of 42.1±6.3 mgL^{-1} was obtained from Ibaka station while Ayadehe station recorded the lowest value of 26.4±1.0 mgL^{-1}. Results showed that higher sulphate levels were obtained in the dry season in all the sampling stations except Nwaniba (Appendix 2).

Sulphates are naturally present in surface waters, but atmospheric precipitation can also add a significant amount of sulphates to surface waters. Results obtained are higher than the mean value (3.3±0.4 mgL^{-1}) reported by Essien *et al.* (2009b) for Qua Iboe estuary, and lower than values reported for River Challawa in Kano (Wakawa *et al.*, 2008), but is lower than the tolerable limits of 500 mgL^{-1} (WHO, 2008). The results compared favourably with values reported for the New Calabar River and about 3 times higher than those reported for some surface waters in Warri (Nduka *et al.*, 2008).

4.1.18 Pearson Correlation Analysis of Physicochemical Parameters

The correlation analysis for the physicochemical parameters in surface water (Table 4.2) showed significant positive correlations ($r \geq 0.500$ at $p<0.05$) between electrical conductivity (EC) and total hardness (r = 0.695), EC and TDS (r = 0.664), EC and SO_4^{2-} (r = 0.501); TDS and hardness (r = 0.737), TDS and NH_4^+ (r = 0.530), TDS and NO_3^-(r = 0.540), TDS and NO_2^- (r = 0.564); alkalinity and Cl^- (r = 0.625), alkalinity and BOD (r = 0.516); NO_3^- and NO_2^- (r = 0.781); and NH_4^+ and NO_3^- (r = 0.659). Significant correlation between conductivity, alkalinity, total hardness, TDS, SO_4^{2-}, NO_3^-, NO_2^-, and NH_4^+ indicate a natural origin and/or a common source of contamination of these parameters.

4.2 TRACE METALS LEVELS IN SURFACE WATER OF CROSS RIVER

Results of trace metal concentrations and seasonal variation of the studied metals in surface water of Cross River are presented in Appendix 3 and Appendix 4 respectively. Mean concentration results for all the studied stations are presented in Table 4.3.

4.2.1 Cadmium

Cadmium level in surface water ranged from 1 µgL^{-1} to 55 µgL^{-1} with mean value of 16±13 µgL^{-1}. The highest mean Cd concentration of 21±16 µgL^{-1} was obtained from Nwaniba station (Table 4.3). The mean Cd level in all the stations exceeded the WHO guideline value (3 µgL^{-1}) for drinking water (WHO, 2008).

4.2.2 Lead

Lead levels in surface water ranged from 1 to 89 µgL^{-1}. Both James Town and Ibaka stations recorded higher levels of Pb while Nwaniba station recorded the least Pb level

Table 4.2. Pearson correlation coefficient (r) of physicochemical properties in Cross River system

	Temp	Alkalinity	Turbidity	TDS	Elect. Cond.	Hardness	DO	COD	BOD_5	Cl^-	F^-	NH_4^+	NO_3^-	NO_2^-	PO_4^{3-}	SO_4^{2-}
Temp.	1															
Alkalinity	0.288	1														
Turbidity	-0.291	0.146	1													
TDS	0.387	0.384	0.324	1												
E. Cond.	0.138	0.232	0.211	0.664[a]	1											
Hardness	0.162	0.403	0.413	0.737[a]	0.695[a]	1										
DO	0.450	-0.081	-0.456	-0.252	0.288	- 0.495	1									
COD	0.301	-0.186	-0.225	-0.018	0.118	- 0.131	0.363	1								
BOD_5	0.547[a]	0.516[a]	-0.069	0.253	0.051	0.000	0.368	0.033	1							
Cl^-	0.033	0.625[a]	0.170	0.119	0.079	0.163	-0.127	-0.127	0.265	1						
F^-	-0.161	0.222	0.473	0.299	0.152	0.245	-0.381	-0.308	0.050	0.299	1					
NH_4^+	0.629[a]	0.326	0.087	0.530[a]	0.409	0.384	0.080	0.100	0.511[a]	0.213	0.068	1				
NO_3^-	0.209	-0.063	0.371	0.540[a]	0.481	0.567[a]	-0.331	0.080	- 0.053	-0.002	0.340	0.659[a]	1			
NO_2^-	0.248	-0.017	0.400	0.564[a]	0.224	0.362	-0.263	-0.263	- 0.263	0.109	0.337	0.655[a]	0.781[a]	1		
PO_4^{3-}	0.185	0.272	-0.122	-0.096	- 0.232	- 0.153	-0.035	-0.035	0.217	0.102	-0.147	0.089	-0.041	0.053	1	
SO_4^{2-}	0.471	0.336	0.107	-0.536	0.501[a]	0.571[a]	-0.012	-0.012	0.343	0.192	0.088	0.371	0.289	0.095	- 0.017	1

[a] *Values are significant at $p<0.05$.*

Table 4.3. Trace metal concentrations (μgL^{-1}) of surface water samples from Cross River

Sampling station	Station code	Metal concentration						
		Cd	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
Okopedi Itu	SC-1	4±2	17±6	9±4	29±9	213±101	18±11	18±8
Ayadehe	SC-2	12±9	25±9	18±14	32±8	75±21	23±8	27±6
Nwaniba	SC-3	21±16	12±5	12±5	20±9	63±24	15±14	15±8
Oron	SC-4	20±18	14±9	16±14	25±19	95±96	47±45	20±15
James Town	SC-5	17±9	28±14	36±17	49±19	138±76	99±50	52±23
Ibaka	SC-6	12±4	28±8	34±15	57±25	114±31	100±46	58±19
	Mean±SD	16±13	22±14	21±16	35±20	112±71	50±49	32±22
	Range	1 – 55	1 – 89	3 – 64	8 – 92	20–331	5 - 191	2 – 91

(Table 4.3). Results obtained compared favourably with River Ijana, Ekpan (25–58 µgL^{-1}) and Esi River, Warri (39 µgL^{-1}) reported by Emoyan *et al.* (2006) and Akporido (2010), respectively. On the other hand, mean results in this study were lower than values reported by Aderinola *et al.* (2009) for Lagos Lagoon. Results obtained are higher than mean values (10 µgL^{-1}) reported by Essien *et al.* (2009b) for asphyxiated and healthy mangrove ecosystem of Qua Iboe estuary. However, results obtained from all stations were above the WHO limit (10 µgL^{-1}) for drinking water (WHO, 2008), indicating adverse Cd pollution.

4.2.3 Chromium

The range of Cr concentration (mean in parenthesis) for all stations was 3 – 64 (21±16) µgL^{-1}. Only two stations, James-Town (36±17 µgL^{-1}) and Ibaka (34±15 µgL^{-1}) recorded high Cr values in surface water (Table 4.3). The mean Cr level did not exceed the maximum allowable concentration for drinking water quality (WHO, 2008). Results obtained exceeded the 20 µgL^{-1} values reported by Essien *et al.* (2009b) for asphyxiated mangrove of Qua Iboe estuary. However, results obtained is comparable with values reported for Cross River estuary (0.036±0.015) by Essien *et al.* (2009a) and Iko River, Eastern Obolo (10 µgL^{-1}) by Benson and Etesin (2008).

4.2.4 Copper

The total Cu concentration in surface water was 35±20 µgL^{-1}. The highest value, 57 µgL^{-1}, was obtained from Ibaka station. From all stations, results obtained were within the permissible limit of 2000 µgL^{-1} recommended for drinking water (WHO, 2008). Cu shows higher levels during the dry season, than in wet season. The results obtained in this study compared favourably with values reported for River Ijana, Ekpan - Delta (20-50 µgL^{-1}) by Emoyan *et al.* (2006), Abuloma River, Port Harcourt (50±10 µgL^{-1}) by Nduka and Orisakwe (2010), Qua Iboe estuary, Ibeno (36±15 µgL^{-1}) by Essien *et al.* (2009b).

4.2.5 Zinc

Zinc levels ranged between 20 µgL^{-1} and 331 µgL^{-1} (112±71 µgL^{-1}) (Table 4.3). Highest concentration, 213 µgL^{-1}, was obtained from Okopedi, followed by 138 µgL^{-1} from James Town. Zn level was significantly higher during the dry season than in the wet season. However, results were within the WHO limit (3000 µgL^{-1}) for drinking water quality. Zn levels obtained in this study were lower than values obtained from other streams and rivers in the western Niger Delta as reported by Asonye *et al.* (2007), but higher than the value (30 µgL^{-1}) reported by Essien *et al.* (2009b) for Qua Iboe estuary, and compare favourably with values from River Ijana, Ekpan reported by Emoyan *et al*. (2006) and Esi River, Warri (107 µgL^{-1}) by Akporido (2010).

4.2.6 Nickel

The range of nickel levels in the river was from 5 to 191 µgL^{-1} with a mean value of 50±4 µgL^{-1} (Table 4.3). The highest value (100±46 µgL^{-1}) was obtained from Ibaka station. Levels obtained are comparable with values reported by Abu and Egenonu (2008) for New Calabar River, Port Harcourt, but lower than values reported by Nduka and Orisakwe (2010) for Ubeji River, Ubeji-Delta State. Mean values from James Town and Ibaka stations exceeded the WHO limit for drinking water quality (WHO, 2008).

4.2.7 Cobalt

The range of cobalt (Co) concentrations in this study was 2 – 91 µgL^{-1} with mean value of 32±22 µgL^{-1} (Table 4.3). The least Co level was obtained from Nwaniba station (15±8 µgL^{-1}). However, maximum levels of 52±23 µgL^{-1} and 58±19 µgL^{-1} were obtained from James Town and Ibaka stations respectively, which did not show high contamination of Co in surface waters.

Correlation matrix analysis of trace metals in surface water showed a fairly strong positive correlations (significant at $p<0.05$, df. = 64) between the pairs Cr and Cu ($r = 0.787$), Cr and Ni ($r = 0.774$), Cr and Co ($r = 0.857$), Cu and Ni ($r = 0.721$), Cu and Co ($r = 0.886$), Ni and Co ($r = 0.804$) and; Co and Pb ($r = 0.608$) (Table 4.4).

4.3 SEDIMENT QUALITY FOR CROSS RIVER

Results of physicochemical characteristics of bottom sediments are presented in Table 4.5 and Appendix 5. The results show the following ranges (means in parenthesis) for temperature, pH, electrical conductivity (EC), nitrate, nitrite, phosphate, sulphate, and TOC: 25.4–32.0 (28.6) ^{o}C, 5.78–7.51 (6.59), 1060–8510 (3400) µScm^{-1}, 72–471 (179) mgkg^{-1}, 4.1–9.4 (6.3) mgkg^{-1}, 75–250 (152) mgkg^{-1}, 49–449 (171) mgkg^{-1}, and 0.57–2.20 (1.10)% respectively (Table 4.5).

Table 4.4. Pearson correlation coefficient (r) of trace metals in surface water from Cross River system

	Cd	Pb	Cr	Cu	Zn	Ni	Co
Cd	1						
Pb	0.085	1					
Cr	0.282	0.470	1				
Cu	0.152	0.556^a	0.787^a	1			
Zn	- 0.009	0.298	0.247	0.316	1		
Ni	0.004	0.358	0.774^a	0.721^a	0.318	1	
Co	0.054	0.608^a	0.857^a	0.886^a	0.279	0.804^a	1

[a] *Values are significant at* $p<0.05$.

Table 4.5. Physicochemical properties of bottom sediment samples from Cross River

Parameters	Sampling stations						Mean concentration and range	
	Okopedi (SC-1)	Ayadehe (SC-2)	Nwaniba (SC-3)	Oron (SC-4)	James Town (SC-5)	Ibaka (SC-6)	Mean±SD	Range
Temp.°C	28.1±2.3	28.2±2.4	28.5±2.6	28.9±2.4	28. 8±2.00	29.3±2.4	28.6±2.2	25.4–32.0
pH	5.86–6.88	6.39–6.77	5.78–7.22	6.21–7.51	6.06–6.86	6.24–6.95	–	5.78–7.51
E. Cond. (μScm^{-1})	3000±870	3450±490	3080±1000	4430±2700	3360±1200	3080±1100	3400±1400	1060–8510
NO_3^- (mgkg^{-1})	213±28	221±29	95±13	376±50	91±12	81±11	179±110	72–471
NO_2^- (mgkg^{-1})	5.7±0.8	6.4±0.9	4.6±0.6	7.8±1.0	6.4±0.9	6.9±0.9	6.3±1.2	4.1–9.4
PO_4^{3-} (mgkg^{-1})	197±37	198±20	122±21	109±19	90±13	154±11	151.6±40.0	75–250
SO_4^{2-} (mgkg^{-1})	201±27	213±28	358±47	64±9	134±18	56±7	171±110	49–449
TOC (%)	0.95±0.13	1.76±0.23	1.54±0.20	0.87±0.12	0.84±0.11	0.65±0.10	1.10±0.43	0.57–2.20
% Sand	63.9±1.8	61.3±1.7	77.1±1.5	83.2±5.3	89.9±4.5	92.1±4.6	77.9±13.0	59.5–97.4
% Silt	11.9±0.5	17.2±1.4	12.3±1.7	9.2±5.0	5.8±2.5	4.0±1.9	10.1±5.0	2.0–18.3
% Clay	24.2±1.4	21.4±0.9	10.6±1.2	7.6±0.3	4.3±2.8	3.9±2.8	12.0±8.4	0.6–25.8

4.3.1 pH

The pH values ranged from 5.78 to 7.51. The highest pH value was obtained from Oron station with values ranging from 6.21 to 7.51 (Table 4.5).

4.3.2 Electrical Conductivity (EC)

Mean conductivity was 3400±1400 µScm^{-1}.

4.3.3 Nitrate and Nitrite

The mean nitrate and nitrite obtained from this study were 179±110 mgkg^{-1} and 6.3±1.2 mgkg^{-1} respectively. The highest nitrate and nitrite concentration in sediments were obtained from Oron station, with mean values of 376 mg kg^{-1} and 7.8 mgkg^{-1} respectively, while Ibaka and Nwaniba stations recorded the least nitrate (81 mgkg^{-1}) and nitrite (4.6 mgkg^{-1}) respectively (Table 4.5).

4.3.4 Phosphates

Phosphate level was 152±40 mgkg^{-1} (Table 4.5). The highest phosphate values obtained from Okopedi and Ayadehe were 198±20 mgkg^{-1} and 197±37 mgkg^{-1} respectively (Table 4.5). Higher value may be due to farming activities and use of phosphate detergents around the river.

4.3.5 Sulphates

Sulphate level was 171±110 mgkg^{-1} (Table 4.5). The highest sulphate value of 358 mgkg^{-1} in sediment was obtained from Nwaniba station during the dry season.

4.3.6 Total Organic Carbon (TOC)

TOC levels in sediments ranged from 0.57 to 2.20%. The highest mean value of 1.76±0.23% was obtained from Ayadehe station (SC-2) (Table 4.5). Mean values obtained were quite lower than values reported for benthic and epipellic sediments by Essien *et al.* (2009b). Davies and Abowei (2009) reported values of 1.43±0.17% for Okpoka Creek. Previous studies have shown that higher TOC values (i.e.>3.0%) are typically associated with fine sediments and lower TOC values with coarse sediments (Salomons and Forstner, 1980; Cho *et al.*, 1999; Essien *et al.*, 2009a & b). Therefore, the relatively low levels of TOC in sediments are indicative of low organic matter associated with coarse sediments. The total organic carbon (TOC) is the sum of all particulate organic carbon (POC) and dissolved organic carbon (DOC).

4.3.7 Particle Size Distribution

The percentages of sand, silt and clay in bottom sediments ranged from 59.5 to 97.4 (77.9±13.0) %, 2.0 to 18.3 (10.1±5.0) % and 0.6 to 25.8 (12.0±8.4) % respectively (Table 4.5). The river system showed a typical high sand composition (>60%) in all the samples particularly at Ibaka station and James Town with maximum values of 92.1±4.6% and 89.9±4.5% respectively. Maximum values for clay and silt were obtained from Okopedi and Ayadehe with percentage values of 24.2±1.4% and 17.2±1.4% respectively. According to Mudrock *et al*. (1997), the sand fraction is not usually a good source of bioavailable contaminants. Therefore, the clay and silt fractions with a greater surface area and more binding sites are more likely to adsorb organic and heavy metal contaminants (ANZECC and ARMCANZ, 2000b; Simpson *et al.*, 2005). The clay and silt fractions are dominated by secondary silicates minerals such as oxides of Al and Fe which adsorb most anthropogenic contaminants. Therefore, Okopedi and Ayadehe stations are more prone to adsorbing anthropogenic contaminants due to high surface area.

4.4 TRACE METALS IN SEDIMENTS FROM CROSS RIVER

The concentrations (µgg^{-1} dry weight) of trace metals in sediments are presented in Appendix 7. The ranges (mean values in parenthesis) for all stations are: 0.04–0.87 (0.50±0.24) for Cd, 32.7–87.6 (59.3±14.2) for Pb, 6.0–26.0 (15.9±5.3) for Cr, 41.1–102.5 (71.8±16.7) for Cu, 107–155 (129±12) for Zn, 2.7–12.0 (6.6±2.3) for Ni and 2.8–11.1 (7.6±2.3) for Co (Table 4.6). Higher metal concentrations were mostly obtained from Ibaka and Oron stations, while the least concentration varied from station to station depending on the different forms of anthropogenic activities taking place in the area.

4.4.1 Cadmium

Level of Cd in bottom sediment was 0.50±0.24 µgg^{-1}. James Town recorded the lowest mean Cd concentration of 0.10±0.07 µgg^{-1} while Ibaka and Okopedi stations recorded elevated concentrations, 0.76±0.15 µgg^{-1} and 0.73±0.05 ugg^{-1}, approximately seven times higher than the value recorded at James Town station (Table 4.6). Cadmium shows relatively similar concentration in the sediments from all stations except James Town. Higher levels were obtained during the wet season than the dry season (Appendix 8).

Table 4.6. Trace metal concentrations (μgg^{-1} dry weight) of sediment samples from Cross River system

Metals	Sampling stations							
	Okopedi	Ayadehe	Nwaniba	Oron	James Town	Ibaka	Mean±SD[b]	Range
Cadmium	0.73±0.05	0.48±0.06	0.56±0.06	0.39±0.06	0.10±0.07	0.76±0.15	0.50±0.24 (48.0)[a]	0.04-0.87
Lead	59.7±4.9	47.3±5.0	67.3±5.3	65.3±4.9	39.0±6.4	77.3±9.9	59.3±14.2 (23.9)[a]	32.7-87.6
Chromium	7.6±1.1	12.8±1.4	14.9±1.7	20.5±3.5	17.3±2.0	23.5±1.8	15.9±5.3 (33.3)[a]	6.0-26.0
Copper	80±8	50±5	70±7	86±6	54±8	92±9	72±17 (23.6)[a]	41-103
Zinc	121±10	130±10	126±11	128±10	125±11	144±10	129±12 (9.3)[a]	107-155
Nickel	7.4±0.5	5.7±0.5	6.8±0.8	10.3±1.4	3.2±0.4	6.0±0.8	6.6±2.3 (35.0)[a]	2.7-12.0
Cobalt	8.0±0.8	7.4±1.0	9.3±1.1	10.0±0.8	3.5±0.7	7.3±0.9	7.6±2.3 (30.2)[a]	2.8-11.10

[a] Coefficient of variation, CV (%) in parenthesis; [b] SD = Standard deviation

4.4.2 Lead

The average Pb level obtained in this study was 59.3±14.2 µgg^{-1}. Higher values of Pb were obtained from Ibaka (77.3±9.9 µgg^{-1}) and Nwaniba (67.3±5.3 µgg^{-1}) stations (Table 4.6). Seasonal values revealed marked increase during the wet season than dry season (Appendix 8). Lead is known to be sorbed onto sediments in river and marine environment (Mostafa *et al.*, 2009). The high Pb may be ascribed to localized anthropogenic inputs from heavy traffic of tankers, cars and commercial cargo boats are common. Mean Pb values from all stations recorded in this study were higher than those reported for Ntawuogba Creek, Port Harcourt (2.28±2.50 mgkg^{-1}) and Ase River, Asaba-Ase (1.15 -24.79 mgkg^{-1}) by Iwegbue *et al.* (2006) and Iwegbue *et al.* (2007) respectively.

4.4.3 Chromium

Chromium levels in the sediments ranged from 6.0 to 26.0 µgg^{-1} with mean of 15.9±5.3 µgg^{-1} (Table 4.6). The highest Cr level (23.5±1.8 µgg^{-1}) was obtained from Ibaka station. Higher values were obtained during the wet season (Appendix 8). The high Cr recorded for Ibaka station during the wet season could be due to untreated wastewater released from abattoir located by the bank of the river near sampling point. However, values obtained from Oron and Ibaka stations were comparable with mean value (21.16±2.19 mgkg^{-1}) reported by Iwegbue *et al.* (2007) for Ase River, Asaba-Ase, Delta State.

4.4.4 Copper

The average Cu level obtained in this study was 71.8±17.3 µgg^{-1}. The highest Cu concentration was obtained from Ibaka station with a mean value of 92±9 µgg^{-1} (Table 4.6). From all the stations studied, results showed higher Cu values during the wet season except Ibaka station (Appendix 8). Mean values obtained far exceeded values reported for Ase River by Iwegbue *et al.* (2007), and Gulf of Aden, Yemen (Mostafa *et al.*, 2009). The mean values obtained were 72±17 µgg$^{-1,}$ and this is about twice the values reported by Essien *et al.* (2009a) for Cross River estuary. The high levels of Cu in sediments may be ascribed to high inputs of organic matter coming from domestic sewage and local food fermentation activity at the bank of the river. From all stations, Cu concentrations exceeded the recommended values for unpolluted sediments (US-EPA, 2009).

4.4.5 Zinc

Zinc concentration in sediments ranged (mean level in parenthesis) from 107–155 (129 ±12) µgg^{-1} dry weight (Table 4.6). Maximum and minimum mean values were obtained from Ibaka (144±10 µgg^{-1}) and Okopedi (121±10 µgg^{-1}). The wet season recorded higher Zn levels than dry season (Appendix 8). Higher values were attributed to the natural geology of the area.

4.4.6 Nickel

Nickel concentration in sediments ranged from 2.7 to 12.0 µgg^{-1} with mean level of 6.6±2.3 µgg^{-1}. Nickel levels occurred in the order: SC-4>SC-1>SC-3>SC-6>SC-2>SC-5 (Table 4.6). Higher values of Ni were obtained during the wet season for all sampling stations (Appendix 8). Maximum value, 10.3±1.4 µgg^{-1}, obtained in this study was lower than values reported by Essien *et al.* (2009b) for Qua Iboe River estuary and slightly higher than values reported by Iwegbue *et al.* (2007) for Ase River, Asaba-Ase, Delta State. Mean results for the entire river system compare favourably with values reported by Emoyan *et al*. (2006) for Ijana River, Ekpan, Delta State.

4.4.7 Cobalt

Cobalt concentrations in sediments ranged between 2.8 and 11.1 (7.6±2.3) µgg^{-1} (Table 4.6). Higher Co concentrations were obtained from Oron (10.0±0.9 µgg^{-1}) and Nwaniba (9.3±1.1 µgg^{-1}) stations, while James Town station had the least concentration of 3.5±0.7 µgg^{-1}. The Co values obtained from the river were slightly lower than the 6.0–27.5 µgg^{-1} reported by Mostafa *et al.* (2009) for the Hadramout coastal area of Yemen.

4.4.8 Correlation Analysis of Sediment Metals

The inter-elemental correlation analysis of trace metals in sediment shows some strong positive correlations between the pairs Pb and Cd (r = 0.749), Pb and Cu (r = 0.874) and Co and Ni (r = 0.876) (Table 4.7). The significant correlations between the metals - Cd, Pb, Cu, Ni and Co indicate a natural origin and or a shared contamination source for these metals.

Table 4.7. Pearson correlation coefficients for trace metals in sediments of Cross River

Metals	**Cd**	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
Cd	1						
Pb	0.749[a]	1					
Cr	- 0.085	0.441	1				
Cu	0.626[a]	0.874[a]	0.426	1			
Zn	0.279	0.530	0.637[a]	0.432	1		
Ni	0.379	0.580[a]	0.040	0.633[a]	0.097	1	
Co	0.520	0.692[a]	0.020	- 0.550	0.186	0.876[a]	1

[a] *Values are significant at $p<0.05$.*

4.5 EVALUATION OF POLLUTION STATUS OF METALS IN SEDIMENTS FROM CROSS RIVER

Two different approaches were used for assessing the pollution status of bottom sediments in Cross River:

(a) The Enrichment Factor (EF) analysis and,

(b) Comparison of levels obtained in this study, with sediment quality guidelines.

4.5.1 Enrichment Factor (EF) Analysis

The EF represents the actual contamination level (Acevedo-Figueroa *et al*., 2006; Sakan *et al*., 2010), and is used to determine whether levels of metals in the sediments are of anthropogenic origin. The factor was calculated as suggested by Loska and Wiechula (2003) and Suthar *et al.* (2009) using the equation below:

$$\mathrm{EF}(\%) = \frac{(C_x - C_{min})}{(C_{max} - C_{min})} \times 100$$

Where,

C_x = the mean metal concentration in sediment sample (μgg^{-1} dry weight),

C_{max} = the maximum metal concentration in sediment (μgg^{-1}) determined during the study,

C_{min} = the minimum metal concentration (μgg^{-1}) determined during the study.

Results of analysis showed that Cd enrichment factor, EF (Cd) ranged from 6.6 to 86.7, EF (Pb) from 11.5 to 81.2, EF (Cr) from 7.9 to 87.5, EF (Cu) from 13.7 to 82.6, EF (Zn) from 29.5 to 76.0, EF (Ni) from 5.2 to 81.7 and EF (Co) from 8.4 to 86.7. The maximum EF value for most metals (Cd, Pb, Cr, Cu and Zn) in the river system was recorded at Ibaka station (SC-6) while Ni and Co showed maximum EF at Oron station (Table 4.8) suggesting point source of metal pollution. When EF approaches unity, the source is considered to be of lithogenic origin. On the other hand, James Town showed lower EF values for Cd (6.6%), Pb (11.5%), Ni (5.2%) and Co (8.4%).

4.5.2 Sediment Quality Guidelines (SQGs)

Comparison of results with sediment quality guidelines (SQGs)

The sediment quality guidelines used in this study are National Oceanic and Atmospheric Administration (NOAA), Florida Department of Environmental Protection (FDEP), Canadian Council for Ministers of the Environment (CCME) and Ontario

Table 4.8. Enrichment factor values, EF (%) for metals in sediments from Cross River system

Sampling Station	**Station code**	**Enrichment factor, EF (%)**						
		Cd	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
Okopedi	SC-1	82.9	49.1	7.9	62.3	29.5	50.1	62.5
Ayadehe	SC-2	52.4	26.5	34.2	13.7	48.1	31.8	55.4
Nwaniba	SC-3	62.0	63.1	44.6	46.7	39.3	44.5	78.2
Oron	SC-4	41.8	59.3	72.5	72.0	44.4	**81.7**	**86.7**
James Town	SC-5	6.6	11.5	56.7	20.9	38.2	5.2	8.4
Ibaka	**SC-6**	**86.7**	**81.2**	**87.5**	**82.6**	**76.0**	35.1	54.0

Sediment Quality Guidelines (Tables 4.9). The metal concentration from each station was compared with a series of these universal guidelines on sediment toxicity limits (ANZECC and ARMCANZ, 2000a,b; CCME, 1999). Sediment quality guidelines values referred to as the effects range-low or threshold effects level (ERL or TEL) and effects range-median or probable effects level (ERM or PEL) (Long *et al.*, 1995) were used to propose the sediment quality criteria for the studied trace metals except for cobalt. Each set of guidelines delineate three ranges in chemical concentrations where adverse effects are observed rarely (<ERL or <TEL), occasionally (ERL-ERM or TEL-PEL) and frequently (>ERM or >PEL) (Table 4.9).

Comparison of sediment quality from Cross River with NOAA, FDEP and CCME sediment quality guidelines revealed that most of the stations recorded intermediate, very low or no contamination level with respect to the different sediment quality guidelines. The mean Cd level (0.50 µgg^{-1}) is below the ERL, TEL and LEL values of the NOAA, FDEP and Ontario and guidelines values ranked as non-polluted.

About 36% of all the samples from different sampling stations recorded Cd values greater than the TEL value (0.68 mgkg^{-1}) of FDEP guideline. Mean Pb concentration (59.3 µgg^{-1}) is greater than the ERL values of 46.7 µgg^{-1} and less than ERM values (218 µgg^{-1}) of the NOAA guideline, indicative of intermediate pollution for almost all the stations. Results obtained showed that levels of Pb (100%) and Zn (70%) from most of the stations analysed revealed values greater than threshold effect level (TEL) of the FDEP guideline thereby ranking Pb and Zn as showing intermediate contamination level. Copper and Zn showed intermediate level of contamination owing to the greater levels of ERL, TEL and LEL values of the adopted guidelines. However, results obtained were below the ERM, PEL and SEL values which could cause severe effects on the aquatic fauna.

According to Wang and Qin (2006), the metals Pb, Cu and Zn coincides with motorways and are associated with vehicular emissions. Therefore, the influence of vehicular emissions is characterised by Pb and to a lesser extent by Cu and Zn. On the other hand, agricultural activities/materials and other human activities could lead to the introduction of Pb, Cu and Zn to the surrounding soils and hence into the rivers (Alloway, 1995). Nickel concentration in all samples is less than the ERL/ERM values,

Table 4.9. Comparison of sediment metal concentration (µgg^{-1} dry weight) of Cross River with sediment quality guidelines (SQGs)

Metal	Mean levels (this study)	NOAA		FDEP		CCME (marine)		CCME (fresh)		Ontario		Contamination level
		ERL[†]	ERM[a]	TEL[b]	PEL[‡]	IG[c]	PEL[‡]	IG[c]	PEL[‡]	LEL[d]	SEL[e]	
Cd	0.50±0.24 (0.04-0.87)	1.2	9.6	0.68	4.21	0.7	4.2	0.6	3.5	0.6	10	Low or no contamination
Pb	59.3±14.2 (32.7-87.6)	46.7	218	30.2	112	30.2	112	35.0	91.3	31	250	Intermediate
Cr	15.9±5.3 (6.0-26.0)	81	370	52.3	160	52.3	160	37.3	90.0	26	110	Low or no contamination
Cu	71.8±17.3 (41-103)	34	270	18.7	108	18.7	108	35.7	197	16	110	Intermediate
Zn	129±12 (107-155)	150	410	124	271	124	271	123	315	120	820	Intermediate
Ni	6.6±2.3 (2.7-12.0)	20.9	51.6	15.9	42.8	n.g*	n.g*	n.g*	n.g*	16	75	No contamination
Co	7.6±2.3 (2.8-11.1)	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	50*	50*	Not ranked

[†] ERL: Effects range low; [a]ERM: Effects range median; [b]TEL: Threshold effects level; [c]IG: Interim Guideline; [‡]PEL: Probable effects level; [d]LEL: Low effect level; [e]SEL: severe effect level; *n.g = no guideline; SQG = Sediment quality guideline.

indicating no contamination. Similar conclusions derived from TEL/PEL of the FDEP, CCME, and Ontario guidelines although lower than the NOAA, these criteria were still lower than the proposed guideline value. But Cr shows no contamination with values < ERL or TEL. The highest Cr value (26.0 µgg^{-1}) obtained from Ibaka station (SC-6) is lower than the ERL (81 µgg^{-1}) and TEL (52.3 µgg^{-1}) values of NOAA and FDEP guidelines respectively.

4.6 SPECIATION OF TRACE METALS IN SEDIMENTS

The pollution studies of trace metals in sediments cannot be better understood without the examination of the distribution pattern of the metal species. The results of speciation studies, fraction-specific concentration and percentage fractionation, of trace metals in the sediment samples are presented in Appendices 9 and 10 respectively. Summary results of speciation of trace metals in sediment samples among the stations are presented in Table 4.10, and in Figures 4.1 – 4.4.

Assuming that bioavailability is related to solubility, then metal bioavailability decreases in the order of exchangeable > reducible > oxidisable > residual fraction (Ma and Rao, 1997). The residual phase represents metals largely embedded in the crystal lattice of the sediment fraction and should not be available for remobilization except under very harsh condition (Naji *et al.*, 2010). The distribution of trace metals among the three-steps BCR-SEP (exchangeable-water and acid soluble, reducible and oxidisable) and the residual fraction essentially recorded highest metal partitioning of all metals under study in the reducible fraction (Step 2). Generally, the distribution pattern of Cd, Pb, Cr, Cu, Zn, Ni and Co among four BCR fractions follows the order:

reducible > oxidisable > exchangeable > residual for Cd;
reducible > residual > oxidisable > exchangeable for Pb, Ni and Co;
reducible > oxidisable > residual > exchangeable for Cr and Cu; and,
reducible > exchangeable > oxidisable > residual for Zn.

The result shows that chemical partitioning of trace metals in the sediment varies in the river. Cadmium is found to be the most bioavailable (89.3%) of the analysed metals. The trend of bioavailability of the seven trace metals in sediments follows the order: Cd>Zn>Cu>Cr>Co>Ni>Pb. All the metals dominate in the reducible fraction, followed by the residual fraction (as in Pb, Ni and Co) and the oxidisable fraction (as in Cd, Cr and Cu). A significantly higher percentage of Zn binding to the non-residual fractions is

Table 4.10. Fractionation of trace metal levels (with standard deviation and % fractionation in parenthesis) of modified BCR protocol for Cross River

Fractions	Metal concentration (in µgg^{-1} dry weight)						
	Cd	Pb	Cr	Cu	Zn	Ni	Co
Exchangeable	0.14±0.07 (25.2)	2.4±1.6 (3.7)	0.7±0.5 (3.7)	12.0±3.4 (16.0)	40.6±4.1 (30.0)	0.9±0.4 (12.7)	1.2±0.4 (14.5)
Reducible	0.18±0.09 (34.1)	30.8±7.5 (48.4)	6.9±2.3 (41.0)	34.9±10.2 (46.4)	45.9±2.8 (34.7)	2.8±1.0 (39.5)	3.2±1.0 (40.4)
Oxidisable	0.17±0.09 (30.0)	6.4±1.1 (10.3)	5.6±1.9 (33.1)	15.6±4.4 (20.7)	25.0±2.0 (18.5)	1.2±0.4 (17.3)	1.4±0.4 (18.2)
Residual	0.06±0.03 (10.8)	24.1±6.8 (37.5)	3.8±1.4 (22.3)	12.6±3.6 (16.8)	22.6±1.3 (16.8)	2.1±0.7 (30.5)	2.2±0.8 (26.9)
∑ non-residual steps	0.49±0.02 (89.3)	39.7±15.4 (62.4)	13.1±3.3 (77.8)	62.4±12.3 (83.1)	113.0±11.3 (83.2)	4.9±1.0 (69.5)	5.8±1.1 (73.1)
∑ 3-steps + Residual	0.55±0.29	63.8±16.0	17.4±6.3	75.2±21.4	136.0±7.9	6.9±2.6	7.9±2.5
Pseudo-total	0.54±0.29	64.0±16.5	17.2±6.3	76.7±20.9	137.0±9.5	7.0±2.5	8.4±2.7

found in sediments. High percentage of Cu in the non-residual fractions is indicative that Cu is more mobile and freshly deposited in sediments.

4.6.1 Speciation of Cadmium

Cadmium recorded about 89 % of total Cd concentration in the bioavailable (non-residual) fraction. Cadmium was predominantly distributed in the reducible fraction representing about 34.1% of total concentration and the least concentration of 10.8% distributed in the residual fraction. The percentage distribution of Cd follows the order: acid reducible>oxidisable>exchangeable>residual [Fig. 4.1(i)].

The mean Cd concentration was 0.54±0.29 μgg^{-1}. The highest Cd concentration was obtained from Ibaka (SC-6) and Nwaniba (SC-3). The distribution of Cd in the residual fraction is attributed to natural sources such as chemical weathering of igneous and metamorphic rocks, as well as decomposition of biota detritus. Arain *et al*. (2008) reported that high Cd was extracted predominantly in the exchangeable fraction which represents the metal bound to carbonates or sorbed by the exchangeable fraction.

4.6.2 Speciation of Lead

The residual fraction recorded 37.5% of the total Pb in sediments leaving about 62.4% in the non-residual (bioavailable) fractions. The highest total Pb concentration was found in the reducible fraction, 48.4% (30.8±7.5μgg^{-1}) [(Fig 4.1 (ii)]. From all stations studied, only Okopedi and Nwaniba recorded the highest bioavailable (50.4%) in the reducible fraction giving only 2.4% Pb distributed in the exchangeable fraction attributable to anthropogenic input of Pb into the river. The distribution pattern of Pb among the fractions followed the order: reducible>residual>oxidisable>exchangeable [Fig. 4.1 (ii)]. Generally, Pb concentrations in the non-residual fraction increases with total Pb concentration suggesting that Pb in sediments is mostly due to anthropogenic input (Fan *et al*., 2002).

The different distribution pattern of Pb among the stations confirmed the anthropogenic source in these sediments with Ibaka (SC-6) station recording higher mobility and availability than other stations. Among all the metals studied, Pb shows the highest percentage fractionation in the residual fraction with about 37.5%, due to lithogenic origin such as chemical weathering of igneous and metamorphic rocks, as well as

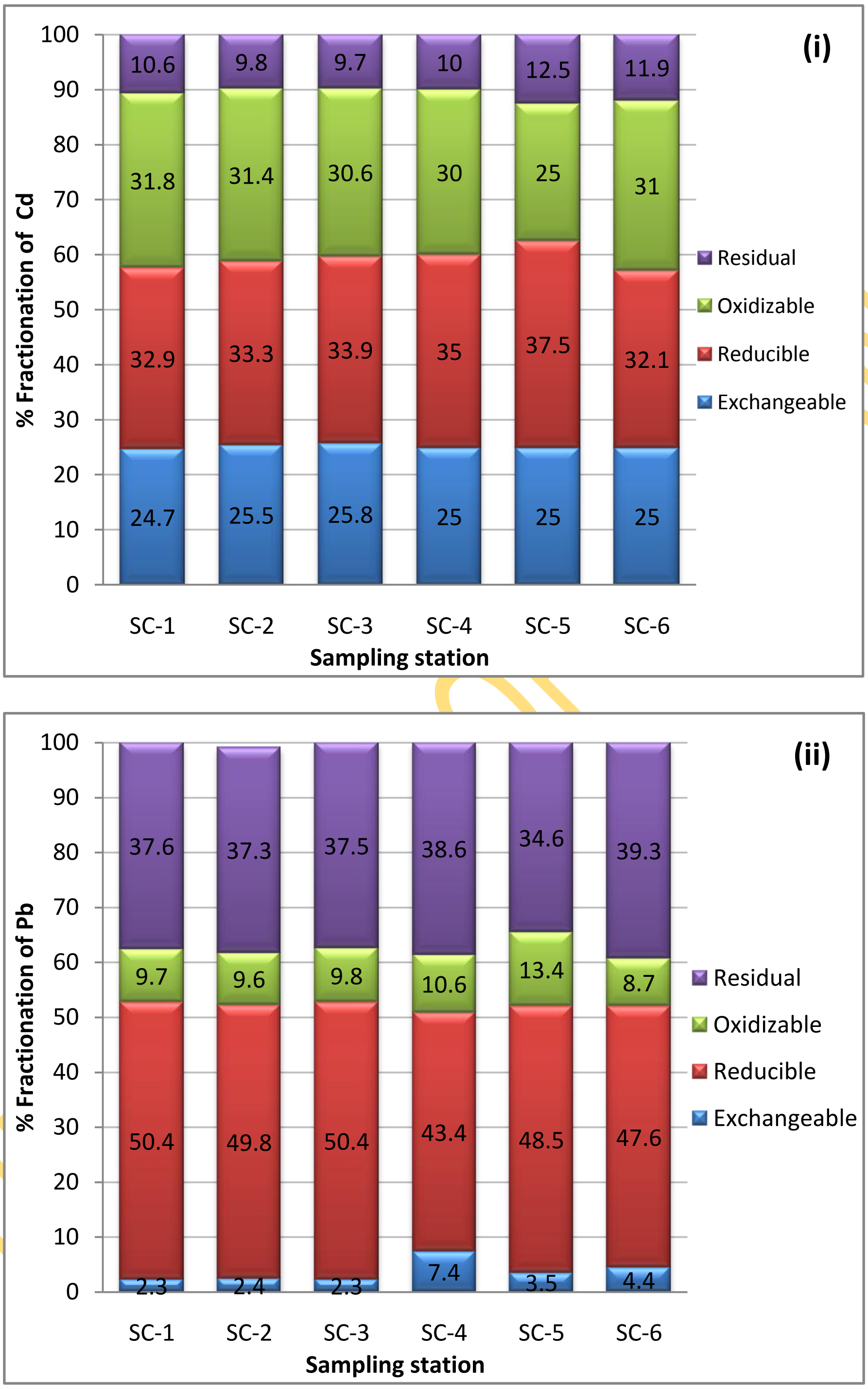

Fig. 4.1. Speciation of Cd (i) and Pb (ii) in sediments of Cross River

decomposition of biota detritus. This agrees with the report of Sutherland and Tack (2003) that high fraction of Pb was in the reducible fraction. Korfali and Jurdi (2011) added that Pb behaviour is governed by sediment carbonate under reducing conditions. Lead distribution shows a strong affinity for the reducible fraction, which accounted for about 48.0 % followed by the residual fraction which accounted for about 36 - 38 % of total metal in the river system.

4.6.3 Speciation of Chromium

The highest distribution of Cr (41.0%) was found in the reducible fraction followed by oxidisable fraction (33.1%). In all, the bioavailable fractions accounted for 77.8% of the total Cr concentration in sediments. The distribution of Cr followed the order: acid reducible > oxidisable > residual > exchangeable [Fig. 4.2 (i)]. This trend agrees with the report by Arain *et al*. (2008) who found low Cr distribution in acid exchangeable fraction of lake sediment samples. Higher Cr in the reducible fraction was reported and attributed to the oxidizing conditions of sediments that render the insoluble forms of the ion (Korfali and Jurdi, 2011).

4.6.4 Speciation of Copper

Copper shows higher speciation in the reducible fraction, followed by the oxidisable-organic fraction of sediments. Cu content of the bioavailable fractions were recorded as: 83.1% of the total. The distribution pattern for Cu followed the order: acid reducible > oxidisable > residual > exchangeable [Fig. 4.2 (ii)]. The variation of Cu shows that only about 17.0% of the total concentration was found in the residual fraction. However, this does not agree with the report that ~44% of total Cu concentration was distributed in non-residual fraction for sediments from Pearl River Estuary and Daya Bay, Southern China by Yu *et al*. (2010). Under reduced conditions, Cu is bound to the organic sediment fraction where organic contents under reduction conditions increase (Korfali and Jurdi, 2011).

4.6.5 Speciation of Zinc

The distribution pattern in Zn for sediment samples follows the order: reducible > exchangeable > oxidisable > residual [Fig. 4.3 (i)]. Results obtained shows that the bioavailable (non-residual) fraction recorded mean concentration of 113±11 μgg^{-1} (83.2%) of the total Zn concentration with only 16.8% partitioned in the residual

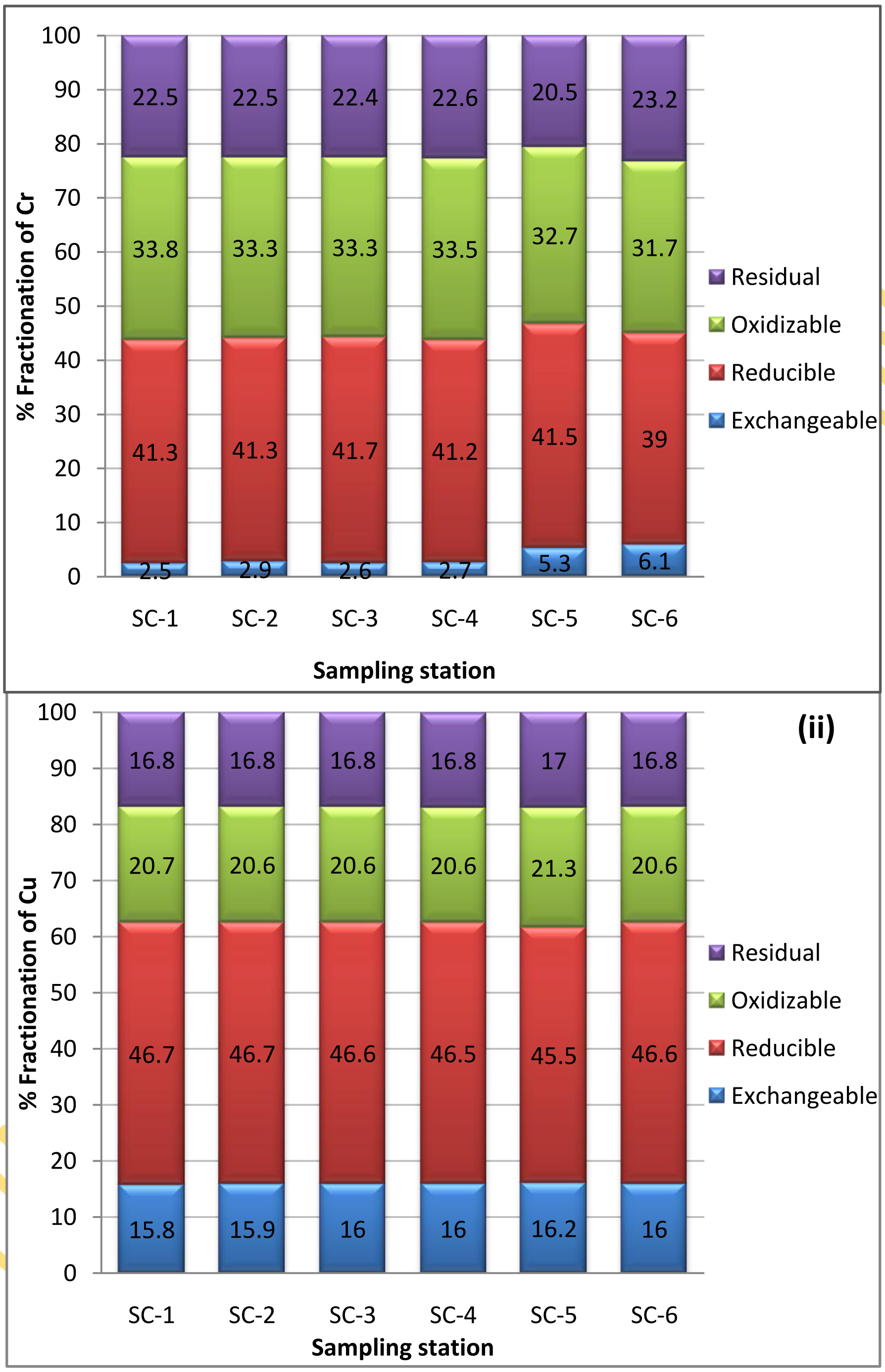

Fig. 4.2. Speciation of Cr (i) and Cu (ii) in sediments of Cross River

fraction. This, however, is far greater than 30.0% for all the non-residual fractions reported by Yu *et al*. (2010) for Pearl River estuary sediments. Apart from Cd, Zn records the highest non-residual concentration of 83.2%. This distribution did not agree with the report of Naji *et al*. (2010) for Klang River, who reported the order: residual > acid reducible > oxidisable-organic > exchangeable. The authors reported mean value of 60.22 % for the non-residual fraction and a higher percentage of Zn (45%) in the oxidisable-organic fraction attributable to different types of organic matter discharged into the Klang River. In most stations, Zn concentrations were dominated in the bioavailable fractions and less than 20% in the residual fraction indicating non-lithogenic origin in the river system.

4.6.6 Speciation of Nickel

The mean concentration of the bioavailable fraction for Ni was 4.9±1.0 μgg^{-1} representing about 69.5% of total metals in the sample (Table 4.10). The order of Ni distribution among the three bioavailable and residual fractions was of the order: reducible (39.5%) > residual (30.5%) > oxidisable (17.3%) > exchangeable (12.7%) [Fig. 4.3 (ii)]. Ni in the residual fraction was attributed to natural sources such as chemical weathering of igneous and metamorphic rocks, as well as decomposition of biota detritus. Ni speciation in the reducible fraction mainly depends on the oxidizing conditions of the sediment.

4.6.7 Speciation of Cobalt

Cobalt shows highest distribution in the reducible fraction (40.4%). The non-residual (bioavailable) fraction recorded 73.1% distribution with mean value of 5.8±1.1 μgg^{-1} (Table 4.10). The least metal distribution was found in the exchangeable (acid-soluble) fraction with value of 14.5%. The distribution pattern of Co follows the order: reducible > residual > oxidisable > exchangeable (Fig. 4.4). Only 26.9% of Co was found in the residual fraction, and this was probably due to natural levels in the environment.

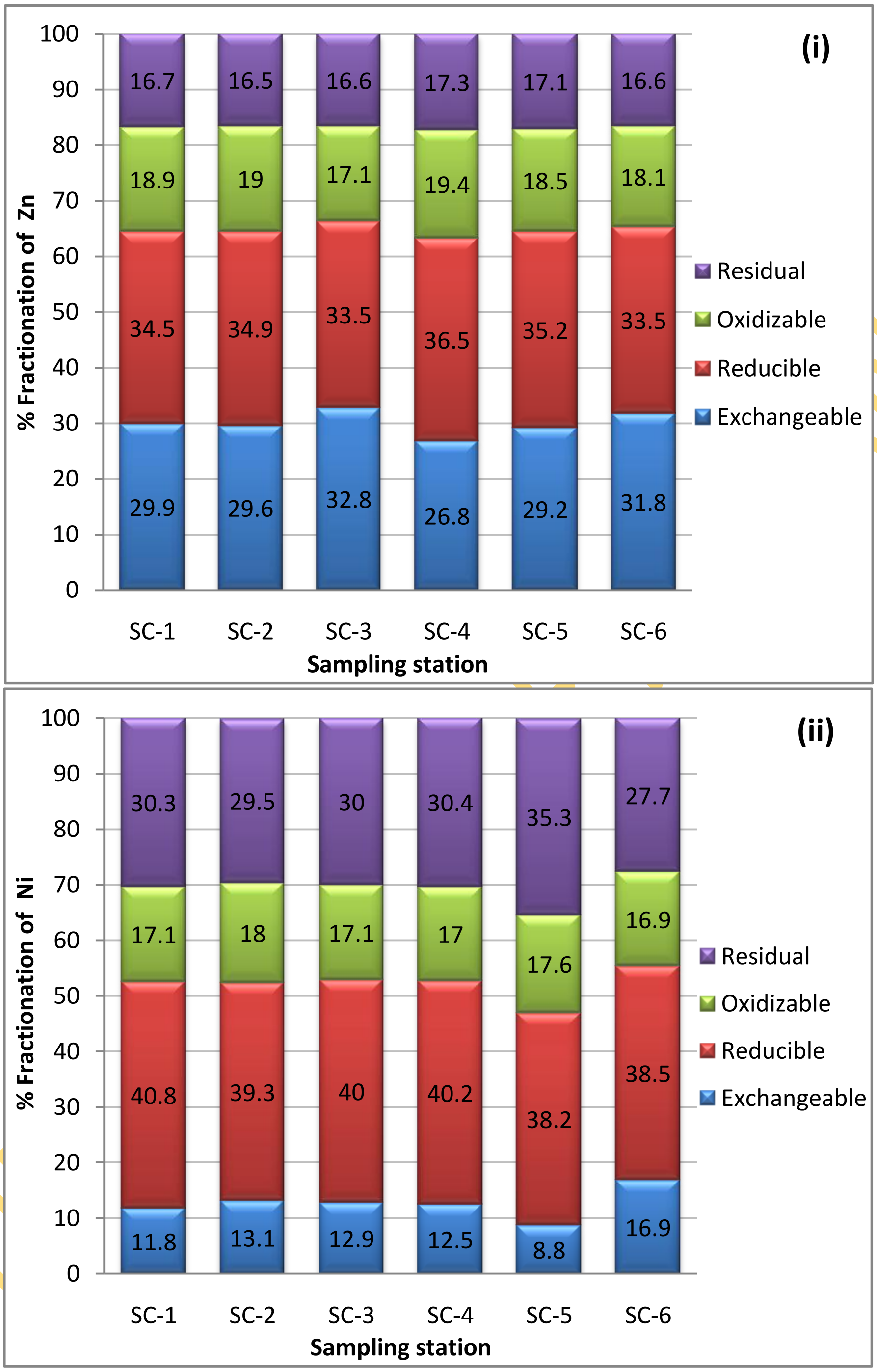

Fig. 4.3. Speciation of Zn (i) and Ni (ii) in sediments of Cross River

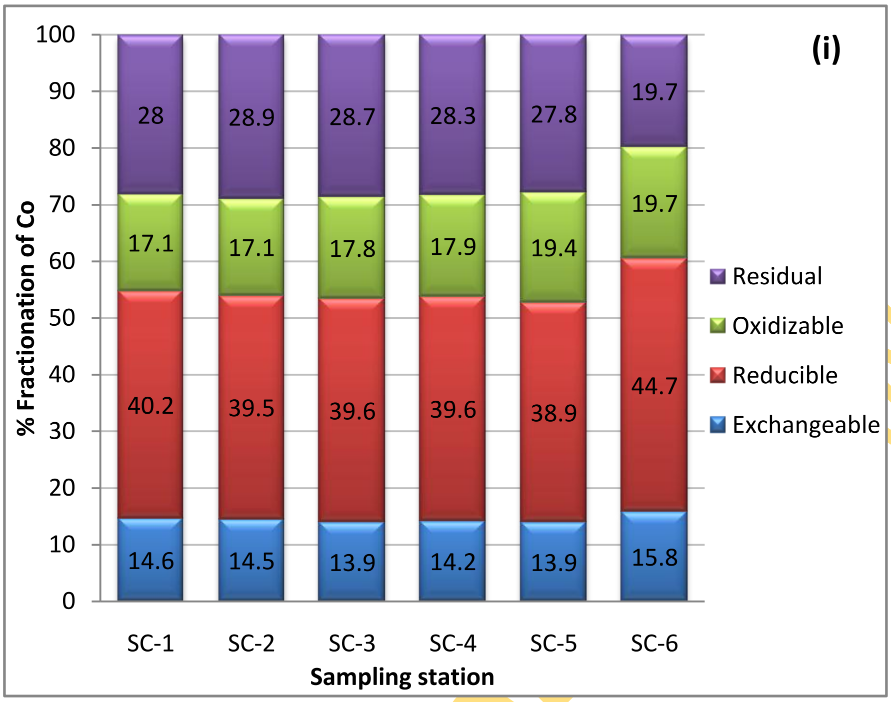

Fig. 4.4. Speciation of Co in sediments of Cross River

4.7 ASSESSMENT OF TRACE METALS CONTAMINATION IN SEDIMENT FRACTIONS

The determination of contamination factor of trace metals is very important for indication of the degree of risk of trace metals to the environment (Nemati *et al*., 2009; Naji *et al*., 2010). The individual contamination factors (ICF) for the various sampling stations were calculated using the results of speciation (fractionation) study. The ratio of the sum of concentration of the three non-residual fractions of the modified BCR procedure to that of the residual fraction for each sampling station was calculated using the equation below:

$$ICF_{metal} = \frac{C_{non-residual\ fraction}}{C_{residual}}$$

Also, the global contamination factor (GCF) for each sampling station was also calculated by summing ICF for all the metals, as follows:

$$GCF = \sum_{i=1}^{n} \mathrm{CFi}$$

The individual and global contamination factors for the seven sediment trace metals (Cd, Pb, Cr, Cu, Zn, Ni and Co) analysed are presented in Table 4.11. The highest ICF factor for all trace metals are: 9.33 for Cd (Nwaniba), 1.89 for Pb (James-Town), 4.43 for Cr (James-Town), 5.01 for Cu (James-Town), 5.03 for Zn (Ibaka), 2.57 for Ni (Ibaka) and 4.05 for Co (Ibaka) with the lowest contamination factor value of 1.54 for Pb obtained from Ibaka (Ibaka) station. Nwaniba, James-Town and Ibaka stations recorded the highest contamination for Cd, Pb-Cr-Cu and Zn-Ni-Co, respectively.

The individual contamination factor (ICF) is a reflection of the existing degree of contamination of a water body by a pollutant and a measure of the risk to the food chain. Therefore, highest risk of these trace metals was found at Ibaka station. Conversely, the least risks of the metals were calculated at Oron stations (SC-4). The mean individual contamination factor in sediments for all sampling stations follows the order: Cd > Zn > Cu > Cr > Co > Ni > Pb. On the other hand, the global contamination factor (GCF) analysed from the individual contamination factor (ICF) values shows that the upstream and downstream stations were highly impacted by metal pollutants. The highest GCF value is 29.24, ranging from 28.24 – 29.24. Therefore, the results obtained in this study showed that Nwaniba and Ibaka stations had the highest potential risk to fauna and flora.

Table 4.11. Individual and global contamination factors of trace metals in sediments from Cross River

Stations	ICF							GCF
	Cd	Pb	Cr	Cu	Zn	Ni	Co	
Okopedi	8.44	1.66	3.52	4.95	5.01	2.36	2.52	28.46
Ayadehe	9.20	1.66	3.43	4.96	5.02	2.34	2.51	29.12
Nwaniba	9.33	1.66	3.42	4.95	5.02	2.34	2.51	**29.24**
Oron	9.00	1.59	3.42	4.94	5.00	2.33	2.51	28.80
James Town	7.00	1.89	4.43	5.01	5.00	2.27	2.65	28.24
Ibaka	7.40	1.54	3.48	4.95	5.03	2.57	4.05	29.03
Mean	8.40	1.67	3.62	4.96	5.01	2.37	2.79	
Min	7.00	1.54	3.42	4.94	5.00	2.27	2.51	
Max	9.33	1.89	4.43	5.01	5.03	2.57	4.05	

4.8 CHEMICAL SPECIATION OF METALS IN SURFACE WATER USING PHREEQCI MODEL

Aqueous metal speciation was modelled using PHREEQCI version 2.18.5134 computer geochemical model in order to assess the chemical species/complexes present in the water, and the saturation states of the various minerals in water. Surface water contains natural organic matter and particles, both of which react with metals to reduce their bioavailability. Often, more than 90% of the metal present in the water is adsorbed on to particles or complexed with organic matter (Tepavitcharova *et al.*, 2011). Therefore, speciation of metals in water is critical to understanding metal behaviour in an aquatic system as well as metal speciation in sediment. The forms of chemical species of toxic metal in a water column, i.e. the organic and inorganic metal complexes and the free solvated metal ion could be used as a predictor of bioavailability to a particular aquatic organism. The free ion activity model (Morel and Herring, 1993), states that there is a correlation between the toxicity of a metal to an organism and the thermodynamic activity of the free aqua metal ion in solution.

The chemical behaviour of the metals and their species in water systems depends on the anion concentrations (e.g. OH^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, Cl^-, PO_4^{3-}, NO_2^-, NO_3^-) and the metal ability to coordinate predominantly with some of the anions. The solution composition of water quality parameters used for speciation modelling is presented in Table 4.12. The water speciation data of the different significant species of trace metal in solution showing their molar concentrations and percentage distribution are presented in Appendix 11.

4.8.1 Speciation of Cadmium

The different Cd species distributed were the chloride complexes, $CdCl^+$, $CdCl_2$, $Cd(Cl_3)^-$, the bicarbonate species, $Cd(HCO_3)^+$, the free hydrated Cd^{2+} and Cd(OH)Cl. The total Cd concentration in surface water was 1.43×10^{-7} M. Dissolved Cd in natural water system occurs in the +2 oxidation state. The uncomplexed free hydrated ion, Cd^{2+}, showed predominance ranging from 5.3 to 16.4% in all the stations sampled [Fig. 4.5 (i)] with James Town station (16.4%) recording maximum values. Cadmium species was dominated by inorganic chloride complex, $CdCl^+$ (79.5 – 82.3%), while $CdCl_2$ recorded percent abundance ranging from 4.0 to 10.2% with Okopedi station recording the highest $CdCl_2$ species.

Table 4.12. Solution composition (molL^{-1}) of water quality parameters in Cross River

Parameters	Sampling station					
	SC-1	**SC-2**	**SC-3**	**SC-4**	**SC-5**	**SC-6**
Ionic strength (M)	**$1.96x10^{-2}$**	**$8.46x10^{-3}$**	**$2.04x10^{-2}$**	**$2.94x10^{-2}$**	**$8.27x10^{-3}$**	**$2.02x10^{-2}$**
Alk ($CaCO_3$)	$5.64x10^{-4}$	$4.68x10^{-4}$	$6.15x10^{-4}$	$1.18x10^{-3}$	$4.86x10^{-4}$	$1.02x10^{-3}$
HCO_3	$6.63x10^{-4}$	$5.89x10^{-4}$	$4.83x10^{-3}$	$4.08x10^{-3}$	$9.92x10^{-4}$	$7.01x10^{-3}$
Ammonia	$1.14x10^{-5}$	$1.50x10^{-5}$	$4.29x10^{-5}$	$2.65x10^{-5}$	$3.29x10^{-5}$	$3.22x10^{-5}$
Nitrite	$1.29x10^{-6}$	$1.72x10^{-6}$	$2.37x10^{-5}$	$2.79x10^{-6}$	$4.72x10^{-6}$	$4.51x10^{-6}$
Nitrate	$2.27x10^{-4}$	$3.56x10^{-4}$	$2.06x10^{-3}$	$5.53x10^{-4}$	$1.01x10^{-3}$	$1.06x10^{-3}$
DO	$5.12x10^{-4}$	$5.39x10^{-4}$	$4.04x10^{-4}$	$4.46x10^{-4}$	$5.14x10^{-4}$	$4.42x10^{-4}$
Chloride	$3.72x10^{-2}$	$1.50x10^{-2}$	$3.66x10^{-2}$	$5.58x10^{-2}$	$1.38x10^{-2}$	$3.65x10^{-2}$
Fluoride	$1.01x10^{-5}$	$4.27x10^{-6}$	$2.80x10^{-5}$	$1.99x10^{-5}$	$2.05x10^{-5}$	$1.50x10^{-5}$
Phosphate	$2.10x10^{-6}$	$1.94x10^{-6}$	$3.72x10^{-6}$	$3.01x10^{-6}$	$8.72x10^{-7}$	$1.52x10^{-6}$
Sulphate	$2.86x10^{-4}$	$2.75x10^{-4}$	$3.29x10^{-4}$	$3.18x10^{-4}$	$2.83x10^{-4}$	$4.39x10^{-4}$
Cadmium	$3.56x10^{-8}$	$1.07x10^{-7}$	$1.87x10^{-7}$	$1.78x10^{-7}$	$1.51x10^{-7}$	$1.07x10^{-7}$
Lead	$8.22x10^{-8}$	$1.21x10^{-7}$	$5.80x10^{-8}$	$6.77x10^{-8}$	$1.35x10^{-7}$	$1.35x10^{-7}$
Chromium	$7.77x10^{-8}$	$1.55x10^{-7}$	$1.04x10^{-7}$	$1.38x10^{-7}$	$3.11x10^{-7}$	$2.94x10^{-7}$
Copper	$4.57x10^{-7}$	$5.04x10^{-7}$	$3.15x10^{-7}$	$3.94x10^{-7}$	$7.72x10^{-7}$	$8.99x10^{-7}$
Zinc	$3.26x10^{-6}$	$1.15x10^{-6}$	$9.65x10^{-7}$	$1.46x10^{-6}$	$2.11x10^{-6}$	$1.75x10^{-6}$
Nickel	$3.07x10^{-7}$	$3.92x10^{-7}$	$2.56x10^{-7}$	$8.03x10^{-7}$	$1.69x10^{-6}$	$1.71x10^{-6}$
Cobalt	$3.06x10^{-7}$	$4.58x10^{-7}$	$2.55x10^{-7}$	$3.40x10^{-7}$	$8.83x10^{-7}$	$9.86x10^{-7}$

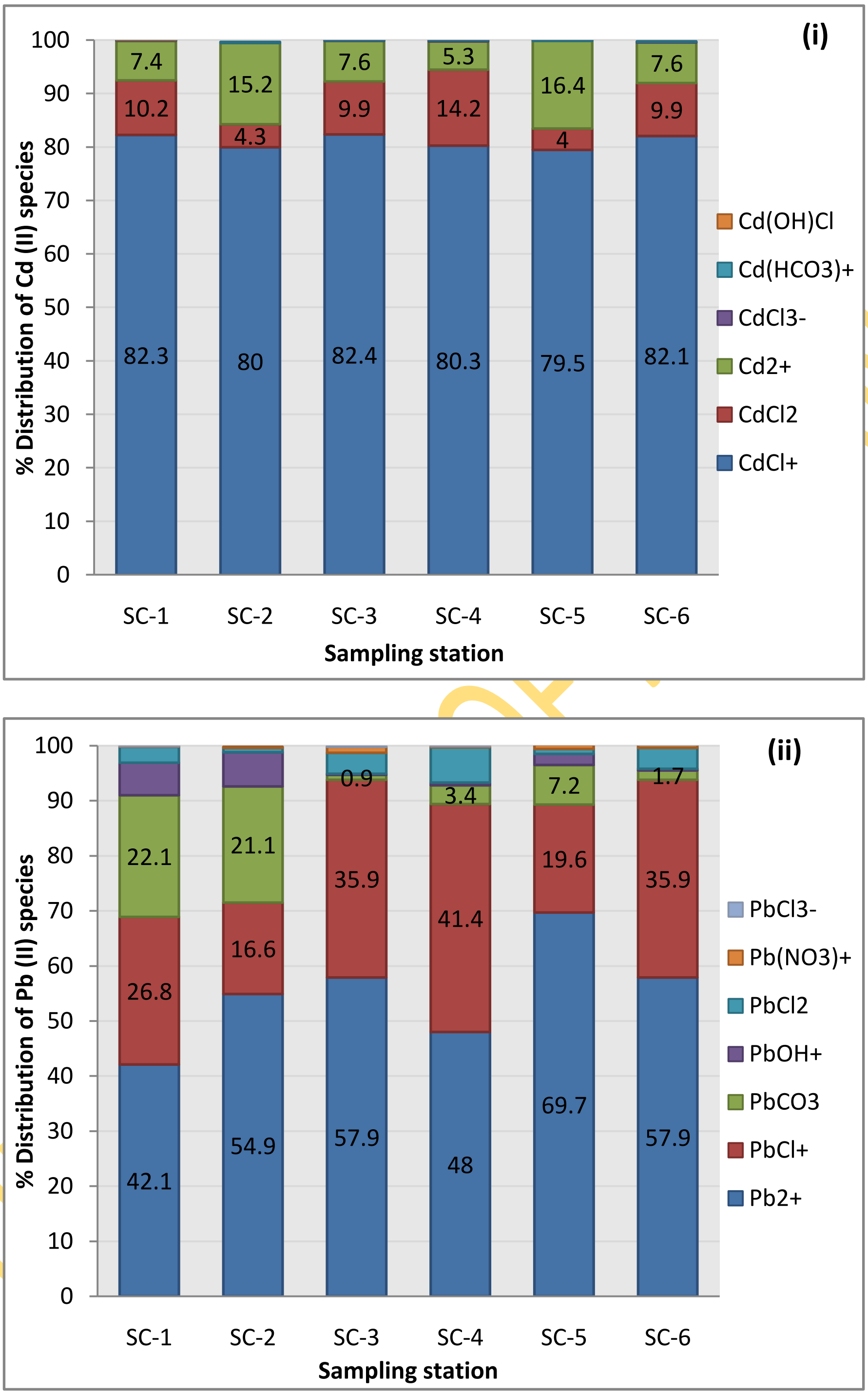

Fig. 4.5. Distribution of Cd (II) (i) and Pb (II) (ii) species in Cross River surface water

Other significant Cd species like $CdCl^{-}$, and $Cd(HNO_3)^+$ also recorded (8.9%) is undissolved and occurs as precipitates ($CdCl_2$), sorbed ions or as surface coatings on minerals or as suspended organic matter. Other possible species are $Cd(HCO_3)^+$ and $CdCl_3^-$ which account for about 0.1% each.

4.8.2 Speciation of Lead

Five different lead species showed significant distribution in the river system including, the free hydrated species (Pb^{2+}), chloride complex ($PbCl^+$) and neutral $PbCl_2$ salt, neutral $PbCO_3$ salt, $PbOH^+$ and $PbNO^+$ species. The free hydrated ion (Pb^{2+}) showed predominance (42.1 – 69.7%), followed by $PbCl^+$ (16.6 – 41.4%), $PbCl_2$ (0.8 – 6.4%), $PbCO_3$ (0.9 – 22.1%), and $PbOH^+$ was between 0.2 and 5.9% while only 0.1 – 1.1% was recorded for $Pb(NO_3)^+$ [Fig. 4.5 (ii)]. Amongst the different stations, the free hydrated species recorded distribution ranges between 42.1 and 69.7% with James Town station (low I = 0.0083M) having the highest distribution. The carbonate species showed significant distribution at Okopedi (22.1%), Ayadehe (21.1%) and James Town (7.2%) though not predominant, as reported earlier by Ettler *et al*. (2008) for waters polluted by municipal solid waste landfill leachate. Tepavitcharova *et al*. (2011) reported higher Pb^{2+} species at lower ionic strength (I=0.36) while higher values for $Pb(Cl_4)^{2-}$ was reported at higher ionic strength (about I=0.98).

4.8.3 Speciation of Chromium

Chromium is found in natural water system in two main oxidation states as, Cr(III) and Cr(VI). While Cr(III) is needed for metabolism, Cr(VI) is toxic and carcinogenic to living organisms and is highly mobile. From the result, Cr(III) ion was the dominant Cr species in solution with the hydroxyl complexes $Cr(OH)^{2+}$ (25.7–89.4%) and $Cr(OH)_2^+$ (6.5–69.7%) showing significant abundance [Fig. 4.6 (i)]. The uncomplexed hydrated species (Cr^{3+}) and neutral hydroxyl salt ($Cr(OH)_3$) were generally below 5% in all stations of the river. The complexed species dominated the solution system. Higher values were recorded for complexed hydroxyl species $Cr(OH)_2^+$ at Okopedi (89.4%), Ayadehe (89.1%), and James Town (73.3%) while Nwaniba (69.7%), Oron (51.2%) and Ibaka (67.3%) recorded higher distribution values for $Cr(OH)^{2+}$ as the predominant species. The free hydrated species (Cr^{3+}) showed significant concentration only at Nwaniba (4.2%) and Ibaka (3.5%) stations. The presence of the complexed hydroxyl species rendered the metal non-bioavailable to the aquatic biota.

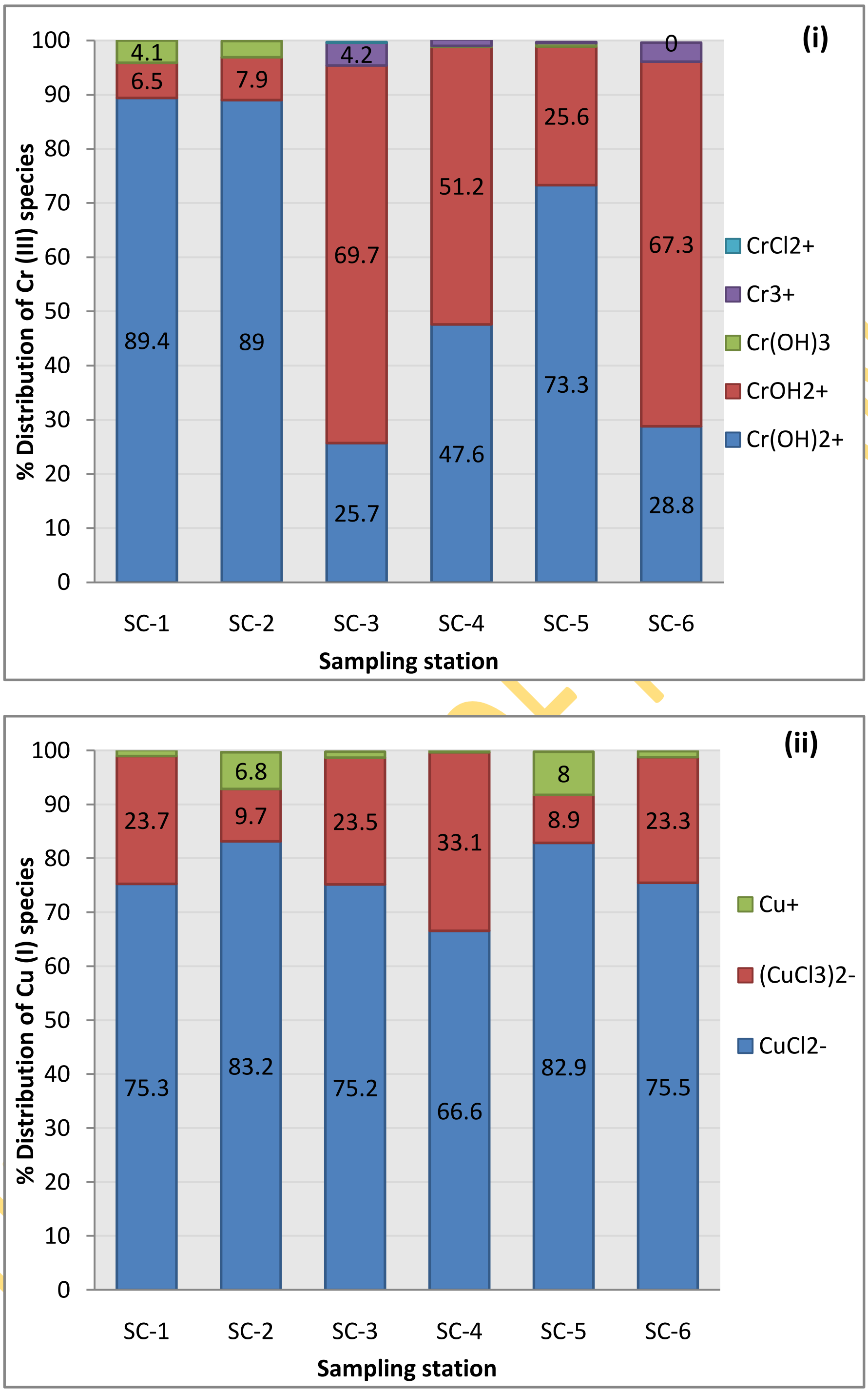

Fig. 4.6. Distribution of Cr (III) (i) and Cu (I) (ii) species in Cross River surface water

4.8.4 Speciation of Copper

Dissolved copper in natural water system occurs in two oxidation states, i.e. Cu(I) and Cu(II). The speciation results showed that about 68.3% of the total Cu concentration was dominated by Cu(I), while 31.7% existed as Cu(II). The most toxic copper species is the free cupric ion (Cu^{2+}), but other forms like $CuOH^{+}$ may be of concern when pH increases above 7.5. The complexed Cu(I) species indicated dominance of complexed chloride species, $CuCl_2^{-}$ (66.6-83.2%) and $CuCl_3^{2-}$ (8.9-33.1%) and the free hydrated Cu^{+} ion (0.5-8.9%) [Fig. 4.6 (ii)]. The significant Cu (II) species in solution were the free hydrated Cu^{2+} ion (36.2-88.1%), neutral $CuCO_3$ salt (3.3-46.5%), and the complexes of $CuOH^{+}$ (0.9-13.4%) and $CuCl^{+}$ (1.2-6.3%). Other significant species distributed included the neutral $CuSO_4$ salt and the complexed $Cu(PO_4)^{-}$ [Fig. 4.7 (i)]. The maximum content of the free hydrated Cu^{2+} species was obtained at Nwaniba station (88.1%) and Ibaka (84.9%) while Okopedi station recorded the least (36.2%) due to the predominance of the neutral $CuCO_3$ (46.5%). Okopedi and Ayadehe stations indicated comparable dominance of both the free hydrated ion and the neutral carbonate salt ($CuCO_3$) due to their comparable pH and alkalinity levels.

The model result also indicated that the neutral sulphate salt ($CuSO_4$) showed significant abundance in all the stations studied ranging from 0.8 to 2.9% with Ibaka station recording the highest distribution. Higher percentages of Cu^{2+} species recorded in this study agrees with values reported for seawater and hyper saline waters at higher ionic strength (I=0.37, 0.96) (Tepavitcharova *et al*., 2011). The competing nature of the neutral carbonate salt ($CuCO_3$) at Okopedi and Ayadehe stations thereby reduces bioavailability of the free hydrated species of Cu^{2+}. Copper toxicity is mostly attributed to the free Cu^{2+} and $CuOH^{+}$, and not the inorganic complexes. In some cases, $Cu_2(OH)_2^{2+}$ is also toxic although no significant distribution was recorded in this study.

4.8.5 Speciation of Zinc

Zinc has only one significant oxidation state, Zn (II). Results from the model indicate that the free hydrated species (Zn^{2+}) is the most soluble and dominant chemical species in surface water ranging from 89.7 to 94.3% of the total Zn in solution. Other significant species included complexes of $ZnCl^{+}$ (1.9-5.8%), $Zn(HCO_3)^{+}$ (0.8-1.6%) and neutral salts of $ZnSO_4$ (1.8-3.1%) and $ZnCl_2$ (~0.1%). The highest content of the free hydrated species, Zn^{2+} (94.3%) was recorded at James Town station [Fig. 4.7 (ii)].

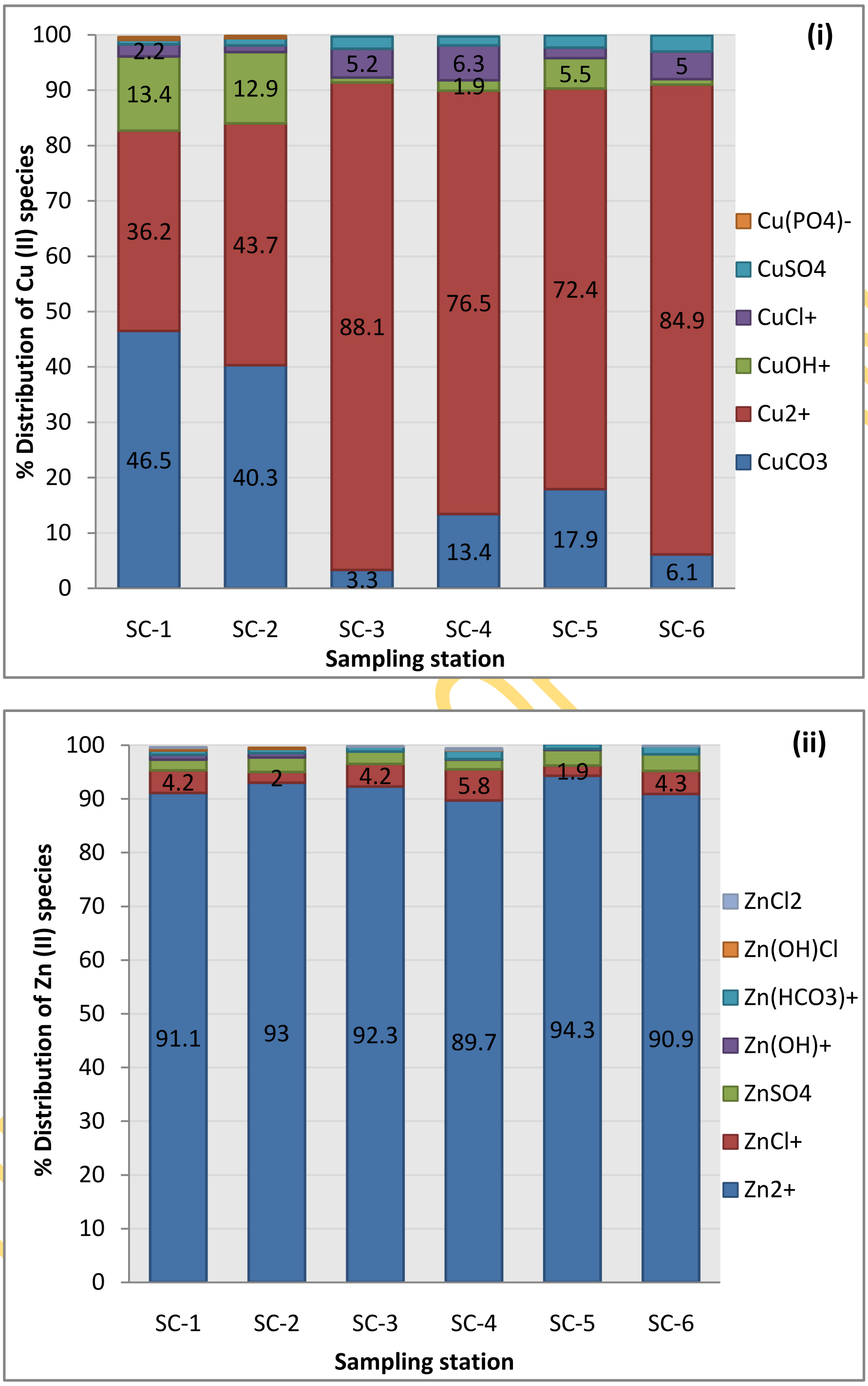

Fig. 4.7. Distribution of Cu (II) (ii) and Zn (II) (ii) species in Cross River surface water

4.8.6 Speciation of Nickel

Nickel like Zn has only one significant oxidation state of +2. The free hydrated species (Ni^{2+}) is the most soluble chemical species recording approximately 98% distribution in all the stations of the river system studied. Other significant chemical species included the neutral sulphate ($NiSO_4$), the chloride ($NiCl^+$) and nitrate ($NiNO_3^+$) complexes recording approximately 0.1 – 0.3% distribution [Fig. 4.8 (i)].

4.8.7 Speciation of Cobalt

Cobalt may occur in solution both as Co(II) and Co(III) oxidation states with Co(II) dominating. The free hydrated species (Co^{2+}) was predominant, ranging between 67.6% and 98.2% of total Co^{2+} concentration in all stations. The complexed species available in the system also included the $HCoO_2^-$ (0.3-30.1%), $CoCl^+$ (1.3-4.4%) and $Co(NO_3)^+$ (~0.1%). Among the stations studied, James Town station recorded the highest the distribution of the free hydrated species, Co^{2+}. The complexed species, $HCoO_2^-$, showed significant levels at Okopedi (30.1%) and Ayadehe (15.3%) stations. Okopedi and Ayadehe stations recorded about 67.6% and 83.4% of the free ionic Co^{2+} respectively, followed by the complexed species, $H(CoO_2)^-$ (30.1% and 15.3%), while Nwaniba, Oron and Ibaka stations recorded 96.5%, 95.6% and 96.8% Co^{2+} and 3.2%, 4.4% and 3.2% as $CoCl^+$ respectively [Fig. 4.8 (ii)].

4.9 CALCULATION OF SATURATION INDICES

It is very common that the interaction of surface water with certain mineral phases may endanger the water quality. A water sample, when collected, is usually no longer in contact with the mineral phases, and these phases may not be accessible. It is of interest then to determine with what mineral phases the water is saturated or nearly so. The calculated activities of the dissolved ions in water may be combined to produce the appropriate activity product which may be compared with the solubility equilibrium constant to show the degree of saturation of the water with various minerals considered.

The saturation index (SI) is approximately equal to zero when water is at equilibrium (balanced); that is, there is no thermodynamic tendency for net dissolution or net precipitation of the mineral. When the SI > 0, the water is supersaturated with that

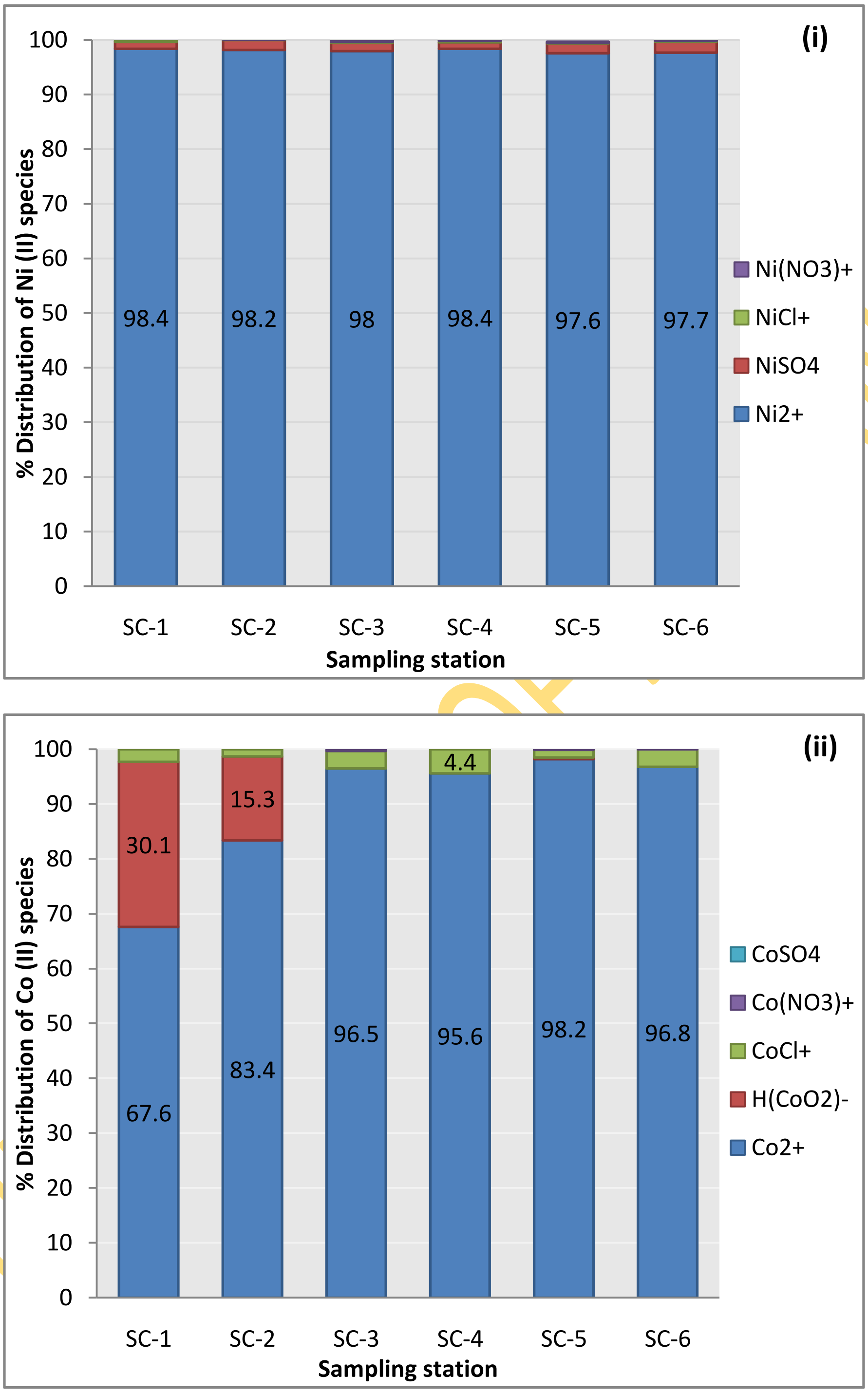

Fig. 4.8. Distribution of Ni (II) (i) and Co (II) (ii) species in Cross River surface water

mineral and would tend to precipitate. When $SI < 0$, the water is below saturation (undersaturated) with respect to the mineral and dissolution of the solid phases would be expected, and the water may be more likely to have a greater corrosive potential. Due to thermodynamic and analytical errors, there will be a range of uncertainty for the SI that must be taken into account. This uncertainty will vary according to both the complexity of the mineral stoichiometry and input data errors.

The partial pressure of carbon dioxide (P_{CO_2}) and saturation indices (SI) for the different mineral phases (Table 4.13) were calculated for the surface water samples using the PHREEQC Interactive Version 2.18.0.5134 program with Lawrence Livermore National Library (LLNL) thermodynamic (llnl.dat) database. The surface water chemistry exchanges matter with the various minerals and gases within any system resulting in a dissolution or precipitation of minerals. Equilibrium calculations are most commonly used to assess whether surface water is in equilibrium with respect to one or more minerals. The dissolution processes for most mineral phases examined would be considered with a relatively large reservoir of CO_2 (g) in the surface water. The high P_{CO_2} values provide dissolved CO_2 which means that the H_2CO_3 supplies the impurities in most of the mineral phase dissolution.

PHREEQC model is based on the ion association theory and can be used for speciation modelling for dilute aqueous solution with ionic strength less than 0.5. The surface water samples from Cross River system studied have ionic strength (I) in the range of 0.0083 to 0.0294 M. Speciation modelling provides saturation indices that indicate which reaction is thermodynamically possible, which mineral may be dissolving and which may be precipitating in an aquifer system. The primary purpose of speciation modelling is to calculate mineral saturation indices, which are indicators of saturation state of a mineral with respect to a given water composition. In Cross River, the surface water is undersaturated in most stations which indicate that most of the elements are more likely to be found as dissolved species. The minerals - $CdCr_2O_4$, $CuCr_2O_4$, $PbHPO_4$ and Pb-Pyromorphite, $Pb_5(PO_4)_3Cl$ showed some degrees of oversaturation in all the stations and the saturation index values for these minerals are in the range of 3.41 to 10.70, 2.88 to 10.52, 0.74 to 2.08 and 2.33 to 11.01 respectively

(Table 4.13). Except for the minerals mentioned above, approximately 87% of the samples indicate under

Table 4.13 Saturation Indices of some mineral phases in Cross River system

Phases	**Saturation Indices (SI)**						**log Ksp**	**Formula**
	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6		
Ionic strength (x 10^{-2}M)	1.96	0.846	2.04	2.94	0.287	2.02		
Anglesite	-3.60	-3.19	-3.56	-3.67	-3.02	-3.07	-7.91	$PbSO_4$
Cerrusite	-0.78	-0.64	-2.33	-1.69	-1.06	-1.69	-3.24	$PbCO_3$
CrO_2	-0.65	-0.63	-4.19	-2.92	-1.55	-3.49	-19.14	CrO_2
$CdCr_2O_4$	9.78	10.70	3.41	5.73	9.00	4.53	15.00	$CdCr_2O_4$
$CuCr_2O_4$	10.09	10.52	2.88	5.16	9.01	4.70	16.22	$CuCr_2O_4$
Cuprite	-1.30	-0.68	-4.51	-4.16	-1.14	-3.48	-1.91	Cu_2O
Hydrocerrusite	-3.49	-3.13	-9.75	-7.64	-5.01	-7.95	1.85	$Pb_3(OH)_2(CO_3)_2$
Malachite	-2.76	-2.35	-7.49	-6.43	-3.36	-6.16	5.90	$Cu_2(OH)_2CO_3$
Nantokite	-3.41	-3.33	-3.45	-3.54	-3.01	-3.01	-6.77	CuCl
Otavite	-3.33	-2.68	-4.14	-3.65	-3.07	-4.10	-1.77	$CdCO_3$
Paralaurionite	-2.39	-2.55	-3.98	-3.44	-3.03	-3.56	0.20	PbClOH
$Pb_3(PO_4)_2$	-1.55	-0.92	-6.83	-5.51	-3.24	-6.25	-19.97	$Pb_3(PO_4)_2$
$PbHPO_4$	1.80	2.08	0.74	0.99	1.44	0.78	-15.73	$PbHPO_4$
Pyromorphite	10.27	11.01	2.33	4.46	7.58	3.39	-47.90	$Pb_5(PO_4)_3Cl$
Smithsonite	-2.42	-3.01	-4.48	-3.63	-3.31	-3.93	0.44	$ZnCO_3$
Sphaerocobaltite	-2.88	-2.76	-4.34	-3.54	-2.96	-3.45	-0.26	$CoCO_3$
Tenorite	-0.86	-0.69	-4.03	-3.41	-1.50	-3.43	7.65	CuO
Tsumebite	-3.47	-2.96	-10.87	-9.20	-5.46	-9.76	2.53	$Pb_2Cu(PO_4)(OH)_3{:}3H_2O$
Zincite	-2.72	-3.39	-6.38	-5.37	-4.28	-5.97	11.20	ZnO
$ZnCO_3{:}H_2O$	-2.19	-2.77	-4.24	-3.41	-3.07	-3.71	0.14	$ZnCO_3{:}H_2O$
CO_2	-2.48	-2.40	-0.86	-1.02	-1.78	-0.70	-7.83	CO_2
O_2	-0.67	-0.65	-0.77	-0.73	-0.67	-0.73	-2.89	O_2

saturation with respect to other mineral phases studied as a reflection of some minor presence in the river bed or system. Therefore, surface water composition was largely controlled by the dissolution of chromate and phosphate minerals in the river basin.

4.10 SURFACE WATER QUALITY OF QUA IBOE RIVER

The results of physicochemical and trace metals analysis (as presented in Appendices 12 and 14) of surface water samples from Qua Iboe River system were used to assess the water quality and to determine the pollution status of the river. The mean levels of physicochemical properties are presented in Table 4.14.

4.10.1 Temperature

Average temperature of the surface water was 29.6±2.9 ^{o}C, and dry season samples recorded higher temperature values (Appendix 13).

4.10.2 pH

pH ranged from 6.49 to 7.34 pH. The highest pH value was obtained from lwuokpom 1 station (SQ-1) while the least value (pH 6.49) was obtained from Eketai station.

4.10.3 Total Alkalinity

Mean alkalinity was 61±35 mgL^{-1} and ranged from 17 to 132 mgL^{-1} (Table 4.14).The highest concentration 93±17 mg L^{-1} was obtained from Iwuokpom 2 station. Higher alkalinity values were obtained during the dry season as revealed at Iwuokpom 2 station with value of 101 mgL^{-1} (Appendix 13). The mean value in this study is higher than values, 13.9±3.8 mgL^{-1}, 1.65 mgL^{-1}, and 1.76-28.0 mgL^{-1} reported for Esi River, Warri (Akporido, 2010), Ethiope River (Agbaire and Obi, 2009) and Ogunpa River (Onianwa *et al.*,2001) and lower than values (47.1-226.0 mgL^{-1}) reported for Elechi Creek (Obire *et al.*, 2003). However, at all stations, results obtained are within national and international guideline value of 200 mgL^{-1} for drinking water quality (FEPA. 1991; WHO, 2008).

4.10.4 Turbidity

Turbidity levels ranged between 25.4 and 85.4 (50.5±16.0) NTU (Table 4.14). The highest turbidity concentration (70.4±11 NTU) was obtained from Atabong station.

Table 4.14. Physicochemical properties of surface water samples from Qua Iboe River

Parameters*	Sampling stations/Code						Mean±SD	Range
	Iwuokpom 1 (SQ-1)	Iwuokpom 2 (SQ-2)	Iwuochang (SQ-3)	Eketai (SQ-4)	Atabong (SQ-5)	Marina (SQ-6)		
Temperature[a]	28.9±2.8	29.2± 2.9	29.8±3.0	29.5±2.7	30.1±3.2	30.1±3.11	29.5±2.8	25.1–34.6
pH (range)	7.01-7.34	6.92-7.27	6.69-7.21	6.49-6.82	6.52-6.97	6.54-6.88	6.89±0.24	6.49–7.34
Alkalinity	81.0±15	93±17	57.5±22	25.0±10	33.4±14	28.3±8.8	61.3±35.1	17–132
Turbidity[b]	40.0±4.9	37.7± 5.3	56.2±5.2	32.2±4.2	70.4±11.0	52.7±5.0	50.5±16.0	25.4–85.4
TDS	668±94	833±150	390±87	154±26	264±81	202±28	495±315	113–1300
E. Conductivity[c]	1630 ±190	1990±220	972±210	385±66	661±61	504±78	1210±740	288-3182
Total Hardness	27±10	24±5	21±2	242±79	669±200	579±260	222±290	17-1003
Dissolved Oxygen	7.0±1.4	7.3±1.5	5.8±1.5	6.9±0.9	5.3±0.4	6.3±0.9	6.4±1.3	3.9–9.3
COD	25.3±1.7	20.5±1.3	19.2±1.5	24.6±2.7	18.9±1.6	18.2±1.9	21.9±3.8	14.4–30.9
BOD_5	2.94±0.40	2.81±0.44	2.76±0.52	3.25±0.67	2.76±0.48	2.78±0.63	2.80±0.73	1.14–4.20
Chloride	1150±280	1330±330	714±190	292±92	498±150	338±73	860±550	172–2422
Fluoride	1.05±0.08	1.05±0.07	0.14±0.03	0.06±0.03	0.10±0.05	0.17±0.04	0.53±0.48	0.003–1.21
NH_3-N	0.36±0.29	0.34±0.25	0.49±0.26	0.64±0.33	0.61±0.29	0.47±0.24	0.46±0.29	0.01–1.13
NO_3^--N	1.9±0.7	3.0±0.8	4.5±1.4	4.6±1.1	9.8±2.7	6.1±1.8	4.6±2.9	1.3–14.4
NO_2^--N	0.03±0.03	0.05±0.02	0.09±0.c02	0.10±0.03	0.17±0.03	0.10±0.03	0.09±0.05	0.01–0.21
PO_4^{3-}	0.11±0.04	0.07±0.02	0.07±0.02	0.13±0.02	0.11±0.02	0.12±0.02	0.10±0.03	0.02–0.15
SO_4^{2-}	33.2±11.0	30.7±13.0	32.4±9.8	38.1±4.2	40.0±4.0	41.8±4.4	36.2±9.8	10.3–54.7

*All units are expressed in mgL^{-1} unless otherwise stated, [a]Temperature in °C, [c] Electrical conductivity as µScm^{-1}, [b] Turbidity in NTU.

The mean turbidity was comparable with those of other rivers in the Niger Delta and other parts of the world. Turbidity range of 21.0-29.4 NTU was reported for Orogodo River by Rim-Rukeh *et al.* (2006), while Omo-Irabor *et al.* (2008) reported 33.3 mgL^{-1} for rivers in Western Niger Delta and Dulo (2008) reported mean value of 41.5 NTU for Nairobi River. Turbidity values obtained from all stations exceeded the WHO limit (2.5 NTU) for drinking water quality (WHO, 2008).

4.10.5 Total Dissolved Solids (TDS)

TDS levels ranged from 113 to1300 (495±315) mgL^{-1}. The highest value of 1300 mgL^{-1} was obtained from one of the downstream stations, Iwuokpom 2 with a mean value of 833±150 mgL^{-1}. This was attributable to marine intrusion from the coast of Atlantic Ocean. Seasonal values obtained showed higher levels recorded during the dry season. 668±94 and 833±150 mgL^{-1}.

4.10.6 Electrical Conductivity (EC)

Electrical conductivity (EC) values ranged from 288-3180 µScm^{-1} (Table 4.14). The highest value of 1990±220 µScm^{-1} was obtained from Iwuokpom 2 station, while Eketai station recorded the lowest concentration of 385±66 µScm^{-1}. Higher values of conductivity were obtained during the dry season (Appendix 13).

4.10.7 Total Hardness

Total hardness ranged from 17 mgL^{-1} to 1003 mgL^{-1} (Table 4.14), with highest values of 479±350 mgL^{-1} recorded during the dry season for Marina station (Appendix 13).

4.10.8 Dissolved Oxygen (DO)

Dissolved oxygen values ranged from 3.9 to 9.3 mg/L and averaged 6.4±1.3 mgL^{-1} (Table 4.14), indicating the presence of adequate dissolved oxygen to maintain aquatic life. The highest DO value of 7.3±1.5 mgL^{-1} was obtained at Iwuokpom 2 followed by 7.0±1.4 mgL^{-1} at Iwuokpom 1. Higher values occurred during the dry season than the wet season. Atabong station recorded the lowest DO level with a mean value of 5.3±0.5 mgL^{-1}.

4.10.9 Chemical Oxygen Demand (COD)

The COD values obtained ranged from 14.4 to 30.9 (21.9±3.8) mgL^{-1} (Table 4.14). The highest COD value of 25.3±1.7 mgL^{-1} was obtained from Iwuokpom 1 while Marina recorded the least value of 18.2±1.9 mgL^{-1}. The COD values were significantly higher during the dry season with the highest values of 26.2±1.8 and 26.5±1.8 mgL^{-1} recorded at Iwuokpom 1 and Eketai stations respectively.

4.10.10 Biochemical Oxygen Demand (BOD)

The BOD values obtained ranged from 0.89 to 4.20 mgL^{-1}, with Eketai station recording the highest average BOD value of 3.25±0.67 mgL^{-1} (Table 4.14). Higher BOD values were obtained during the dry season. The BOD levels reported fell within the recommended and 0 - 6 mgL^{-1} limit for drinking water quality (WHO, 2008), and also within limit of 10 mgL^{-1} recommended by FEPA (1991).

4.10.11 Chloride

Chloride levels ranged from 172 to 2420 mgL^{-1} with mean value of 860±550 mgL^{-1} (Table 4.14). Highest chloride level was obtained from Iwuokpom 2 station with mean value of 1330±330 mgL^{-1}, while the lowest mean chloride value of 292±92 mgL^{-1} was obtained at Eketai station. Higher chloride levels were obtained during the dry season (Appendix 13). The wet season samples recorded low chloride levels which may be attributed to increased dilution by rainwater. Higher levels of chloride were recorded at the downstream stations (Iwuokpom 1 and Iwuokpom 2), attributable to the influence of intrusion of saline water from the Atlantic Ocean. The chloride content in this study, generally, is above the permissible levels of WHO guideline limits (250 mgL^{-1}) for drinking water quality (WHO, 2008). Values obtained are higher than those obtained for Esi River, Warri (1.45±0.92 mgL^{-1}) (Akporido, 2010) and Ogunpa River (70.5-688.0 mgL^{-1}) (Onianwa *et al.*, 2001).

4.10.12 Fluoride

Fluoride concentration ranged from 0.003 mgL^{-1} to 1.21 mgL^{-1}. Both Iwuokpom1 and Iwuokpom 2 stations recorded highest fluoride level of 1.05±0.07 mgL^{-1} in this study. The lowest value was obtained at Eketai station with mean value of 0.06±0.03 mgL^{-1}

(Table 4.14). The concentrations are within the permissible level for drinking water and water for fish production (HACH, 2003).

4.10.13 Ammonia

Average concentration of ammonia was 0.46±0.29 mgL^{-1} (Table 4.14). Eketai station (SQ-4) recorded the highest concentration of 0.64±0.33 mgL^{-1}. Higher concentrations occurred during the wet season (Appendix 13).

4.10.14 Nitrate

Nitrate levels ranged from 1.3 to 14.4 mgL^{-1} with mean of 4.6±2.9 mgL^{-1}. Maximum and minimum nitrate values, 9.8±2.7 mgL^{-1} and 1.9±0.7 mgL^{-1}were obtained from Atabong and Iwuokpom 1 stations respectively (Table 4.14). The wet season samples recorded the highest nitrate values during the wet season except Atabong and Marina whose source of nitrate is attributed to municipal sewage discharge into the river. Nitrate levels in this study did not exceed the WHO maximum permissible limit of 50 mgL^{-1} (WHO, 2008).

4.10.15 Nitrite

Nitrite levels obtained ranged from 0.01 to 0.21 mgL^{-1} with mean value of 0.09±0.05 mgL^{-1} (Table 4.14). Atabong station recorded the highest mean value of 0.17±0.03 mgL^{-1}. Higher nitrite levels were obtained during the dry season than wet season (Appendix 13).

4.10.16 Phosphate

Average phosphate level in this study was 0.10±0.03 mgL^{-1}, with the highest value, 0.13±0.02 mgL^{-1}, obtained at Eketai station. Low phosphates values were recorded in this study compared with reports from other surface water bodies in the Niger Delta (Rim-Rukeh *et al.*, 2006; Nduka *et al.*, 2008). High phosphate from Eketai was attributable to the use of phosphate detergents and use of phosphate fertilizers in nearby agricultural farmlands which enters the stream through surface runoff as reported by Adeyemo *et al.* (2008) for river sediment in Ibadan. Phosphate levels in this study are within the WHO tolerable limit of 2.0 mgL^{-1} (WHO, 2008)

4.10.17 Sulphate

The average sulphate level obtained in this study is 36.2±9.8 mgL^{-1} with Marina recording the highest mean value of 41.8±4.4 mgL^{-1}, while the least value, 30.7±12.7 mgL^{-1}, was obtained from Iwuokpom 2. Results obtained showed that higher levels of sulphate were obtained during the dry season in all the sampling stations (Appendix 13). This was attributable to surface run-off from surrounding agricultural farmlands using sulphate fertilizers for nutrient enrichment. Sulphate levels in this study were far higher than mean value (3.3±0.4 mgL^{-1}) reported for Qua Iboe River estuary by Essien *et al.* (2009b). However, results obtained were within the tolerable limits of 500 mgL^{-1} (WHO, 2008).

4.10.18 Correlation Analysis of Physicochemical Parameters

The correlation matrix analyses of physicochemical variables in Qua Iboe River surface water (Table 4.15) showed strong positive correlations, significant at $P<0.05$, between the pairs alkalinity and TDS ($r = 0.864$), alkalinity and EC ($r = 0.905$), alkalinity and chloride ($r = 0.883$), alkalinity and fluoride ($r = 0.873$); TDS and EC ($r = 0.982$), TDS and chloride ($r = 0.892$), TDS and fluoride ($r = 0.898$); EC and chloride ($r = 0.926$), EC and fluoride ($r = 0.912$). TDS showed the highest positive correlations with electrical conductivity ($r = 0.982$). The significant correlation between the pairs is indicative of a common source of contamination.

4.11 TRACE METAL LEVELS IN SURFACE WATER OF QUA IBOE RIVER

Results of trace element concentration and seasonal metal variation in surface water samples are presented in Table 4.16 and Appendix 14 respectively.

4.11.1 Cadmium

The mean Cd concentration was 41±49 μgL^{-1} with Iwuochang (100±32 μgL^{-1}) and Atabong (105±43 μgL^{-1}) recording the highest significant Cd level. The downstream stations near the Atlantic coast Iwuokpom 1 and Iwuokpom 2 stations recorded very low levels of Cd, 3±1 μgL^{-1} and 4±4 μgL^{-1} but the significantly high level at Iwuochang could be related to the detritus materials and wastes dumped at the bank of the river. On the other hand, high level obtained at Atabong was attributed to automobile tyre wear from nearby highway and regular burning of automobile tyres by butchers at the river

Table 4.15: Pearson correlation coefficient (r) of physicochemical properties of Qua Iboe River

Parameters	Temp	Alkalinity	Turbidity	TDS	Elect. Cond.	Hardness	DO	COD	BOD_5	Cl^-	F^-	NH_3–N	NO_3^-–N	NO_2^-–N	PO_4^{3-}	SO_4^{2-}
Temp.	1															
Alkalinity	0.264	1														
Turbidity	0.189	0.108	1													
TDS	- 0.073	0.864[a]	0.032	1												
E. Cond.	- 0.073	0.905[a]	0.046	0.982[a]	1											
Hardness	- 0.111	- 0.680[a]	0.243	- 0.598[a]	- 0.611[a]	1										
DO	0.601[a]	0.397	0.395	0.178	0.257	- 0.381	1									
COD	0.192	0.442	- 0.180	0.400	0.449	- 0.435	0.394	1								
BOD_5	0.605[a]	0.307	0.086	0.075	0.133	- 0.280	0.517	0.337	1							
Cl^-	0.063	0.883[a]	0.094	0.892[a]	0.926[a]	- 0.583[a]	0.258	0.484	0.171	1						
F^-	- 0.021	0.873[a]	- 0.120	0.898[a]	0.918[a]	- 0.589[a]	0.349	0.500	0.122	0.853[a]	1					
NH_3–N	0.564[a]	- 0.160	- 0.011	- 0.362	- 0.294	0.187	0.350	0.140	0.431	- 0.242	- 0.320	1				
NO_3^-–N	0.118	- 0.571	0.395	- 0.559	- 0.574	0.655[a]	- 0.327	- 0.497	0.019	- 0.544	- 0.640[a]	0.073	1			
NO_2^-–N	0.481	- 0.431	0.407	- 0.543	- 0.495	0.562[a]	- 0.067	- 0.158	0.135	- 0.424	- 0.600[a]	0.467	0.750[a]	1		
PO_4^{3-}	0.548[a]	- 0.237	- 0.087	- 0.393	- 0.328	0.304	0.430	0.359	0.298	- 0.263	- 0.221	0.532[a]	0.149	0.496	1	
SO_4^{2-}	0.544[a]	- 0.061	0.161	- 0.261	- 0.147	0.280	0.439	0.129	0.376	- 0.021	- 0.178	0.494	0.194	0.480	0.582[a]	1

[a] [a] *Values are significant at* $p<0.05$

Table 4.16. Mean trace metal concentrations (μgL^{-1}) of surface water samples from Qua Iboe River

Sampling station	Metal concentration						
	Cd	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
Iwuokpom 1	3±1	27±9	17±6	48±15	205±89	26±10	46±18
Iwuokpom 2	4±4	19±6	18±8	35±12	141±73	16±5	32±12
Iwuochang	100±32	14±7	40±14	34±14	104±36	12±4	18±27
Eketai	6±3	11±14	51±50	19±7	68±26	8±5	7±3
Atabong	105±43	79±53	110±35	210±85	250±81	200±57	126±42
Marina	60±26	30±11	55±22	97±29	223±83	169±69	104±36
Mean±SD	41±49	31±30	45±39	70±71	163±89	62±82	55±48
Range	1 – 167	1 – 220	3 – 171	9 – 345	34 – 391	2 – 311	3 – 195

bank. Results obtained in this study compares favourably with values reported for Iko River, Akwa Ibom (40 µgL^{-1}) by Benson and Etesin (2008) but lower than values reported for Ubeji Creek, Delta (740 µgL^{-1}), Okirika River, Port Harcourt (160±40 µgL^{-1}), and Abuloma River, Port Harcourt (150±20 µgL^{-1}) by Nduka and Orisakwe (2010). The mean Cd levels exceeded the WHO guideline limit of 3 µgL^{-1} for drinking water (WHO, 2008).

4.11.2 Lead

Average Pb level in surface water was 31±30 µgL^{-1} ranged from 1 to 220 µgL^{-1}. The highest Pb value (79±53 µgL^{-1}) was obtained from Atabong while Eketai station recorded the least value of 11±14 µgL^{-1}. High Pb at Atabong station was attributable to discharged effluents from filling stations located around the site and also to the cumulative effect of exhaust emissions from heavy duty trucks along the highway. However, mean values from all stations exceeded the WHO maximum guideline value (10 µgL^{-1}) for drinking water (WHO, 2008). Results obtained compared favourably with River Ijana (25-58 µgL^{-1}) and Esi River, Warri (39 µgL^{-1}) reported by Emoyan *et al.* (2006) and Akporido (2010), respectively.

4.11.3 Chromium

The mean Cr level of 45±39 µgL^{-1} (3 to 171 µgL^{-1}) was obtained in this study. Apart from Iwuokpom 1 and Iwuokpom 2 stations all the other stations studied recorded mean values which exceeded the 20 µgL^{-1} level reported by Essien *et al.* (2009b) for asphyxiated mangrove ecosystem of Qua Iboe River estuary. However, the result compares with those reported for River Ijana (37 - 67 µgL^{-1}) by Emoyan *et al.* (2006). The mean Cr levels at stations Iwuochang and Atabong exceeded the maximum allowable concentration for drinking water (WHO, 2008).

4.11.4 Copper

Copper level in surface water ranged from 9 to 345 µgL^{-1} with mean value of 70±71 µgL^{-1}. The maximum level was obtained from Atabong station (210±85 µgL^{-1}) followed by Marina (97±29 µgL^{-1}) (Table 4.16). However, results obtained from all stations were below the maximum limit of 2000 µgL^{-1} recommended for drinking water (WHO, 2008). High Cu level was obtained during the dry season than in wet season. The high Cu level in Atabong station was indicative of high organic matter input from municipal/domestic sewage into the river as reported by Khan and Khan (2003) for littoral sediments in Chittagong, Bangladesh. However, values obtained in this study compares favourably with reports for Okirika River (80±10 µgL^{-1}) and Lagos Lagoon by Nduka and Orisakwe (2010) and Aderinola *et al.* (2009) respectively (197 µgL^{-1}).

4.11.5 Zinc

The range (mean value in parenthesis) of Zn obtained in this study is 34–391 (163±89) µgL^{-1} (Table 4.16). Almost all the stations except Eketai (68±26 µgL^{-1}) recorded high Zn levels. The highest value was obtained from Atabong (250±81 µgL^{-1}) followed by Marina (223±83 µgL^{-1}) both located within Eket urban. Zinc levels were significantly higher during the dry season, attributed to heavy sewage discharge from urban sewage lines in Eket urban. Zinc is frequently associated with sewage (Muniz *et al.*, 2004).

The high Zn levels obtained from the downstream stations near Atlantic coast are attributed to materials originating from the natural mineral composition of the coastal areas which is rich in sulphide (Prieto *et al.*, 2008). However, from all the studied stations, Zn level fell within the WHO guideline limit of 3.0 µgL^{-1} for drinking water (WHO, 2008).

4.11.6 Nickel

Nickel levels in this study ranged from 2 µgL^{-1} to 311 µgL^{-1} with mean value of 62±82 µgL^{-1}. Atabong station recorded the highest mean value of 200±57 µgL^{-1} while Eketai recorded the lowest value of 8±5 µgL^{-1} in this study. Results obtained show higher Ni levels than those reported for asphyxiated mangrove swamp of Qua Iboe River by Essien *et al.* (2009b), but lower than values reported for Ubeji River (Nduka and Orisakwe, 2010) all in the Niger Delta.

4.11.7 Cobalt

The mean Co level in this study was 55±48 µgL^{-1} with values ranging from 3 to 195 µgL^{-1}. Eketai station recorded the lowest Co level (7±3 µgL^{-1}) while the highest level (126 µgL^{-1}) was obtained from Atabong station. Almost all stations except Iwuochang recorded higher levels of Co during the dry season with maximum value of 159±26 µgL^{-1} for Atabong and 131±29 µgL^{-1} for Marina (Table 4.16, Appendix 15). Cobalt is a transition metal that is a micronutrient for the growth of plants and animals.

Concentrations of cobalt in natural water are generally less than a few micrograms per liter (Hem, 1989).

The Pearson correlation coefficient analysis of trace metals concentrations shows significant strong correlations ($r \geq 0.800$, $p < 0.05$, df.=70) between the pairs: Cu and Ni, Cu and Co; Zn and Co and Ni and Co (Table 4.17). But, few metals shows moderately positive correlations ($r \geq 0.500$), including the pairs: Cd and Pb (0.528), Cd and Cr (0.675), Cd and Cu (0.672), Cd and Ni (0.605), Cd and Co (0.528); Pb and Ni (0.695), Cr and Zn (0.524) and Ni and Zn (0.685).

4.12 SEDIMENT QUALITY OF QUA IBOE RIVER SYSTEM

Mean results of physicochemical characteristics of bottom sediments are presented in Table 4.18.

4.12.1 pH

The pH value obtained from sediment ranged from 6.56 to 8.11. Iwuokpom 1 station recorded the highest pH value which ranged from 6.67 to 8.11 (Table 4.18). However, there was no significant variability in the pH range across all the stations under study.

4.12.2 Electrical Conductivity (EC)

Mean conductivity level obtained for the river system was 9460±4700 μScm^{-1}. Higher values were obtained from Iwuokpom 2 (15200±2500 μScm^{-1}) and Iwuochang (13500±2400 μScm^{-1}) attributable to chloride influence owing to the tidal intrusion of marine water from Atlantic Ocean.

4.12.3 Nitrate and Nitrite

Mean value (range in parenthesis) of nitrate obtained was 167±30 $mgkg^{-1}$ (113 – 234 $mgkg^{-1}$) while nitrite 6.1±1.6 $mgkg^{-1}$ (3.0 – 9.1 $mgkg^{-1}$) was obtained for nitrite. The highest nitrate level with mean concentration of 205±29 $mgkg^{-1}$ was recorded at Iwuochang station while Iwuokpom 2 recorded the highest NO_2^- concentration of 7.2±1.9 $mgkg^{-1}$ (Table 4.18).

Table 4.17. Pearson correlation coefficient (r) of trace metals in surface water from Qua Iboe River system

Metals	Cd	Pb	Cr	Cu	Zn	Ni	Co
Cd	1.000						
Pb	0.528^a	1.000					
Cr	0.675^a	0.711^a	1.000				
Cu	0.672^a	0.880^a	0.794^a	1.000			
Zn	0.414	0.703^a	0.524^a	0.729^a	1.000		
Ni	0.605^a	0.695^a	0.715^a	0.865^a	0.685^a	1.000	
Co	0.528^a	0.764^a	0.647^a	0.889^a	0.831^a	0.882^a	1.000

^{a} *Values are significant at p<0.05.*

Table 4.18. Physicochemical properties of bottom sediments from Qua Iboe River

Parameters	Sampling stations							
	Iwuokpom 1	Iwuokpom 2	Iwuochang	Eketai	Atabong	Marina	Mean±SD	Range
Temp. °C	29.5±2.5	29.7±2.4	29.8±2.5	29.7±2.6	30.0±2.9	30.0±2.8	29.8±2.42	26.1–34.4
pH	6.67–8.11	6.56–7.55	6.92–7.95	6.61–7.15	6.78–7.11	7.02–7.24	–	6.56–8.11
E. Cond. (μScm^{-1})	4980±4300	15200±2500	9680±2800	5380±3300	13500±2400	8030±1300	9460±4700	1400–19400
NO_3^- - N ($mgkg^{-1}$)	150±15	162±37	205±29	183±17	150±17	156±13	167±30	113–234
NO_2^- - N ($mgkg^{-1}$)	6.4±1.8	7.2±1.9	6.6±1.6	5.1±1.3	6.0±1.4	5.4±1.3	6.1±1.6	3.0–9.1
PO_4^{3-} ($mgkg^{-1}$)	339±140	118±41	324±160	93±37	185±57	160±64	203±130	28–471
SO_4^{2-} ($mgkg^{-1}$)	247±42	466±160	242±46	268±52	210±27	158±23	265±120	123–606
TOC (%)	0.56±0.37	1.73±0.79	1.23±0.13	0.67±0.10	0.51±0.30	0.38±0.25	0.85±0.61	0.11–2.34
TOM (%)	0.97±0.63	2.99±1.40	2.12±0.23	1.16±0.13	0.87±0.52	0.66±0.42	1.46±1.10	0.19–4.03
% Sand	72.2±3.2	63.0±3.3	60.7±3.3	84.6±1.8	57.3±0.8	75.6±2.8	68.9±10.0	57.5–85.9
% Silt	9.8±0.4	14.2±1.9	16.3±1.5	8.4±0.6	15.3±0.5	9.8±1.7	12.3±3.3	7.8 – 17.8
% Clay	18.1±3.0	22.8±1.4	23.1±1.7	7.0±1.3	27.4±0.6	14.5±1.2	18.8±7.0	6.2 – 27.9

4.12.4 Phosphate

The mean phosphate concentration (range in parenthesis) for sediment samples was 203±130 (28 – 471) mgkg^{-1}. The highest mean phosphate values, 339±140 mgkg^{-1} and 324±160 mgkg^{-1} (Table 4.18), were obtained from stations Iwuokpom 1 and Eketai respectively, attributable to the use of phosphate detergents.

4.12.5 Sulphate

The mean sulphate concentration obtained in this study was 265±120 mgkg^{-1}, (Table 4.18). The highest level (466 mgkg^{-1}) was obtained from Iwuokpom 2 station. Higher sulphate values are ascribed to the influence of atmospheric precipitation significantly encountered during dry season, due to the impact of gas flaring by Exxon-Mobil in the area.

4.12.6 Total Organic Carbon (TOC)

The mean TOC levels in sediments ranged from 0.11 to 2.34%, with the highest mean value of 2.99±1.36% obtained from Iwuokpom 2 (Table 4.18). Low levels of TOC in sediments are indicative of low organic matter associated with coarse sediments. Other organic carbon containing substances in sediments may include wood debris, ash, soot, oil and tar.

4.12.7 Particle Size Distribution

Bottom sediment samples indicated variable percentages of sand, silt and clay whose ranges were between 57.5 and 85.9%, 7.8 and 17.8%, and 6.2 and 27.9% respectively (Table 4.18). Mean values showed that sand was the major component in all sediment samples with maximum percentage value of 84.6±1.8 % obtained from Eketai station. .

The high sand fraction (>70.0 %) recorded was attributable to high activity level at different stations, making the area sandy. Clay fraction was found to be predominant (>20.0 %) at Atabong, Iwuochang and Iwuokpom 2 stations where the sand level was a bit low while silt fraction was < 20.0 % in all the stations under study. Davies and Abowei (2009) reported lower values for sand (57.86±2.65%), silt (17.47±1.68%), and clay (24.67±1.33%) for the lower reaches of Okpoka Creek, a tributary of the Upper Bonny Estuary in the Niger Delta.

4.13 TRACE METALS CONCENTRATION IN SEDIMENTS OF QUA IBOE RIVER

Metal concentrations (µgg^{-1} dry weight) in sediments samples from Qua Iboe River are presented in Appendix 18. The ranges (mean values in parenthesis) of metal levels for all stations were - 0.34–3.56 (1.59±0.87), for Cd, 1.85–33.2 (13.4±6.2) for Pb, 5.0–51.0 (20.9±14.0) for Cr, 18.8–81.6 (45.3±16.0) for Cu, 86–158 (122±18) for Zn, 0.91–14.2 (4.9±3.0) for Ni and 0.7–11.2 (5.5±2.9) for Co (Table 4.19). Higher metal levels obtained from Atabong station rendered the station to be a serious pollution risk.

4.13.1 Cadmium

Average Cd level in sediment was 1.59±0.87µgg^{-1}. The highest concentration was obtained from Atabong with value 2.96±0.57 µgg^{-1} while the least value was 0.88±0.56 µgg^{-1} recorded at Iwuokpom 2 (Table 4.19). The high Cd at Atabong may be ascribed to automobile tyre wear from highways and the daily burning of automobile tyre at the bank of the river. High Cd concentration was obtained during the rainy season than dry season owing to the inputs associated with urban run-off.

4.13.2 Lead

Average Pb concentration in sediment samples was 13.4±6.2 µgg^{-1}. Higher Pb values were obtained from Atabong 19.4±8.6 µgg^{-1}, and Eketai, 16.2±3.7 µgg^{-1} stations of the river system (Table 4.19). Seasonal levels in sediments revealed marked increase during the rainy season (Appendix 19). Lead showed some high level of homogenous concentrations in all stations studied and the relatively high concentration at Eketai and Atabong stations might also be attributable to point source of contamination ascribed to localized anthropogenic inputs from automobiles. Lead is known to be sorbed onto sediments in river and marine environment (Mostafa *et al.*, 2009).

4.13.3 Chromium

The concentration of Cr in this study ranged from 5.0 to 51.0 µgg^{-1} (20.9±14.0 µgg^{-1}) (Table 4.19). The highest Cr level was obtained from Atabong as 45.4±6.9 µgg^{-1}. Results obtained showed that higher values of Cr were recorded during the wet season than dry season (Appendix 19). High Cr levels recorded for Atabong station may be due to untreated waste water released daily from the abattoir located near sampling points, as reported by Muniz *et al.* (2004) for sediments of Montevideo Habour, Uruguay.

Table 4.19. Mean trace metal concentration (μgg^{-1} dry weight) of sediment samples from Qua Iboe River

Metals	Sampling stations							
	Iwuokpom 1	Iwuokpom 2	Iwuochang	Eketai	Atabong	Marina	Mean±SD[†]	Range
Cadmium	1.23±0.60	0.88±0.56	1.42±0.89	1.52±0.52	2.96±0.57	1.51±0.45	1.59±0.87	0.34-3.56
Lead	14.5±5.0	11.6±2.7	11.9±3.2	16.2±3.7	19.4±8.6	6.5±4.9	13.4±6.2	1.9–33
Chromium	19.5±13.0	13.7±1.8	8.7±3.4	27.5±8.8	42.6±6.9	13.4±4.7	20.9±14.0	5.0 - 51.0
Copper	51±25	33±12	46±16	44±10	56±11	42±11	45±16	19–82
Zinc	130±7	131±16	114±8	104±11	139±14	111±21	122±18	86–158
Nickel	5.96±1.7	4.13±1.4	3.11±0.9	4.85±1.3	9.09±4.3	2.39±1.6	4.92±3.0	0.91–14.20
Cobalt	8.03±1.1	7.13±1.0	2.71±2.1	6.15±2.8	6.73±3.2	2.40±0.7	5.52±2.9	0.70–11.22

[†] SD = Standard deviation

4.13.4 Copper

The mean Cu content was 45±16 µgg^{-1} with highest concentration obtained from Atabong station (56±11 µgg^{-1}) (Table 4.19). Mean values obtained far exceeded values reported for Ase River by Iwegbue *et al.* (2007), and Gulf of Aden, Yemen (Mostafa *et al.*, 2009). This is about two times higher than values reported by Essien *et al.* (2009a) for Cross River estuary. The high Cu level in sediments may be ascribed to high inputs of organic matter discharged through domestic sewage into the river. Copper concentrations in this study exceeded the recommended value for unpolluted sediments (US-EPA, 2009).

4.13.5 Zinc

Zinc concentration in sediments ranged from 86 to 158 µgg^{-1} and the mean level was 122±18 µgg^{-1} (Table 4.19). The highest mean Zn level, 139±14 µgg^{-1}, was obtained from Atabong station followed by Iwuokpom 2 (131±16 µgg^{-1}). Higher Zn values were recorded during the wet season than dry season (Appendix 19).

4.13.6 Nickel

The mean Ni concentration (range in parenthesis) in sediment was 4.9±3.0 µgg^{-1} (0.9-14.2 µgg^{-1}) (Table 4.19). Higher Ni values were obtained during the wet season for all sampling stations. Maximum level, 9.1±4.3 µgg^{-1} and minimum level, 2.39±1.6 µgg^{-1} was obtained from Atabong and Marina stations respectively. Results obtained in this study are lower than values reported by Essien *et al.* (2009b) for asphyxiated sediments of Qua Iboe estuary.

4.13.7 Cobalt

The mean Co concentration in this study was 5.52±2.90 µgg^{-1}. Maximum Co concentration ranged between 0.7 and 11.2 (5.5±2.9) µgg^{-1} (Table 4.19). High Co concentration, 8.0±1.1 µgg^{-1}, was obtained at Iwuokpom 1, and least value, 2.4±0.7 µgg^{-1} was from Marina. Cobalt levels in this study were slightly lower than values (6.0–27.5 µgg^{-1}) reported for sediment from the Hadhramout coastal area of Yemen by Mostafa *et al.* (2009).

4.13.8 Correlation Analysis of Sediment Metals

Correlation matrix analysis for metals in sediments results showed strong positive correlations between the pairs Cd and Cr, Pb and Ni and Ni and Co ($r > 0.700$, $p<0.05$, df. = 34) (Table 4.20). The relationship between the levels of different metals in sediments indicate fair relationship between Cd, Cr, Pb and Co which is a reflection of point source pollution.

4.14 EVALUATION OF POLLUTION STATUS OF QUA IBOE RIVER

4.14.1 Enrichment Factor (EF) Analysis

The enrichment factor (EF) analyses for sediment metal of Qua Iboe River are presented in Table 4.21. Results of analysis show the enrichment factor for the metals as: EF (Cd) from 16.6 to 81.4, EF (Pb) from 14.8 to 56.2, EF (Cr) from 8.0 to 81.7, EF (Cu) from 22.0 to 59.8, EF (Zn) from 25.2 to 73.1, EF (Ni) from 11.2 to 61.5, and EF (Co) from 16.2 to 69.6. The maximum EF (%) values for all metals were significant at Atabong station except for Co whose highest enrichment was obtained at Iwuokpom 1 station. The trend suggests point source of metal pollution mainly due to effect of municipal effluent discharges into the river at Atabong location.

4.14.2 Comparison of Sediment Quality with Other Sediment Quality Guidelines

As discussed earlier in Section 4.5.2, the results of trace metals in sediments from Qua Iboe River system were compared with different sediment quality guidelines (Table 4.22). Cadmium shows intermediate contamination as the mean concentration of 1.50 μgg^{-1} is greater than the ERL, TEL and LEL values of the NOAA, FDEP and Ontario guideline values respectively. Copper and Zn shows intermediate contamination owing to the greater levels of ERL, TEL and LEL values of the adopted guidelines. However, levels found in sediments were quite below the ERM, PEL and SEL values which could cause severe effects on the aquatic fauna.

On the other hand, agricultural and other human activities could lead to the introduction of Pb, Cu and Zn to the surrounding soils and hence into sediments (Alloway, 1995). Nickel concentrations in all samples are quite less than the ERL/ERM values, indicating no contamination. Similar conclusions derived from TEL/PEL of the FDEP, CCME, and Ontario guidelines, although lower than the NOAA, these criteria were still lower than the proposed guideline value. The mean Pb, Cr and Ni concentrations is quite less than

Table 4.20. Pearson correlation coefficients for trace metals in sediments of Qua Iboe River

Metals	Cd	Pb	Cr	Cu	Zn	Ni	Co
Cd	1						
Pb	0.357	1					
Cr	0.739[a]	0.560	1				
Cu	0.153	0.695[a]	0.237	1			
Zn	0.220	0.535	0.375	0.351	1		
Ni	0.438	0.876[a]	0.665[a]	0.665[a]	0.620[a]	1	
Co	0.017	0.696[a]	0.477	- 0.417	0.571	0.725[a]	1

[a] *Values are significant at* $p<0.05$.

Table 4.21. Enrichment factor values, EF (%) for metals in sediments of Qua Iboe River

Sampling Station	Station code	Enrichment factor, EF (%)						
		Cd	Pb	Cr	Cu	Zn	Ni	Co
Iwuokpom 1	SQ-1	27.5	40.6	31.5	51.7	60.7	38.0	69.6
Iwuokpom 2	SQ-2	16.6	31.3	18.8	22.0	62.6	24.2	61.1
Iwuochang	SQ-3	33.5	32.0	8.0	43.7	39.1	16.5	19.1
Eketai	SQ-4	36.7	46.1	48.9	39.4	25.2	29.6	51.8
Atabong	SQ-5	81.4	56.2	81.7	59.8	73.1	61.5	57.3
Marina	SQ-6	36.2	14.8	18.3	36.5	35.3	11.2	16.2

Table 4.22. Comparison of sediments metals levels (µgg^{-1} dry wt.) for Qua Iboe River system with sediment quality guidelines (SQGs)

Metal	Mean levels and range in parenthesis	NOAA guideline		FDEP guideline		CCME guideline (marine)		CCME guideline (fresh water)		Ontario guideline		Contamination level
		ERL[†]	ERM[a]	TEL[b]	PEL[‡]	IG[c]	PEL[‡]	IG[c]	PEL[‡]	LEL[d]	SEL[e]	
Cd	1.59±0.87 (0.34-3.56)	1.2	9.6	0.68	4.21	0.7	4.2	0.6	3.5	0.6	10	Intermediate
Pb	13.4±6.2 (1.9-33.2)	46.7	218	30.2	112	30.2	112	35.0	91.3	31	250	Low or no contamination
Cr	20.9±13.5 (5.0-51.0)	81	370	52.3	160	52.3	160	37.3	90.0	26	110	Low or no contamination
Cu	45.3±15.8 (18.8-81.6)	34	270	18.7	108	18.7	108	35.7	197	16	110	Intermediate
Zn	122±18 (86-158)	150	410	124	271	124	271	123	315	120	820	Low or no contamination
Ni	4.9±3.0 (0.9-14.2)	20.9	51.6	15.9	42.8	n.g*	n.g*	n.g*	n.g*	16	75	No contamination
Co	5.5±2.9 (0.7-11.2)	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	n.g*	50	50	Not ranked

[†] ERL: Effects range low; [a]ERM: Effects range median; [b]TEL: Threshold effects level; [c]IG: Interim Guideline; [‡]PEL: Probable effects level; [d]LEL: Low effect level; [e]SEL: severe effect level; *n.g = no guideline; SQG = Sediment quality guideline.

the ERL/ERM values of the NOAA and TEL/PEL values of FDEP guidelines indicating no contamination. From the results, none of the metals recorded concentrations greater than the upper range values (ERM, PEL and SEL) of the different SQGs which adversely affect the sediment dwelling fauna.

4.15 SPECIATION OF TRACE METALS IN SEDIMENTS OF QUA IBOE RIVER

The trend in the distribution of the seven trace metals in sediments among the four BCR fractions follows the order: Cd>Zn>Cu>Cr>Co>Ni>Pb. All the metals dominated in the reducible fraction, followed by the residual fraction (as in Pb, Ni and Co) and the oxidisable fraction (as in Cd, Cr and Cu). A significantly higher percentage of Zn binding to the non-residual fractions was found in sediments.

4.15.1 Speciation of Cadmium

About 88.7% of total Cd was distributed among the non-residual fractions thereby rendering Cd bioavailable to aquatic organisms. Cd is predominantly distributed in the reducible fraction representing about 36.2% of total concentration with only 11.4% distributed in the residual fraction. The percentage Cd distribution follows the order: acid reducible>oxidisable>exchangeable>residual [Fig. 4.9(i)]. The highest Cd concentration in Qua Iboe River system was obtained at Marina with the highest value for the sum of three-steps and residual fraction, 3.60 μgg^{-1}, giving 101.1% recovery (Appendix 20). Cadmium level in the residual fraction was attributable to natural sources.

Cd speciation is found to be highly variable, perhaps because it is a typical anthropogenic element and mostly enters the aquatic environment through the discharge of industrial effluents and municipal run-off. On average, ~ 88.6 % of Cd is mainly distributed among the non-residual fractions, which makes it the most mobile element in this study (Table 4.23). Comparing it with other metals, each fraction of Cd takes on apparent differences between samples, ~18.8 – 26.9% of its total content is measured in the first step of extraction with mean value of ~23.4%, and ~32.5 – 41.4%, and ~23.1 – 31.8% are found in the second and third stages with mean values of 36.2% and 29.1%, respectively.

Table 4.23. Fractionation of trace metal levels (% fractionation in parenthesis) of modified BCR protocol for Qua Iboe River

Fraction	Metal concentration (in μgg^{-1} dry weight)						
	Cd	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
Exchangeable	0.49±0.25 (23.4)	0.6±0.3 (4.3)	0.9±0.5 (4.9)	6.2±2.3 (16.1)	35.5±7.6 (31.2)	0.4±0.1 (12.7)	0.6±0.3 (14.4)
Reducible	0.77±0.34 (36.2)	5.8±1.0 (48.8)	8.5±6.0 (39.7)	17.5±4.5 (46.2)	38.6±6.6 (34.2)	1.5±0.7 (40.7)	1.7±0.7 (40.7)
Oxidisable	0.60±0.20 (29.1)	1.4±0.3 (11.7)	6.9±4.9 (32.2)	8.0±2.4 (21.0)	20.6±2.8 (18.3)	0.7±0.3 (17.0)	0.8±0.4 (18.9)
Residual	0.25±0.13 (11.4)	4.5±1.0 (36.1)	4.6±2.6 (23.3)	6.3±1.6 (16.7)	18.4±3.7 (16.3)	1.1±0.5 (29.7)	1.1±0.6 (25.9)
∑ non-residual steps	1.85±0.14 (88.7)	7.7±2.8 (64.0)	16.3±4.0 (76.8)	31.7±6.1 (83.3)	94.8±9.6 (83.7)	2.6±0.6 (70.4)	3.0±0.6 (74.0)
∑3-steps + R^{a}	2.11±0.22	12.1±2.5	20.9±3.3	38.0±5.4	113.0±10.3	3.72±0.48	4.10±0.46
Pseudo-total	2.13±0.86	13.2±1.9	22.3±15.0	38.9±10.0	114.0±20.1	3.91±1.79	4.04±2.00

[a] R = Residual fraction,

4.15.2 Speciation of Lead

The distribution of Pb in the residual fraction accounts for an average of 36.1 % of its total content in sediments. For the Pb in non-residual fractions (~ 64.0%), a major portion 48.0% (5.8±1.0 μgg^{-1}) is bound to the Fe/Mn oxides (i.e. reducible fraction) with about one third of it associated with the acid soluble and oxidisable fractions. The distribution pattern of the fractions follows the order: reducible>residual>oxidisable>exchangeable [Fig. 4.9(ii)]. The formation of stable complexes with Fe and Mn dioxide (Ramos *et al*., 1994) may be the reason why reducible Pb is more abundant than the other two non-residual fractions of Pb. The reducible Pb predominating in non-residual fractions has been reported by many researchers (e.g. Li *et al*., 2001; Ip *et al*., 2007; Gao *et al*., 2008; Sutherland and Tack, 2003).

4.15.3 Speciation of Chromium

On average, about 76.7% of Cr is mainly distributed among the non-residual fractions, which makes it one of the most mobile elements in this study (Table 4.23). Only about 2.6 – 7.0% of its total content was found in the exchangeable fraction with a mean of 4.9%, and 39.7% and 32.2% was found in the reducible and oxidisable fractions respectively [Fig. 4.10(i)]. This shows that large proportion of Cr deposited in the sediment can be remobilized as a result of the mineralization of organic matter under oxic conditions. This trend agrees with the report by Arain *et al*. (2008) who asserted low Cr distribution in acid exchangeable fraction of lake sediment samples. Korfali and Jurdi (2011) reported higher percentage of Cr in the reducible fraction, attributable to the oxidizing conditions of sediments that render the insoluble forms of the iron.

4.15.4 Speciation of Copper

Copper shows higher percentage distribution in the reducible fraction, followed by the oxidisable-organic fraction. The mean percentages of Cu in the non-residual (bioavailable) fractions are recorded as 83.3% (Table 4.23). The distribution pattern for Cu follows the order: acid reducible > oxidisable > residual > exchangeable [Fig. 4.10(ii)]. The speciation shows that only about 17.0% of the total concentration was found in the residual fraction. Li *et al*. (2007) reported that the non-residual fractions of Cu are mainly associated with the oxidisable phase, occurring as organically complexed

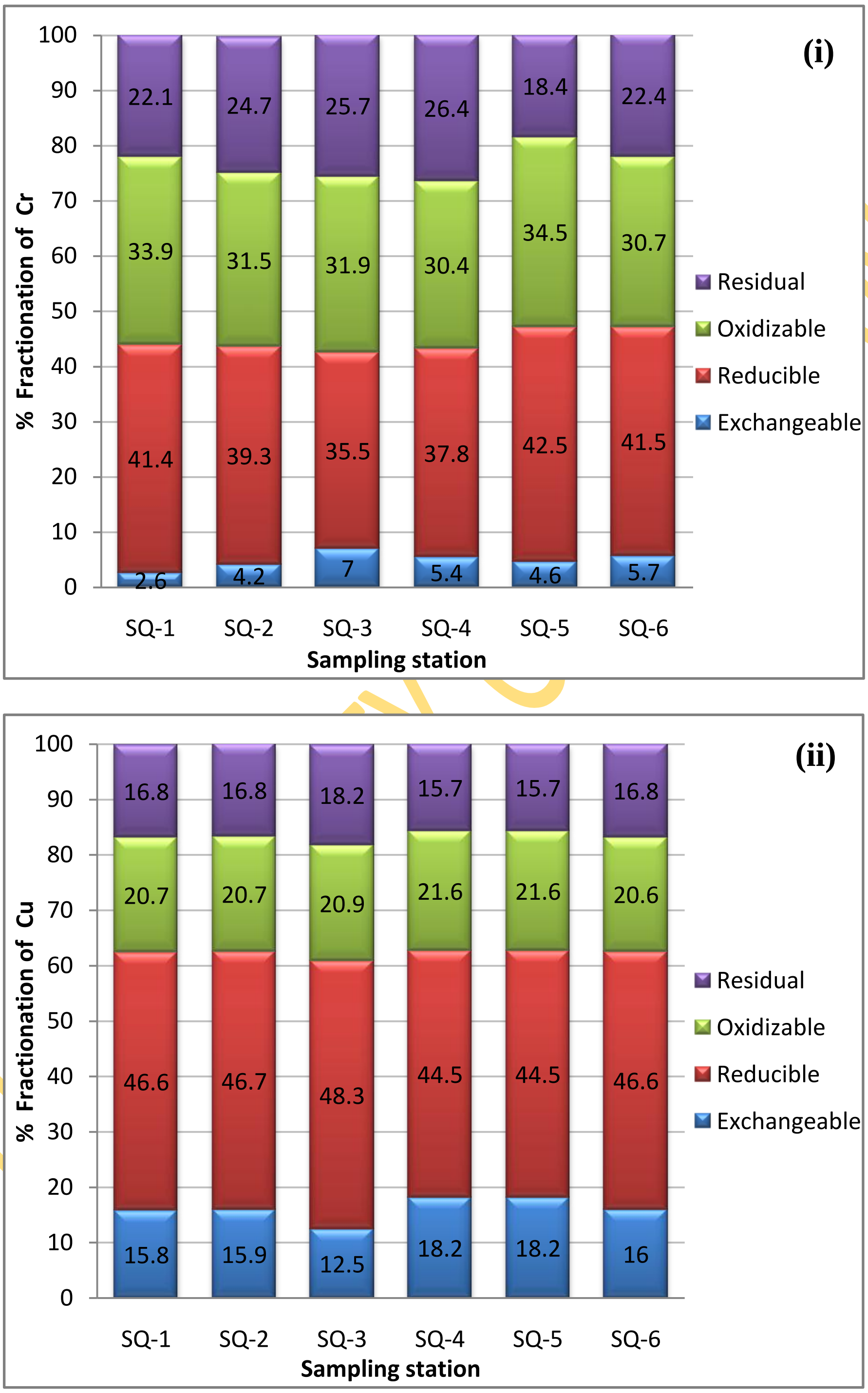

Fig. 4.10. Speciation of Cr (i) and Cu (ii) in sediments of Qua Iboe River

metal species mainly because Cu shows high affinity with humic substances, which are a fraction of natural organic matter chemically active in complexing such metals. But in this study, the non-residual fractions of Cu show a different pattern, perhaps owing to the influence of early diagenetic processes with the acid reducible fraction showing higher affinity for Cu.

4.15.5 Speciation of Zinc

Mean concentration of Zn metal in the bioavailable fraction was 94.8±9.6 μgg^{-1} representing about 83.7% distribution [Fig. 4.11 (i)]. This, however, was far greater than 30.0% value reported by Yu *et al.* (2010) for the non-residual fractions. Zinc concentrations in most sampling stations were dominated in the non-residual fractions with less than 20% in the residual fraction indicating non-lithogenic origin in the river system. This, however, makes Zn mobile in aqueous system and bioavailable to flora and fauna.

4.15.6 Speciation of Nickel

The mean concentration of the total Ni in the bioavailable fraction was recorded as 2.6±0.6 μgg^{-1} (70.4%). The distribution pattern follows the order: reducible (40.7%) > residual (29.7%) > oxidisable (17.0%) > exchangeable (12.7%) [Fig.4.11 (ii)]. The concentration distributed in the residual fraction was attributed to natural sources such as chemical weathering of igneous and metamorphic rocks, as well as decomposition of biota detritus. Nickel speciation in this fraction mainly depends on the oxidizing conditions of the sediment.

4.15.7 Speciation of Cobalt

The highest mean distribution for Co was 40.7%, found in the reducible fraction. The non-residual (bioavailable) fraction recorded mean value of 74.0%. The least distribution was (14.4%) was found in the exchangeable (acid-soluble) fraction. About 25.9% of Co ranging from 17.5 to 28.4% was distributed in the residual fraction Fig. 4.12 (i)].

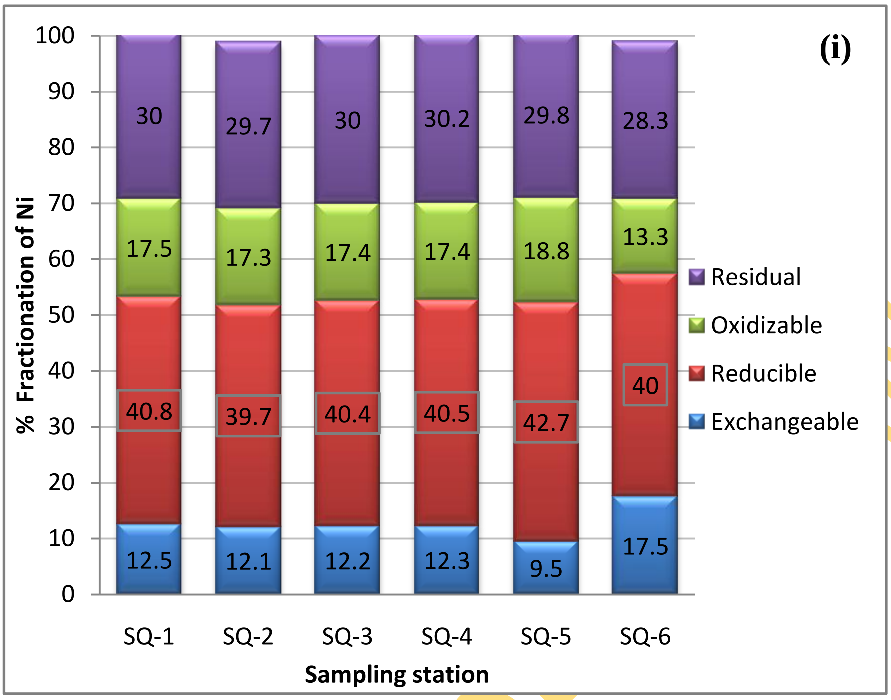

Fig. 4.11. Speciation of Zn (i) and Ni (ii) in sediments of Qua Iboe River

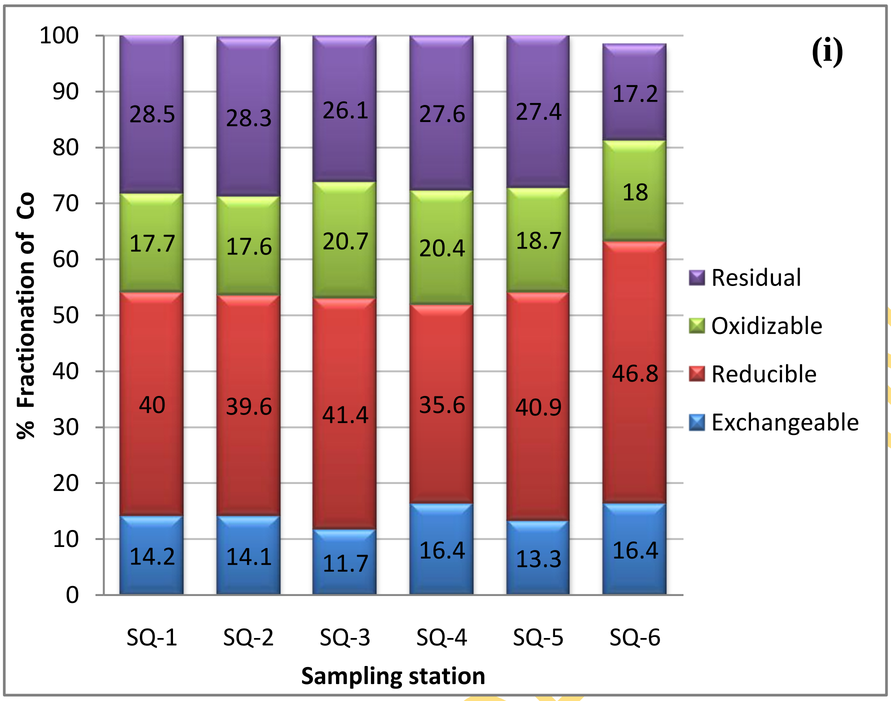

Fig. 4.12. Speciation of Co (i) in sediments of Qua Iboe River

4.16 ASSESSMENT OF TRACE METAL CONTAMINATION IN SEDIMENT FRACTIONS

The individual and global contamination factors (as earlier discussed in Section 4.7) for Cd, Pb, Cr, Cu, Zn, Ni and Co analysed are presented in Table 4.24. The highest ICF values for each individual element obtained were: 9.77 for Cd, 1.90 for Pb, 4.43 for Cr, 5.37 for Cu, 5.45 for Zn, 2.50 for Ni and 4.72 for Co with the least individual contamination value of 1.59 recorded for Pb at Eketai (SQ-4) station. The individual contamination factor (ICF) is a reflection of the risk of contamination of a water body by a pollutant. Therefore, Atabong and Marina stations indicated the highest risk of these metals in Qua Iboe River system. The mean individual contamination factor in sediments for all sampling stations follows the order: Cd>Zn>Cu>Cr>Co>Ni>Pb.

The global contamination factor (GCF) analysis shows that both the upstream and downstream stations were highly impacted by metal pollutants. The highest GCF value for Qua Iboe River was 32.36 ranging from 25.07 to 32.36. Hence, the results obtained in this investigation shows that the three stations (Eketai, Atabong and Marina), all located within the urban area recorded highest potential risk to flora and fauna.

4.17 CHEMICAL SPECIATION OF METALS IN SURFACE WATER OF QUA IBOE RIVER USING PHREEQCI MODEL

The solution composition of water quality parameters used for speciation modelling in Qua Iboe River is presented in Table 4.25. The modelling data showed that the trace metals Cd, Pd. Cr, Cu, Zn, Ni and Co form several complexes. Results of chemical speciation of metals in water shows that the predominant species are the free hydrated ions of Pb^{2+} (62.0%), Cu^{2+} (70.2%), Zn^{2+} (92.6%), Ni^{2+} (97.6%) and Co^{2+} (97.7%) and as well as the inorganic chloride species $CdCl^{+}$ (82.3%), $CuCl_2^{-}$ (81.2%), $PbCl^{+}$ (27.1%) and the hydroxy species of $CrOH^{2+}$ (40.2%), $Cr(OH)_2^{+}$ (58.7%). Results shows that high percentages of Pb, Zn, Cu and Ni are present as the free hydrated species, Pb^{2+} (75.6 – 82.7%), Zn^{2+} (≈93%), Cu^{2+} (89.3 – 91.5%) and Ni^{2+} (≈97%) in the upstream stations, thereby increasing bioavailability of these metals to the aquatic organisms.

The inorganic hydroxy complexed species - $Pb(OH)_2$ and $Pb(OH)_3$, $Zn(OH)_2$, $Zn(OH)_3^{-}$, $CuCO_3(OH)_2^{2-}$, $Ni(OH)_2$ and $Ni(OH)_3^{-}$) predominates the downstream stations where

Table 4.24. Individual and global contamination factors of trace metals in sediments from Qua Iboe River system

Stations	ICF							GCF
	Cd	Pb	Cr	Cu	Zn	Ni	Co	
Iwuokpom 1	6.85	1.66	3.52	4.95	5.01	2.36	2.52	28.86
Iwuokpom 1	3.19	1.90	3.03	4.97	5.02	2.33	2.52	25.07
Iwuochang	6.91	1.73	2.90	4.49	5.45	2.33	2.83	28.31
Eketai	9.77	1.59	2.78	5.37	5.45	2.32	2.63	31.77
Atabong	7.00	1.89	4.43	5.37	5.00	2.38	2.66	30.20
Marina	7.47	1.89	3.47	4.95	5.03	2.50	4.72	**32.36**
Mean	6.86	1.78	3.36	5.02	5.16	2.37	2.98	
Min	3.19	1.59	2.78	4.49	5.00	2.32	2.52	
Max	9.77	1.90	4.43	5.37	5.45	2.50	4.72	

Table 4.25. Solution composition (molL^{-1}) of water quality parameters in Qua Iboe River

Parameters	Sampling stations					
	SQ-1	SQ-2	SQ-3	SQ-4	SQ-5	SQ-6
Ionic strength (x10^{-2}M)	**1.82**	**2.09**	**1.17**	**0.54**	**0.86**	**0.62**
Alk ($CaCO_3$)	1.62x10^{-3}	1.86x10^{-3}	1.15x10^{-3}	5.00x10^{-4}	6.68x10^{-4}	5.66x10^{-4}
HCO_3	4.50x10^{-4}	4.01x10^{-4}	3.45x10^{-4}	3.96x10^{-3}	1.10x10^{-2}	9.50x10^{-3}
Ammonia	2.57x10^{-5}	2.43x10^{-5}	3.50x10^{-5}	4.57x10^{-5}	4.36x10^{-5}	3.36x10^{-5}
Nitrite	3.50x10^{-6}	3.58x10^{-6}	6.57x10^{-6}	7.14x10^{-6}	1.22x10^{-5}	7.00x10^{-6}
Nitrate	1.35x10^{-4}	2.12x10^{-4}	3.19x10^{-4}	3.27x10^{-4}	6.98x10^{-4}	4.38x10^{-4}
DO	4.36x10^{-4}	4.55x10^{-4}	3.62x10^{-4}	4.31x10^{-4}	3.31x10^{-4}	3.96x10^{-4}
Chloride	3.25x10^{-2}	3.77x10^{-2}	2.02x10^{-2}	8.24x10^{-3}	1.41x10^{-2}	9.54x10^{-3}
Fluoride	5.53x10^{-5}	5.56x10^{-5}	7.27x10^{-6}	3.21x10^{-6}	5.22x10^{-6}	9.06x10^{-6}
Phosphate	3.49x10^{-6}	2.13x10^{-6}	2.10x10^{-6}	4.20x10^{-6}	3.46x10^{-6}	3.72x10^{-6}
Sulphate	3.46x10^{-4}	3.20x10^{-4}	3.38x10^{-4}	3.97x10^{-4}	4.17x10^{-4}	4.36x10^{-4}
Cadmium	2.67x10^{-8}	3.56x10^{-8}	8.90x10^{-7}	5.34x10^{-8}	9.35x10^{-7}	5.34x10^{-7}
Lead	1.31x10^{-7}	9.18x10^{-8}	6.76x10^{-8}	5.31x10^{-8}	3.82x10^{-7}	1.45x10^{-7}
Chromium	1.47x10^{-7}	1.55x10^{-7}	3.45x10^{-7}	4.40x10^{-7}	9.50x10^{-7}	4.75x10^{-7}
Copper	7.56x10^{-7}	5.52x10^{-7}	5.36x10^{-7}	2.99x10^{-7}	3.31x10^{-6}	1.53x10^{-6}
Zinc	3.14x10^{-6}	2.16x10^{-6}	1.59x10^{-6}	1.04x10^{-6}	3.83x10^{-6}	3.41x10^{-6}
Nickel	4.44x10^{-7}	2.73x10^{-7}	2.05x10^{-7}	1.36x10^{-7}	3.41x10^{-6}	2.88x10^{-6}
Cobalt	7.82x10^{-7}	5.44x10^{-7}	3.06x10^{-7}	1.19x10^{-7}	2.14x10^{-6}	1.77x10^{-6}

the ionic strength (I = 0.01 – 0.02M) of the water increases due to increased level of dissolved salts (TDS) with relation to sea water influence. The predominant Zn species at the downstream stations include: $Zn(OH)_2$ with the range 75.0 – 88.1%, followed by $Zn(OH)_3^-$, 10.4-24.0%, $ZnOH^+$, Zn(OH)Cl and $Zn(OH)_4^{2-}$. This therefore reduced bioavailability of the free hydrated species of Zn^{2+} in the downstream stations. The complex, $CuCO_3(OH)_2^{2-}$ recorded percentage distribution ranging from 81.1 – 87.0% in the downstream stations thereby reducing bioavailability of the free aqua ionic species of Cu^{2+}, noting that copper toxicity is attributed to the free Cu^{2+} and $CuOH^+$ and not the inorganic complexes. The dominant hydroxide, carbonate, hydroxocarbonate, and phosphate species of the studied trace metals favour their precipitation in the system due to the low solubility of their salts.

4.17.1 Speciation of Cadmium

In surface water, the available Cd species include: Cd(OH)Cl, $CdCl^+$, $Cd(OH)_2$, $CdOH^+$, $CdCl_2$, Cd^{2+}, $Cd(OH)_3^-$ and $CdHCO_3$. The total Cd concentration was 3.65×10^{-7} M. The free hydrated Cd^{2+} species make up only 10.6% of the total Cd for the rivers (Fig. 4.13) with Eketai station (23.8%) recording maximum values. Cadmium is highly associated with chloride ions (Cl^-) mainly $CdCl^+$. The most soluble Cd species being $CdCl^+$ (82.3%) and Cd^{2+} (10.6%), $CdCl_2$ (6.8%) and $Cd(HCO_3)^+$ (0.3%). The upland stations, Eketai, Atabong and Marina (fresh water) with no sea water intrusion recorded higher levels of $CdCl^+$ species (73.8, 79.6 and 75.7%) respectively, while the other downstream stations, Iwuokpom 1, Iwuokpom 2 and Iwuochang with significant sea water intrusion, recorded higher levels of Cd(OH)Cl species (58.8%, 61.2% and 51.3% respectively), The species $CdCl^+$ and $Cd(OH)_2$ were also significant though not predominant (Fig. 4.13 and Appendix 22). Cadmium complexes with inorganic and/or organic ligands generally reducing the uptake and toxicity of the metal by reducing the concentration of Cd^{2+} (ANZECC and ARMCANZ, 2000b). In seawater, dissolved cadmium is dominated by chloride-complexes (Fergusson, 1990)

4.17.2 Speciation of Lead

The different species of Pb (II) distributed in Qua Iboe River system include- $Pb(OH)_2$, $Pb(OH)_3^-$, $PbOH^+$, $PbCO_3$, $Pb(CO_3)_2^{2-}$, $PbCl^+$, Pb^{2+}, $PbCl_2$, $PbNO_3^+$ with the hydroxyl species dominating the downstream stations while the free hydrated species Pb^{2+} and the chloride complexed ($PbCl^+$) species dominate the upstream stations. At lower ionic

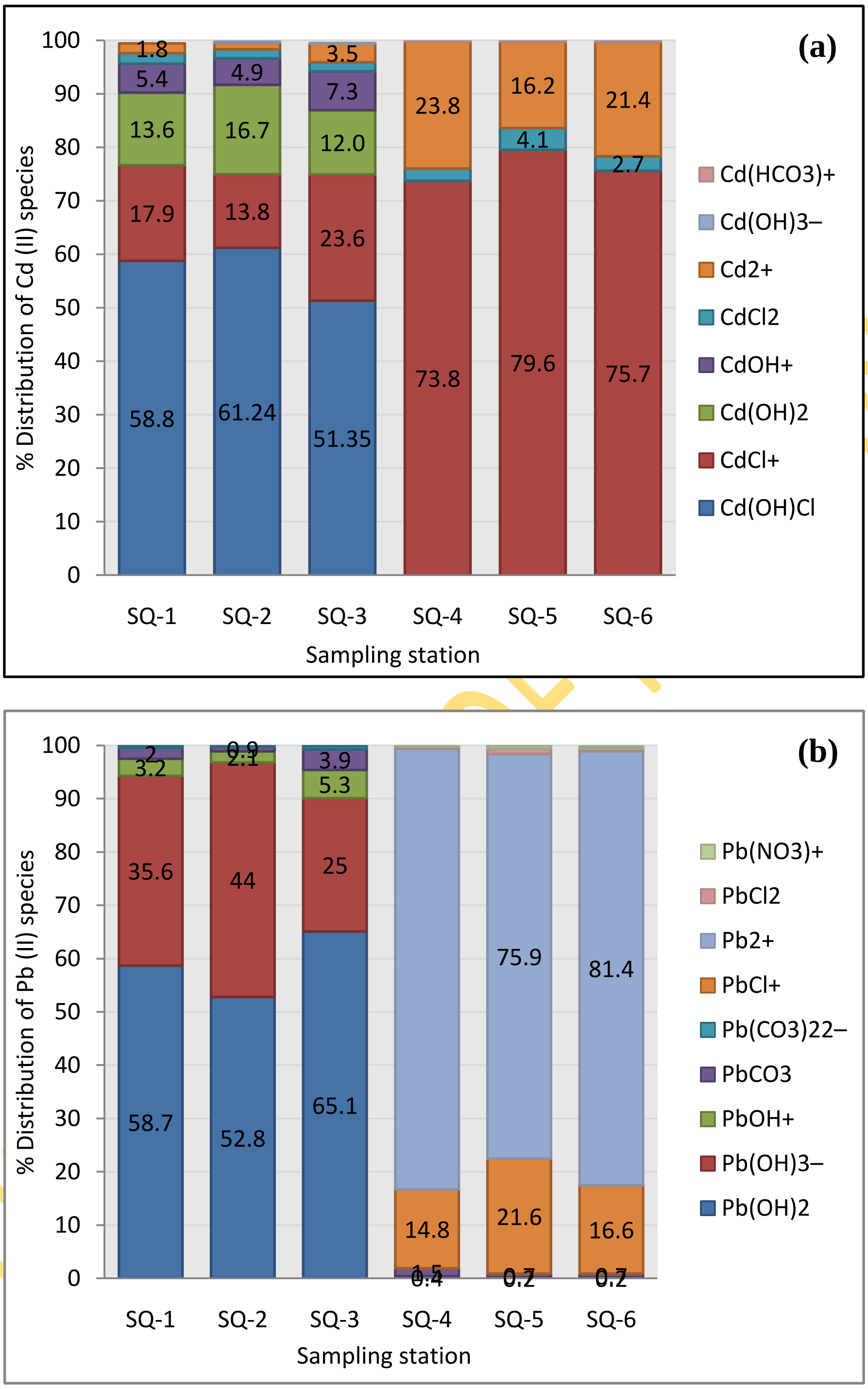

Fig. 4.13. Distribution of Cd (II) (a) and Pb (II) (b) species in Qua Iboe River surface water

strength (I = 0.013M), the free hydrated species is the most soluble chemical species (Pb^{2+}, 62.0%). Among the six stations studied, the free hydrated species, Pb^{2+} showed significant distribution in the upstream stations (fresh water) recording about 82.7% (for Eketai), 75.9% (for Atabong) and 81.4% (for Marina) (Fig. 4.13). The downstream stations recorded higher prevalence of the inorganic hydroxy complexed species - $Pb(OH)_2$ (48.0 – 65.0%), $Pb(OH)_3^-$ (25.0 – 50.0%) and $PbOH^+$ (1.6 – 5.3%) thereby reducing bioavailability of the free hydrated specie. The $PbCO_3$ and $PbCl_2$ fraction is undissolved and occurs as precipitates, sorbed ions and surface coatings on minerals or suspended organic matter (Stumm and Morgan, 1996).

4.17.3 Speciation of Chromium

The different significant chromium species are the hydroxyl complexes: $Cr(OH)_4^-$, $Cr(OH)_2^+$, $CrOH^{2+}$, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, neutral salt $Cr(OH)_3$ and the free hydrated Cr^{3+} ion. The downstream stations recorded very low levels of Cr (III) due to greater prevalence of Cr (VI) species, with CrO_4^{2-} (~100%) being the predominant species attributable to sea water intrusion while the upstream stations recorded significant dominance of Cr(III) complexed species with the hydroxyl complexes $CrOH^{2+}$ (66.1-76.2 %), $Cr(OH)_2^+$ (30.5- 15.2 %) and the free hydrated species, Cr^{3+} (3.1- 8.4 %) as the predominant species in solution [Fig. 4.14 (a) and Appendix 22].

4.17.4 Speciation of Copper

In natural water system, dissolved Cu occurs in two oxidation states, i.e. Cu(I) and Cu(II). All possible chemical species of copper include: $CuCl_2^-$, $CuCl_3^{2-}$, Cu^+ (for Cu (I) and $CuCO_3(OH)_2^{2-}$, CuO_2^{2-}, $CuOH^+$, $CuCO_3$, $Cu(CO_3)_2^{-2}$, $CuPO_4^-$, Cu^{2+}, $CuCl^+$, $CuSO_4$ for Cu(II) (Appendix 22). Out of a total Cu concentration of $11.0x10^{-6}$ M, about 51.0% of total Cu is dominated as Cu(I) while 49.0% occurs as Cu(II). The two complexed species of Cu(I) recorded the following ranged distribution - $CuCl_2^-$ (75.7 - 82.8%) and $CuCl_3^{2-}$ (4.7 – 9.1%) and the free ionic species, Cu^+ (7.7 – 19.8%) as the least in solution in the upstream stations [Fig.4.14 (b)].

The Cu(II) species recorded a total concentration of $5.40x10^{-7}$ molar with the free hydrated Cu^{2+} ion dominating the solution (70.2%). The upstream stations (SQ-4, SQ-5 and SQ-6) recorded distribution values > 90.0% as free hydrated species (Cu^{2+}) while $CuCO_3(OH)_2^{2-}$ showed predominance (81.3 - 87.0%) at the downstream stations

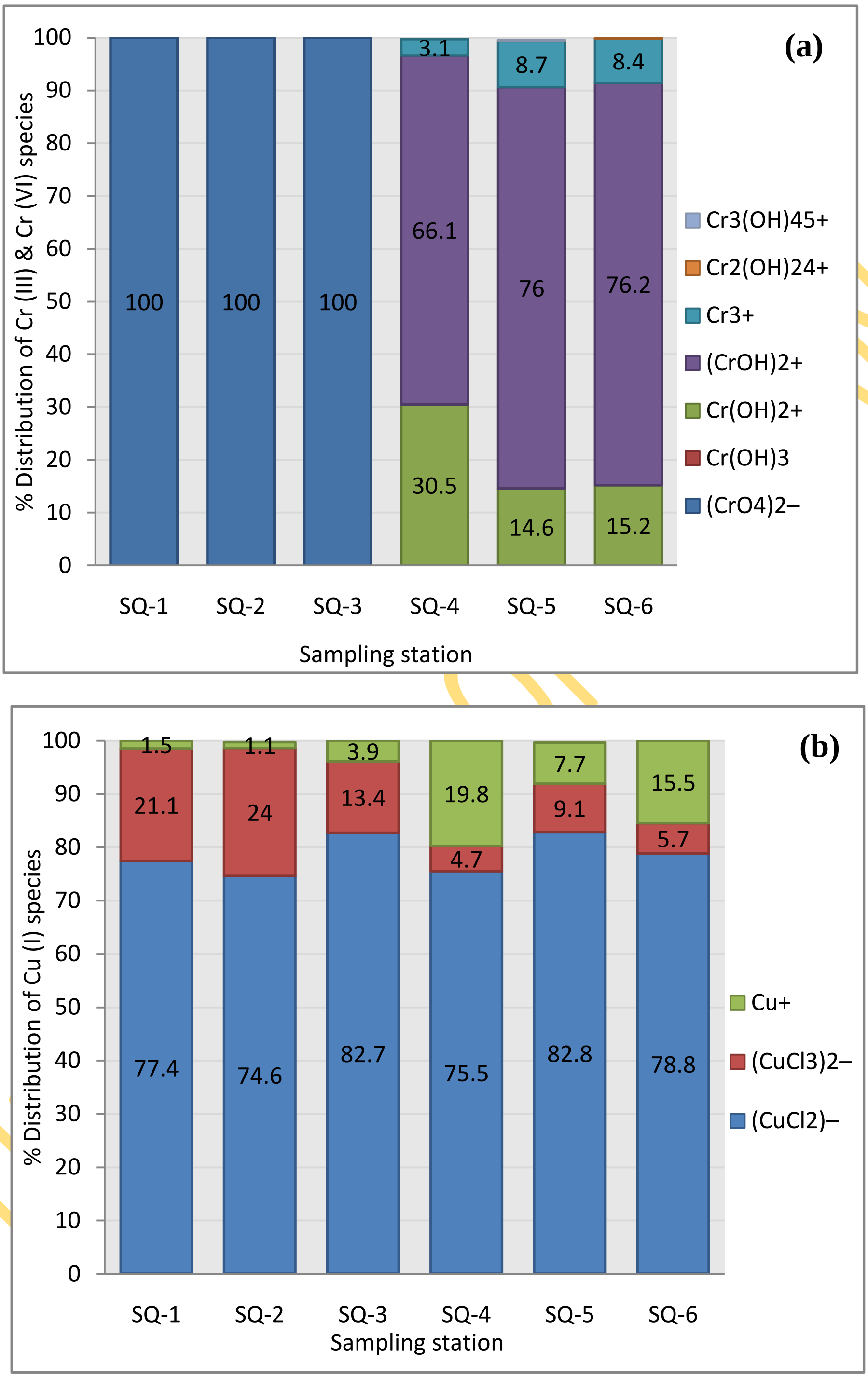

Fig. 4.14. Distribution of Cr (III)/Cr (VI) (a) and Cu (I) (b) species in surface water of Qua Iboe River

[Fig. 4.15 (a)]. Higher percentages of Cu^{2+} species recorded in this study agrees with values reported for seawater and hyper saline waters at higher ionic strength (I=0.37, 0.96) (Tepavitcharova *et al*., 2011). Bioavailability of the free hydrated species of Cu^{2+} is reduced by the predominance of $CuCO_3(OH)_2^{2+}$ in the downstream stations. Copper toxicity is attributed to the free hydrated copper ion (Cu^{2+}) and the hydroxyl species ($CuOH^+$) and not the inorganic complexes (ANZECC and ARMCANZ, 2000b).

4.17.5 Speciation of Zinc

The total concentration of Zn (II) obtained for the river system is 2.50×10^{-6} M. All significant chemical species of Zn in solution includes $Zn(OH)_2$, $Zn(OH)_3^-$, $ZnOH^+$, $Zn(OH)Cl$, $Zn(OH)_4^{2-}$, Zn^{2+}, $ZnCl^+$, $ZnSO_4$, $ZnHCO_3^+$ and $ZnCl_2$ [Fig. 4.15 (b)]. The predominance of the free hydrated species in all the upstream stations (92.4 – 93.2%) was in agreement with the report that the free ion Zn^{2+} was the predominant species in fresh waters of ionic strength 0.01 (Tepavitcharova *et al*., 2011).

The downstream stations with higher ionic strength recorded predominance of different hydroxyl species especially $Zn(OH)_2$ (78.7 - 88.1%) and $Zn(OH)_3^-$ (10.4 – 20.1%) [Fig. 4.15 (b)]. This trend, however, reduces bioavailability of the free hydrated species (Zn^{2+}) in the downstream stations (Bervoets *et al*. 1996).

4.17.6 Speciation of Nickel

Total Ni concentration in surface water of Qua Iboe River was 1.06×10^{-6} M with the availability of the species - $Ni(OH)_2$, $Ni(OH)_3^-$, Ni^{2+}, $NiSO_4$, $NiCl^+$ and $NiNO_3^+$ in solution. The speciation calculation results shows that the most soluble chemical species at the upstream stations (Eketai, Atabong and Marina) was the free hydrated Ni^{2+} (96.9 0 97.4%). However, the downstream stations recorded significant dominance of the hydroxy species, $Ni(OH)_2$ (53.5 – 65.5%) and $Ni(OH)_3^-$ (25.1– 44.7%) thereby reducing bioavailability of the free hydrated species as shown in [Fig. 4.16 (a)]. Nickel like Zn has only one significant oxidation state of +2 and this happens to be the most soluble chemical species in the sample.

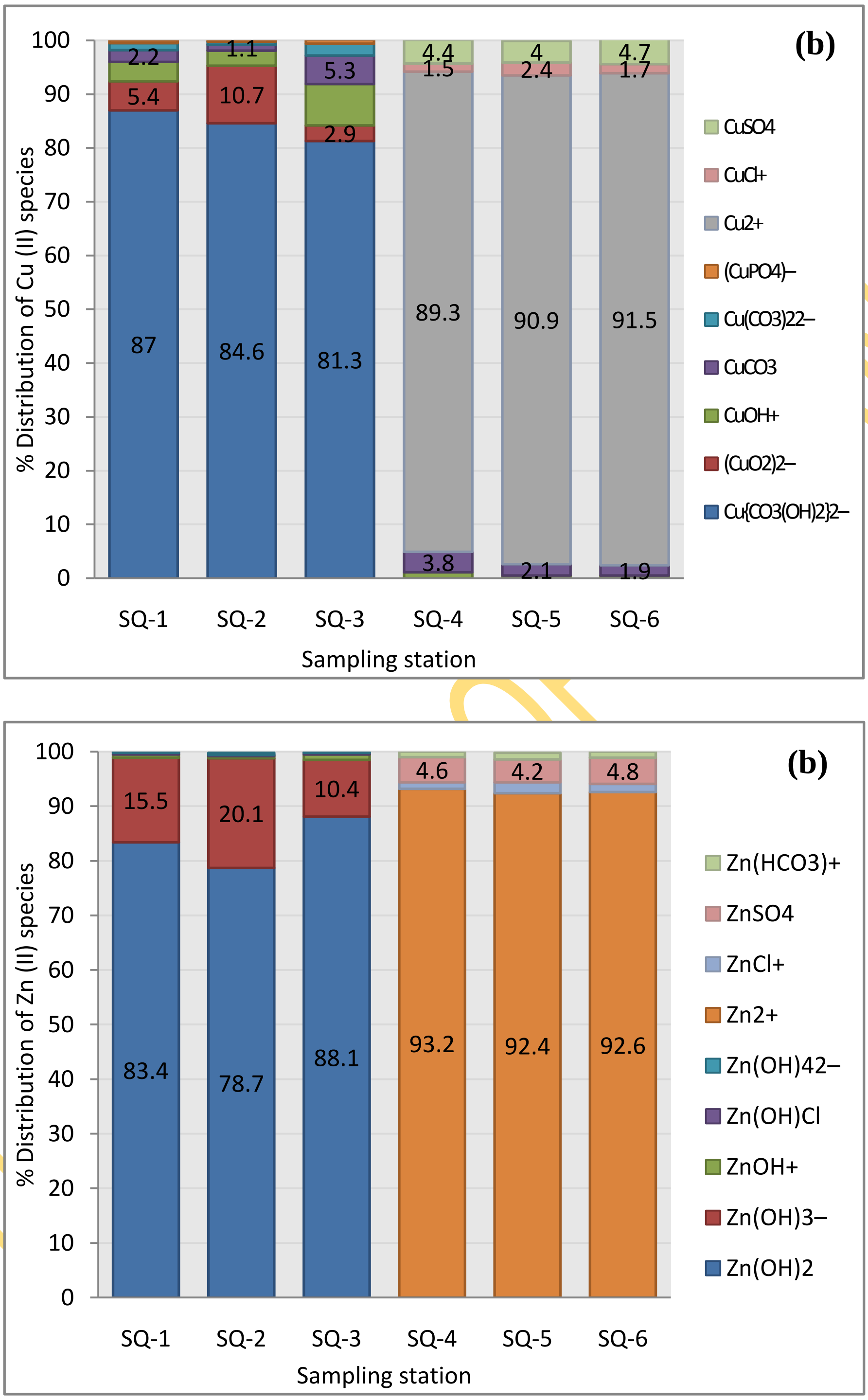

Fig. 4.15. Distribution of Cu (II) (a) and Zn (II) (b) species in surface water of Qua Iboe River

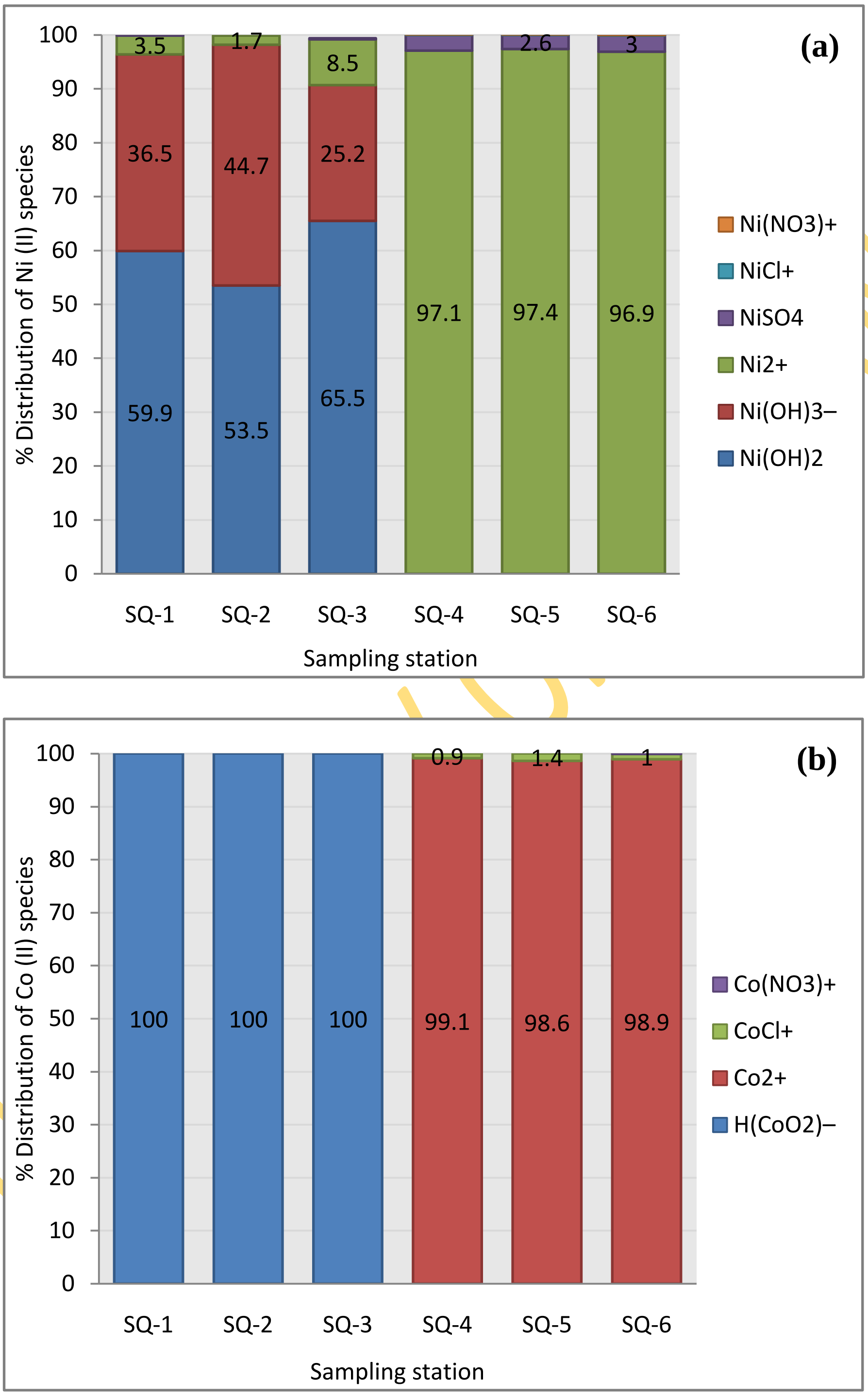

Fig. 4.16. Distribution of Ni (II) (a) and Co (II) (b) species in surface water of Qua Iboe River

4.17.7 Speciation of Cobalt

Only four species of Co, $HCoO_2^-$, Co^{2+}, $CoCl^+$ and $CoNO_3^+$ were significant in this study. From total Co concentration value of 9.3×10^{-7} M, the downstream stations (SQ-1 – SQ-3) recorded 100% distribution of $HCoO_2^-$ as the only predominant species. But the upstream stations (SQ-4 – SQ-6) identified the distribution of the free hydrated species, Co^{2+} (98.6 – 99.2%) as the predominant significant Co species and $CoCl^+$ (0.9 – 1.5%) and $CoNO_3^+$ (0.0 - 0.1%) [Fig. 4.16 (b)]. The presence of the free hydrated specie, Co^{2+}, in all the upstream stations, therefore, renders Co^{2+} bioavailable to aquatic organisms, whereas, the presence of the complexed specie, $HCoO_2^-$ as the predominant species in all the downstream stations reduces bioavailability of the free hydrated species of Co^{2+}.

4.18 CALCULATION OF SATURATION INDICES

The saturation index (SI) (as discussed in Section 4.9) for the different mineral phases were calculated for surface water samples from Qua Iboe River (Table 4.26). The ionic strength for the different stations of Qua Iboe River system studied ranged between 0.0054 and 0.0263. About 77% of the samples recorded negative saturation indices for the different mineral phases as a reflection of undersaturation. Generally, cerrusite ($PbCO_3$) shows moderate under saturation (SI = –0.94), while Pb-pyromorphite ($Pb_5(PO_4)_3Cl$) (SI = 7.69), $CuCr_2O_4$ (SI = 7.25) and $PbHPO_4$ (SI = 1.69) were highly supersaturated showing very high tendency to precipitate out of solution. The mineral phases $Cd(OH)_2$, cuprite (Cu_2O), otavite ($CdCO_3$) and smithsonite ($ZnCO_3$) showed varying degrees of under saturation at different sampling points with low ionic strengths.

The downstream stations, with higher ionic strength (~ 0.02M), showed oversaturation with respect to the minerals - atacamite, $Ni(OH)_2$, tenorite, and zincite. The same minerals at lower ionic strengths (~ 0.01M) in the upstream stations showed varying degrees of under saturation ranging from -12.6 to -10.5 for atacamite, -8.58 to -7.88 for $Ni(OH)_2$, -3.35 to -3.12 for tenorite, and -6.36 to -6.18 for zincite. At low ionic strength also, the upstream stations showed oversaturation for the minerals $CdCr_2O_4$, $CuCr_2O_4$, and $PbHPO_4$. The mineral phase, Pb-pyromorphite ($Pb_5(PO_4)_3Cl$) also showed high oversaturation in all the stations with SI values ranging from +1.45 to +4.96 (Table 4.26).

Table 4.26. Saturation Indices of some mineral phases in Qua Iboe River system

Phase	Saturation Indices (SI)						log K_{sp}	Formula
	SQ-1	SQ-2	SQ-3	SQ-4	SQ-5	SQ-6		
Ionic strength (x 10^{-2}M)	1.82	2.09	1.17	0.54	0.86	0.62		
Anglesite	-7.28	-7.80	-7.12	-3.15	-2.38	-2.70	-7.91	$PbSO_4$
Atacamite	3.04	2.42	3.09	-12.55	-10.53	-11.79	14.26	$Cu_2(OH)_3Cl$
$Cd(OH)_2$	-1.64	-1.41	-0.13	-10.61	-10.25	-10.35	13.73	$Cd(OH)_2$
$CdCr_2O_4$	-4.00	-5.22	-0.14	5.09	4.82	4.15	15.00	$CdCr_2O_4$
Cerrusite	-1.62	-2.13	-1.63	-2.16	-1.61	-2.05	-3.24	$PbCO_3$
$Co(OH)_2$	-7.94	-8.24	-8.15	-8.43	-7.92	-7.98	12.30	$Co(OH)_2$
CrO_2	-7.17	-7.75	-6.13	-3.36	-4.00	-4.28	-19.14	CrO_2
$CuCr_2O_4$	-6.71	-8.27	-4.31	5.13	4.73	3.93	16.22	$CuCr_2O_4$
Cuprite	-1.23	-1.74	-0.84	-3.22	-2.09	-2.56	-1.91	Cu_2O
Hydrocerrusite	-1.52	-2.74	-1.77	-9.14	-7.95	-9.19	1.85	$Pb_3(OH)_2(CO_3)_2$
Malachite	0.25	-0.30	0.53	-6.23	-5.32	-5.85	5.90	$Cu_2(OH)_2CO_3$
Nantokite	-7.13	-7.47	-6.96	-3.45	-2.32	-2.71	-6.77	CuCl
$Ni(OH)_2$	0.89	0.64	0.64	-8.58	-7.88	-7.94	12.75	$Ni(OH)_2$
Otavite	-1.13	-1.22	0.58	-4.13	-3.32	-3.49	-1.77	$CdCO_3$
Paralaurionite	-2.51	-2.79	-2.76	-4.37	-3.71	-4.24	0.20	PbClOH
$Pb_3(PO_4)_2$	-4.41	-6.02	-4.72	-5.92	-5.15	-6.19	-19.97	$Pb_3(PO_4)_2$
$PbHPO_4$	-1.45	-2.16	-1.49	1.06	1.41	1.07	-15.73	$PbHPO_4$
Pyromorphite	4.04	1.45	3.44	3.19	4.96	3.06	-47.90	$Pb_5(PO_4)_3Cl$
Smithsonite	-3.43	-3.92	-3.44	-4.38	-4.07	-4.16	0.44	$ZnCO_3$
Tenorite	2.89	2.77	2.92	-3.34	-3.12	-3.35	7.65	CuO
Tsumebite	0.65	-0.38	0.37	-9.62	-9.00	-9.94	2.53	$Pb_2CuPO_4(OH)_3:3H_2O$
Zincite	0.75	0.58	0.52	-6.18	-6.33	-6.36	11.20	ZnO
$ZnCO_3:H_2O$	-3.19	-3.69	-3.22	-4.16	-3.86	-3.95	0.14	$ZnCO_3:H_2O$
CO_2	-6.95	-7.25	-6.70	-0.94	-0.46	-0.53	-7.83	CO_2
O_2	-0.74	-0.72	-0.82	-0.74	-0.85	-0.78	-2.89	O_2

Sometimes, the water samples showed different saturation states with respect to the mineral phases examined as a function of the ionic strength of the solution. Saturation indices calculations using PHREEQCI model reveals that while the upstream stations recorded marked level of under saturation of the mineral phase atacamite, $Cu_2(OH)_3Cl$ - $Ni(OH)_2$, tenorite - CuO, and zincite - ZnO; the downstream stations with higher ionic strengths showed oversaturation with the same minerals. Also, while the downstream stations experienced under saturation of $CdCr_2O_4$, $CuCr_2O_4$, and $PbHPO_4$, the upstream stations with lower ionic strengths were oversaturated with the same minerals. Therefore, results obtained show that surface water composition is largely controlled by the dissolution of chromate and phosphate minerals.

4.19 COMPARISON OF WATER QUALITY STATUS OF CROSS AND QUA IBOE RIVER WITH OTHER RIVERS IN THE NIGER DELTA AND OTHER PARTS OF THE WORLD

4.19.1 Physicochemical Characteristics

The results of physicochemical characteristics in surface water samples from Cross River and Qua Iboe River were used to assess the water quality in order to determine the pollution status of the two rivers.

The pH values for Cross River and Qua Iboe River ranged from 5.78 to 7.22 and 6.49 to 7.34, respectively. The pH ranges reported were good enough for fresh water except Nwaniba station which recorded acidic pH attributable to the formation of humic acid from decayed organic matter and tree barks dumped into the river. Generally, pH values for the two rivers falls within the range that allows for the survival of fishes and other aquatic animals. Results fell within the WHO guideline value, 6.5 – 8.5 pH units, for drinking water (WHO, 2008).

Mean alkalinity value for Qua Iboe River (61 ± 35 mgL^{-1}) almost doubled that of Cross River (36 ± 19 mgL^{-1}), especially at Iwuokpom 2 (93.0 ± 17 mg L^{-1}) attributable to soil mineral type and watershed bedrock. Increased alkalinity reduces metal bioavailability due to the formation of metal carbonate species. Total alkalinity values in this study were quite higher than values reported for Esi River, Warri (13.9 ± 3.8 mgL^{-1}) by Akporido (2010), Ethiope River (1.65 mgL^{-1}) by Agbaire and Obi (2009) in the region and Ogunpa River (1.76-28.0 mgL^{-1}) by Onianwa *et al.* (2001) (Table 4.27).

Table 4.27. Comparison of water quality parameters with some rivers in Niger Delta and other parts of the world

	Physicochemical parameters (mgL^{-1} except otherwise stated)															Reference
Study area/Rivers	pH	†EC	TDS	Alk.	TH	‡Turb.	DO	BOD	COD	Cl^-	NH_3	NO_3^-	NO_2^-	PO_4^{3-}	SO_4^{2-}	
Orogodo River, Agbor	5.1-6.1	6775-8197	1869-2078	-	-	21-29.4	2.17-3.19	21-38.2	-	-	-	21.4-28.0	-	17.91-28.67	30.9-36.8	Rim-Rukeh *et al.* (2006)
Ethiope River, Delta State	6.82	87.2	0.34	1.65	2.42	-	17.45	4.38	-	-	-	-	-	-	-	Agbaire and Obi (2009)
Western Niger Delta	6.01	206.1	455.3	-	-	33.3	531	10.25	27.75		-	5.83	-	-	23.59	Omo-Irabor *et al.* (2008)
Esi River, Warri State	5.87	-	58	13.9	-	-	3.6	6.2	73	1.45	-	-	-	13.8	11.5	Akporido (2010)
Elechi Creek, Niger Delta	6.4-7.7	-	1240-19800	47.1-226	-	-	4.16-6.62	1.43-8.80	-	-	-	-	-	0.30-14.2	3.77-78.9	Obire *et al.* (2003)
New Calabar River, PH	-	-	6.50-40.10	-	-	-	3.40-9.10	0.25-4.20	10.0-110	-	-	-	-	-	-	Odukuma and Okpokwasili, 1997
Ogunpa River, Ibadan	6.6-8.1	-	0.1-5.9	1.76 – 28.0	-	-	0.2-8.3	13-56.0	11.9-22.4	70.5-688	-	-	-	-	0.001-0.3	Onianwa *et al.* (2001)
Ona River, Ibadan	-	-	-	-	-	-	4.9	-	54.5	-	-	-	-	0.47	20.65	Nubi and Nubi (2010)
River Illo, Otta	-	-	-	-	-	-	2.24	-	782.9	-	76.0	-	-	-	-	Longe and Omole (2008)
Oti River, Ghana	8.15	60.07		44.0	48.0	17.54	8.03	0.33		6.00		0.16		0.001	8.93	Abdul-Razak *et al.* (2009)
Densu River, Ghana	6.54-7.48	136-369	68.3-196	-	-	-	-	6.91-18.8	-	-	0.21-2.1	0.13-5.21	-	0.54-104	7.90-40.57	Fianko *et al.* (2010)
Lake Qarun, Egypt	-	-	-	-	-	-	-	-	-	-	0.378	0.039	0.01	-	-	Abdel-Satar *et al.* (2010)
Nairobi River, Nairobi	7.04	-	-	-	-	41.5	4.32	182.5	49.5		-	-	-	-	-	Dulo (2008)
Gediz Stream, Turkey	8.05	1590	-	-	-	-	11.75	6.1	44.75	-	0.26	-	-	-	-	Akcay *et al.* (2003)
Buyak Menderes R, Turkey	8.15	1645	-	-	-	-	11.65	6.2	42.4	-	0.30	-	-	-	-	Akcay *et al.* (2003)
Biga stream, Turkey	7.51	869.9	-	-	-	-	8.33	136.6	-	-	-	-	-	-	-	Hacioglu and Dulger (2009)
Cross River (This study)	6.62	553	275	36.1	184.2	34.2	7.61	1.94	27.7	1150	0.38	12.25	0.09	0.068	30.9	Present study
Qua Iboe River (This study)	6.91	1205	495	61.3	221.6	50.5	6.42	2.80	21.9	860	0.46	4.63	0.09	0.097	36.2	Present study

† EC = μScm^{-1}, ‡ Turb = Turbidity unit (NTU).

Conductivity values for the two rivers were 550±280 µScm^{-1} and 1210±740 µScm^{-1}. The concentration values from Qua Iboe River doubled that of Cross River due to influence of sea water intrusion from Atlantic Ocean. The EC values obtained are comparable with reports for other rivers in the region (Omo-Irabor *et al.*, 2008).

In Cross River, low water hardness level was reported while some upstream stations (Atabong and Marina) of Qua Iboe River recorded higher levels (669 mgL^{-1}and 579 mgL^{-1}) which exceeded the WHO guideline limit (500 mgL^{-1}) for drinking water (WHO, 2008). The mean DO level for Cross River (7.6±1.5 mgL^{-1}) and Qua Iboe Rivers (6.4±1.3 mgL^{-1}) were greater than 5.0 mgL^{-1}. Therefore, the two rivers are very adequate to support aquatic organisms.

Mean chloride levels for Cross and Qua Iboe River were 880±520 mgL^{-1} and 860±550 mgL^{-1} respectively with Ibaka (1540±180 mgL^{-1}) and Iwuokpom 2 (1330±330 mgL^{-1}) having the highest chloride levels attributable to sea-water intrusion (from Atlantic Ocean). Results were higher than those reported for other surface waters bodies in the region (Nduka *et al.*, 2008) and other parts of Nigeria (Wakawa *et al.*, 2008) [Table 4.27]. However, chloride levels for most stations exceeded the WHO guideline limit of 250 mgL^{-1} for drinking water (WHO, 2008).

Nitrogen in surface water is present as ammonia, nitrite and nitrate nitrogen. Therefore, ammonia, nitrite and nitrate levels in this study were below obnoxious level. Maximum nitrate level obtained from Nwaniba (28.7±9.3 mgL^{-1}) tripled the highest level from Qua Iboe River at Atabong (9.8±2.7 mgL^{-1}). However, the high values recorded in Cross River did not exceed the WHO maximum limit of 50 mgL^{-1} for drinking water (WHO, 2008).

Phosphate levels of 0.07±0.09 mgL^{-1} (Cross River) and 0.10±0.03 mgL^{-1} (Qua Iboe River) were highly comparable, and fell within the WHO desirable limits of 0.35 mgL^{-1} (WHO, 2008). The mean sulphate level for the two rivers, 31.0±9.0 mgL^{-1} (Cross River) and 36.2±9.8 mgL^{-1} (Qua Iboe River) were comparable with no significant difference. There was no threat of phosphate contamination in the two river system.

The general assessment of the surface water quality of the two rivers using Prati Scale classification (Prati *et al*., 1971) showed that Cross River fell in the class of excellent water (Class 1) with respect to pH, DO and BOD and acceptable water (Class 2) with respect to NH_3 and COD. On the other hand, Qua Iboe River fell in the class of acceptable (Class 2) and slightly polluted (Class 3) with respect to the measured parameters. The high chloride concentration rendered the river heavily polluted as reflected in all stations except Ayadehe which showed acceptable class. The results showed spatial distribution of the measured parameters as a reflection of different anthropogenic activities at various stations

4.19.2 Metals in Surface Water

Trace metal concentrations in surface water from the two rivers (Cross and Qua Iboe) were compared with other rivers in the region. Results showed that the two rivers were of good quality compared with other rivers in the region. Mean metal levels from Cross River and Qua Iboe River was of the order: Zn>Ni>Cu>Co>Pb>Cr>Cd and Zn>Cu>Ni>Co>Cr>Pb>Cd respectively. In Qua Iboe River, metal levels were higher than levels obtained in Cross River due to influence of point source pollution. For example, Cd level (41±49 µgL^{-1}) in Qua Iboe River was significantly higher than level (16±13 µgL^{-1}) obtained in Cross River. Levels of Cd were quite below values reported for Ubeji Creek (700 µgL^{-1}), Okirika River (160±40 µgL^{-1}), and Abuloma River (150±20 µgL^{-1}) by Nduka and Orisakwe (2010) but compared favourably with 40 µgL^{-1} reported for Iko River in Akwa Ibom by Benson and Etesin (2008).

However, Pb level in surface water of this study was comparable with other rivers in the region except New Calabar, Okirika, Abuloma and Ubeji Rivers which recorded elevated Pb levels of 850 µgL^{-1}, 590±30 µgL^{-1}, 410±30 µgL^{-1} and 300 µgL^{-1} respectively (Table 4.28). Chromium level in Cross River (21±16 µgL^{-1}) was one-half of the concentration in Qua Iboe River (45±39 µgL^{-1}), although the difference was not significant. However, at Atabong station of Qua Iboe River value obtained far exceeded the WHO guideline limit for drinking water (WHO, 2008). The mean levels of Cd, Pb and Ni in the two rivers exceeded the WHO drinking water guideline limits of 3 µgL^{-1}, 10 µgL^{-1} and 20 µgL^{-1} respectively (Table 4.29). All the other metals analysed – Cr, Cu, Zn and Co did not pose any environmental risk to the biota.

Table 4.28. Comparison of metal concentrations in surface water with some rivers in Nigeria and other parts of the world

Rivers/Study area	Metals concentration (mgL^{-1})							Reference
	Cd	Pb	Cr	Cu	Zn	Ni	Co	
Ubeji Creek, Delta State	700 (640) [a]	300 (220) [a]	ND [c]	5200 (4300) [a]	780 (680) [a]	100 (80) [a]	-	Nduka and Orisakwe (2010)
New Calabar River, PH	-	850	500	2080	70	-	-	Wegwu and Akininwor (2006)
Iko River, Akwa Ibom State	40	4	10	130	350	420	-	Benson and Etesin (2008)
River Ijana, Ekpan- Delta State	10-100	25-58	37-67	20-50	88-122	30-80	-	Emoyan *et al.* (2006)
Esi River, Warri	2.4	39	42	16.1	107	12	-	Akporido (2010)
Abraka River, Delta State	-	10–170	-	-	40–240	10–130	-	Rim-Rukeh *et al.* (2007)
Okirika River, PH-Nigeria	160±40	590±30	230±20	80±10	20±0	650±10	-	Nduka and Orisakwe (2010)
Abuloma River, PH-Nigeria	150±20 (130±0) [a]	410±30 (390±10) [a]	ND [c]	50±10 (40±10) [a]	30±10 (20±10) [a]	520±30 (470±10) [a]	-	Nduka and Orisakwe (2010)
Lagos Lagoon, Nigeria	354	263	60	197	530	140	-	Aderinola *et al.* (2009)
J. A. Alzate Reservoir, Mexico	-	61	79	70	68	34	-	Avila-Perez *et al.* (1999)
Hindon River, India	2.4 – 24.1	30-90.2	31.2-331	BDL [b] - 4373	5-836	-	-	Suthar *et al.* (2009)
Qua Iboe estuary, AKS	-	10 ±6	20 ± 1	36±15	30 ± 1	13 ± 5	-	Essien *et al.* (2009b)
Cross River, Akwa Ibom	16±13	22±14	21±16	35±20	112±71	50±49	32±22	Present study
Qua Iboe River, Akwa Ibom	41±49	31±30	45±39	70±71	163±89	62±82	55±48	Present study

[a] *Wet season values in parenthesis,* [b] *BDL = below detection limit,* [c] *ND = not detected*

Table 4.29. Comparison of results from this study with WHO guidelines for drinking-water and Canadian Water Quality Guidelines for fresh water

Parameters	Mean concentration		WHO guideline (2008)	Canadian WQG (fresh water)
	Cross River	Qua Iboe River		
Temp. °C	29.5±2.5	29.6±2.9	NG	-
pH (pH units)	5.68-7.22	6.49-7.34	6.5-8.5	6.5-9[d]
Alkalinity (mgL^{-1})	36.1±19	61.3±35	n.g[†]	-
Turbidity (NTU)	34.2±18	50.5±16	5.0	-
TDS (mgL^{-1})	275±130	495±320	n.g[†]	-
E. Cond. (μScm^{-1})	553±280	1210±740	250	-
Hardness (mgL^{-1})	184±160	222±290	500	-
DO (mgL^{-1})	7.6±1.2	6.4±1.3	n.g[†] , 7.5[a]	5.5-9.5
COD (mgL^{-1})	27.7±5.4	21.9±3.8	n.g[†]	-
BOD_5 (mgL^{-1})	1.94±0.78	2.80±0.73	n.g[†]	-
Chloride (mgL^{-1})	880±520	860±550	n.g[†]	-
Fluoride (mgL^{-1})	0.31±0.28	0.53±0.48	1.5	1.5
NH_3-N (mgL^{-1})	0.38±0.30	0.46±0.29	n.g[†]	-
NO_3^--N (mgL^{-1})	12.3±9.6	4.6±2.9	50	45
NO_2^--N (mgL^{-1})	0.09±0.15	0.09±0.05	0.003	0.06
PO_4^{3-} (mg L^{-1})	0.07±0.09	0.10±0.03	0.35[a]	-
SO_4^{2-} (mgL^{-1})	31.0±9.0	36.2±9.8	250-500	-
Cadmium (μgL^{-1})	16±13	41±49	3	0.017
Lead (μgL^{-1})	22±14	31±30	10	1 - 7*
Chromium (μgL^{-1})	21±16	45±39	50	8.8[e], 1.0[f]
Copper (μgL^{-1})	35±20	70±71	2000	2-4
Zinc (μgL^{-1})	112±71	163±89	3000	30
Nickel (μgL^{-1})	50±49	62±82	20	25-150
Cobalt (μgL^{-1})	32±22	55±48	n.g[†]	-

[a] = WHO desirable limit; [b] = soft water, [c] = medium water, [d] = hard water, [e] = Cr(III), [f] = Cr(VI), * = hardness dependent, [†]n.g = no guideline value'

4.19.3 Metals in Bottom Sediments of Cross and Qua Iboe River Systems

Metal levels in sediments revealed that the rivers were moderately polluted compared with other rivers in the region and other parts of the world. Results show higher levels for Pb, Cu, Zn, Ni and Co. However, results obtained for others showed lower values compared with values reported for other rivers in the region and other parts of the world (Table 4.30).

Sediment is the main sink and source of trace metals like in river and marine environment (WHO, 1996). Cadmium, for example, was lower than those reported for other rivers in the region: New Calabar River (12.8 µgg^{-1}), Bonny/New Calabar River (16 – 29 µgg^{-1}) and Esi River, Warri (5.5 µgg^{-1}) (Horsfall and Spiff, 2002; Chindah *et al.*, 2004; Akporido, 2010). Mean Cd concentration obtained from Cross River compared favourably with values reported for Orogodo River by Puyate *et al.* (2007). However, results obtained were higher than values reported for some other rivers in other parts of the world (Wade *et al.*, 2008; Villaescusa-Celaya *et al.*, 2000).

Lead level in Cross River (59.3±14.2 µgg^{-1}) was about four-times higher than that of Qua Iboe River (13.4±6.2 µgg^{-1}). Values obtained were higher than values reported for most river sediments in the region except asphyxiated sediments of Qua Iboe estuary (93.0 µgg^{-1}) by Essien *et al.* (2009b). The level in this study compared favourably with values reported for Buyak Menderes River and Gomti River as reported by Akcay *et al.* (2003) and Singh *et al.* (2005) respectively. Lead is known to be sorbed onto sediments in river and marine environment (Mostafa *et al.*, 2009). Chromium level for Cross River (15.9±5.3 µgg^{-1}) slightly compared favourably with that of Qua Iboe River (20.9±14.0 µgg^{-1}). Values obtained were higher than levels reported for other rivers in the region but lower than values reported for some other rivers in other parts of the world: J. A. Alzate reservoir, Mexico (85.0 µgg^{-1}), Montevideo Harbour, Mexico (162.0 µgg^{-1}), Buyak Menderes River, Turkey (160-195 µgg^{-1}), and Hindon River, India (42.9-250.4 µgg^{-1}) (Table 4.30).

The mean Cu concentration in sediments of Cross River (71.8±17.1 µgg^{-1}) and Qua Iboe River (45.3±15.8 µgg^{-1}) were higher than levels reported for other rivers in the region - 2.50 µgg^{-1} for Orogodo River, 1.87 µgg^{-1} for Calabar River, 0.04 µgg^{-1} for Iko River and 5.51 µgg^{-1} for Ntawuogba Creek.(Table 4.30). Zinc, nickel and cobalt in the

Table 4.30. Comparison of results of sediment metals of Cross and Qua Iboe River with other rivers in the Nigeria and other parts of the world

Study area/Rivers	Trace metals concentration (µgg^{-1} dry weight)							Reference
	Cd	Pb	Cr	Cu	Zn	Ni	Co	
Orogodo River, Agbor	0.49	4.39	0.89	2.50	1.26	0.71	-	Puyate *et al.* (2007)
New Calabar River, PH	12.8	41.6	ND	25.5	31.6	3.2	-	Horsfall and Spiff (2002)
Calabar River, Calabar	0.01	0.62	-	1.87	4.25	0.34	0.27	Bassey and Udosen (2007)
Qua Iboe River estuary	-	93.8	0.21	33.5	179.4	37.4	-	Essien *et al.* (2009b)
Iko River, Akwa Ibom	0.05	0.03	0.25	0.04	1.10	2.87	-	Benson and Etesin (2008)
Ntawuogba Creek, PH	0.30	22.28	-	5.51	-	0.89	-	Iwegbue *et al.* (2006)
Esi River, Warri	5.5	21	24	132	165	1.8	-	Akporido (2010)
Bonny/New Calabar River, PH	16-29	3-27	10-83	1-57	3-277	-	-	Chindah *et al.* (2004)
Ase River, Asaba-Ase	2.89±2.97	7.00±10.04	2.34±2.53	3.32±2.37	12.46±4.56	7.04±7.49	-	Iwegbue *et al.* (2007)
Lagos Lagoon, Nigeria	1.15	0.45	0.618	0.60	0.73	0.867	-	Aderinola *et al.* (2009)
Casco Bay, USA (Seaport)	0.4	40.0	68.0	23.0	88.0	26.8	-	Wade *et al.* (2008)
J. A. Alzate Reservoir, Mexico	2.45	26	85	35	145	33	-	Avila-Perez *et al.* (1999)
Montevideo Harbour, Uruguay	-	85	162	89	312	30		Muniz *et al.* (2004)
Buyak Menderes River, Turkey	-	35-75	160-195	130-150	85-185	168-418	30-38	Akcay *et al.* (2003)
Pearl River estuary, China	-	48±14	88±22	47±17	140±142	35±10	-	Ip *et al.* (2007)
Gediz River, Turkey	-	105-140	170-220	108-152	140-180	101-129	32-40	Akcay *et al.* (2003)
Hindon River, India	1.15-3.47	5.07-59.1	42.9-250.4	9.42-195.1	3.98-85.0	-	-	Suthar *et al.* (2009)
Gomti River, India	2.42	40.33	8.15	5.0	41.67	15.17	-	Singh *et al.* (2005)
Baja California, Mexico	0.08-0.64 (0.17)	6 – 21 (13.6)	56-802 (137)	4.9-23 (12.8)	39-188 (68.3)	16-44 (25.3)	-	Villaescusa-Celaya *et al.* (2000)
Hadramout coastal area, Gulf of Aden, Yemen	0.3–2.6 (1.5)	5.3–23 (10.3)	5.7–3.3 (10.9)	3.1–51 (20.4)	10.6–90.6 (55.6)	5.4–24.2 (12.4)	6–27.5 (12.8)	Mostafa *et al.* (2009)
Cross River	0.50±0.24	59.3±14.2	15.9±5.3	71.8±17.1	129±12	6.55±2.3	7.58±2.3	Present study
Qua Iboe River	1.59±0.87	13.4±6.2	20.9±14.0	45.3±15.8	122±18	4.92±3.0	5.52±2.9	Present study

two rivers showed comparable values with no significant difference. The mean Ni level (6.55±2.3 and 4.92±3.0 μgg^{-1}) in this study was significantly higher than other river sediments within the region except Qua Iboe estuary which recorded 37.4 μgg^{-1} as reported by Essien *et al*. (2009b). Ni values were lower than values reported for other water bodies outside Nigeria – Casco Bay USA, (26.8 μgg^{-1}), J. A. Alzate reservoir, Mexico (33.0 μgg^{-1}) and Gediz River, Turkey (101-129 μgg^{-1}).

4.20 SPECIATION MODELLING IN SURFACE WATER OF CROSS AND QUA IBOE RIVER USING PHREEQC MODEL

Mean Cd concentrations in Cross River and Qua Iboe River were 7.66x10^{-7} M and 2.47x10^{-6} M respectively (Table 4.30). The predominant dissolved species present includes $CdCl^{+}$ (80 – 82%), Cd Cl_2 (4 – 14% and the free hydrated ionic species, Cd^{2+} (5 – 16%). The mobile and toxic Cd^{2+} species was however only available in limited amount in the fresh water body. In Qua Iboe River system, the free hydrated species, Cd^{2+} showed significance only in the upstream stations (16 to 23%). The chloride complex species, $CdCl^{+}$ (74 – 80%) and Cd(OH)Cl (51 to 59%) were most significant in the upstream and downstream stations respectively. The trend in Qua Iboe River was however influenced by the marine water intrusion which accelerated the formation of the hydroxide complexes in the downstream stations.

Lead exists in Cross River as the free hydrated species, Pb^{2+} (42 - 70%), $PbCl^{+}$ (16 - 41%) and $PbCO_3$ (1 – 22%). But in Qua Iboe River system, only the free hydrated ion, Pb^{2+} (75 - 83%) and $PbCl^{+}$ (15 – 22%) showed predominance in the upstream stations, and the hydroxyl complexes, $Pb(OH)_2$ (53 – 65%), $Pb(OH)_3^{-}$ (25 – 44%) and $PbOH^{+}$ (2–5%) showed predominance in the downstream stations. Two major hydroxyl complexes of chromium (III); $Cr(OH)_2^{+}$ and $CrOH^{2+}$, showed dominance in Cross River with mean distribution ranging from 26 to 89% and 6.5 to 70% respectively. The free uncomplexed hydrated ion, Cr^{3+} ranged from 0 to 4%. In Qua Iboe River system, significant species were the hydroxyl complexes of $Cr(OH)_2^{+}$ (15 – 31%), $CrOH^{2+}$ (66 – 76%) and the free hydrated ion, Cr^{3+} (3 – 8.7%) showing dominance only in the upstream stations were observed. The free hydrated species was very low (< 10%) and therefore did not pose significant risk to the biota.

In Cross River, about 68.3% of the total Cu concentration existed as Cu(I) while 31.7% existed as Cu(II) while in Qua Iboe River, 51% of the total concentration existed as Cu(I) while 49.0% exists as Cu(II). Only three species of Cu(I) ($1.89x10^{-6}$ M), $CuCl_2^-$ (67 – 83%), $CuCl_3^{2-}$ (9.0 – 33%) and Cu^+ (0.5 – 8.0%) showed significant distribution with $CuCl_2^-$ being the most predominant complexed species. Two significant species of Cu (II) in Cross River were the free hydrated species, Cu^{2+} (36 – 88%) and the $CuCO_3$ (3.3 – 46.5%) species with stations Nwaniba and Ibaka recording ≥ 85% free hydrated Cu^{2+}. But in Qua Iboe River, the free hydrated species, Cu^{2+}, showed dominance in the upstream stations while the hydroxy-carbonate complex, $CuCO_3(OH)_2^{2-}$ showed >80% dominance in the downstream stations due to formation of carbonate and hydroxides. The free hydrated Cu^{2+} species which dominates the upstream stations of Qua Iboe River and Cross River could be as a result of low alkalinity recorded.

Total Zn concentration in Cross River was $1.07x10^{-7}$ M and in Qua Iboe River was $1.52x10^{-5}$ M. The free hydrated species, Zn^{2+} (80 – 94%) dominated in all the stations of Cross River and only in the upstream stations of Qua Iboe River. The downstream stations of Qua Iboe River showed dominance of only the hydroxy salt of $Zn(OH)_2$ (79 - 88%) and $Zn(OH)_3^-$ (10 – 20%).

About 98% of total Ni (II) concentration ($1.76x10^{-6}$ M) in Cross River was distributed as the free un-complexed hydrated species (Ni^{2+}) being the predominant Ni species, whereas, the upstream stations of Qua Iboe River recorded ~97% distribution of free Ni^{2+} as the predominant species while the downstream stations showed predominance of the hydroxy species $Ni(OH)_2$ (54 – 66%) and $Ni(OH)_3^-$ (25 – 45 %). Only about 2 – 8.5% of the free un-complexed Ni^{2+} was distributed in the downstream stations.

Cobalt species in the two river systems were the free hydrated species, Co^{2+}, $HCoO_2^-$ complex and the $CoCl^+$. The free hydrated species showed predominance (>97%) in Cross River and in the upstream stations of Qua Iboe River. At the downstream stations of Qua Iboe River, the most predominant species of Co is $HCoO_2^-$ which is 100% of the total occurrence making the other species of no significance.

4.21 SATURATION INDICES FOR CROSS RIVER AND QUA IBOE RIVER SYSTEM

Surface water composition at different sampling stations of the two rivers (Cross River and Qua Iboe River) systems showed some slight differences in composition. In Cross River, the water was highly oversaturated with respect to $CuCr_2O_4$, $PbHPO_4$ and Pyromorphite ($Pb_5(PO_4)_3Cl$) in all the stations. But in Qua Iboe River system, only the upstream stations, (with low ionic strength I = 0.0054 – 0.0086 M) showed higher degrees of oversaturation while the downstream stations (high ionic strength, I = 0.012 – 0.021 M) showed high under saturation of the same minerals. Atacamite ($Cu_2(OH)_3Cl$), $Ni(OH)_2$, tenorite (CuO), tsumebite ($Pb_2CuPO_4(OH)_3{:}3H_2O$) and zincite (ZnO) showed oversaturation in the downstream stations but was highly undersaturated in all the upstream stations. Cerrusite ($PbCO_3$), cuprite (Cu_2O) and otavite ($CdCO_3$) showed slight undersaturation.

CHAPTER FIVE

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 SUMMARY AND CONCLUSIONS

This study has provided valuable data on the pollution status of the Cross River and Qua Iboe River in Akwa Ibom State, Nigeria. These deal with the physicochemical properties and trace metals levels in surface water and sediment. In addition, it has provided novel data on the speciation of metals in the waters of these rivers, using a unique modelling method.

5.1.1 Physicochemical Characteristics of Cross River and Qua Iboe River

Average levels of all water quality parameters in the two rivers were generally low, except electrical conductivity, and fell within the national and international regulatory standards for drinking water. The quality of the river did not pose serious threat to the survival of aquatic life especially in terms of pH, DO, total hardness, BOD and nutrients concentrations. There was slight non-significant seasonal influence in some physicochemical parameters among the stations studied.

5.1.2 Metal Concentration in Surface Water and Sediment of Cross River and Qua Iboe River

Trace metal levels in surface water were generally lower than levels in sediments. However, levels in surface water showed remarkable contamination of Cd, Pb and Ni which exceeded the regulatory standards, thereby posing pollution threat to the biota. The highest potential contamination risk to flora and fauna was recorded by Cd while Pb recorded the lowest especially at Oron and Ibaka stations. The metal pollution levels in the river may be due to anthropogenic activities in the river.

In Qua Iboe River, average levels were higher than levels in Cross River. Atabong and Marina stations showed values for all metals (except Cu) which exceeded the regulatory guideline limit for drinking water due to municipal discharges. Generally, Cd, Pb and Ni exceeded the regulatory standards for drinking water, posing serious contamination risk to flora and fauna. From EF calculations, Pb and Cd showed significant contribution from anthropogenic sources particularly at Ibaka and Atabong stations. Seasonal distribution of trace metals in surface water and sediments showed higher levels during the wet season than the dry season which may be attributable to surface runoff carrying contaminants from agricultural farmlands, urban highways and municipal drainage channels into the river.

5.1.3 Chemical Speciation of Trace Metals in Sediments from Cross River and Qua Iboe River

There was no significant difference in the distribution patteren of the metals among the four fractions. The distribution of metals in sediments showed that all the metals were very mobile due to higher distribution (62.4 – 89.2 %) in the non-residual fractions, meaning that the metals are less strongly bound to minerals and non-resistant components. This suggests potential toxicity, bioavailability and risk to the biota

5.1.4 Speciation Modelling in Surface Water of Cross River and Qua Iboe River

Speciation modeling calculation results showed that the predominant species in surface water of Cross River were the free hydrated ions of Zn^{2+} (≥90.0%), Ni^{2+} (≥97.0%), Co^{2+} (≥97.7%), Pb^{2+} (≥42.0%) and Cu^{2+} (≥36.2%) as well as the chloride species - $CdCl^{+}$ (≥80.0%), $CuCl_2$ (≥66.0%), $PbCl^{+}$ (≥16.0%) and the hydroxy species of $CrOH^{2+}$ (≥50.0%) and $Cr(OH)_2^{+}$ (≥89.0%).

The pattern of distribution in Qua Iboe River differs significantly due to increased level of metal concentration and ionic strength of the water body. The free hydrated species of Cu^{2+} (≥89.0%), Ni^{2+} (≥97.0%), Pb^{2+} (≥76.0%) and Zn^{2+} (≥92.0%) showed predominance in the upstream stations thereby increasing bioavailability and toxicity of these metals to the aquatic organisms. But due to increased ionic strength in the downstream stations, the free hydrated species concentrations were relatively low and the inorganic complexed species - $Zn(OH)_2$ (≥79.0%), $Ni(OH)_2$ (≥54.0%), $Ni(OH)_3^{-}$ (≥25%), $HCoO_2^{-}$ (100%), $Pb(OH)_2$ (≥53.0%), $CuCO_3(OH)_2^{2-}$ (≥81.0%), $Cd(OH)Cl$ (≥51.0%) and CrO_4^{2-} (≥100.0%) predominates thereby reducing bioavailability and toxicity.

5.1.5 Saturation Indices for Cross River and Qua Iboe River

The saturation indices calculation showed higher SI values for $CuCr_2O_4$, $PbHPO_4$ and pyromorphite ($Pb_5(PO_4)_3Cl$) minerals in all stations of Cross River indicating oversaturation. But in Qua Iboe River, only the upstream stations indicated oversaturation while the downstream stations indicated high undersaturation for the same minerals. Atacamite ($Cu_2(OH)_3Cl$), $Ni(OH)_2$, tenorite (CuO), tsumebite ($Pb_2CuPO_4(OH)_3{:}3H_2O$) and zincite (ZnO) showed undersaturation, implying that these minerals would dissolve when in contact with the solution.

5.2 RECOMMENDATIONS

The following recommendations are therefore made from the study:

(a) Adequate environmental education and awareness on safe handling/use of fertilizers and pesticides in order to minimize the contribution of agricultural practices to water pollution should be given to farmers and residents of riverine/coastal communities.

(b) In Qua Iboe River system, metal levels were found to be high. This requires adequate pollution-control programs and stricter environmental regulations for water and sediment quality by the relevant monitoring agencies of government. This will help put in place measures that will mitigate further pollution of the water body in order to support the protection and management of the coastal ecosystems.

(c) Routine monitoring of the surface water and sediment quality should be given priority attention owing to the the trans-boundary nature of water pollution.

(d) Since some of the chemical species are responsible for the metal toxicity and bioavailability in aquatic systems, more analytical data on chemical speciation of surface water systems in Nigerian rivers and streams should be generated using the PHREEQCI model.

(e) Further research on the pollution status and chemical speciation studies of the quality of underground water within the region should be carried out.

REFERENCES

Abbasi, S.A. 2002. *Water Quality Indices: State of the Art Report*. National Institute of Hydrology, Scientific Contribution No. INCOH/SAR-25/2002, Roorkee, INCOH. 73pp.

Abdel-Satar, A. M., Goher, M. E. and Sayed, M. F. 2010. Recent environmental changes in water and sediment quality of Lake Qarum, Egypt. *Journal of Fisheries and Aquatic Science* 5(2): 56–69.

Abdul-Razak, A., Asiedu, A. B., Entsua-Mensah, R. E. M. and de-Graft-Johnson, K. A. A. 2009. Assessment of the water quality of the Oti River in Ghana. *West African Journal of Ecology* 15*:* 1-12.

Abowei, J. F. N. 2010. Salinity, dissolved oxygen, pH and surface water temperature conditions in Nkoro River, Niger Delta, Nigeria. *Advance Journal of Food Science and Technology* 2(1): 36-40.

Abu, G. O. and Egenonu, C. 2008. The current pollution status of the New Calabar River in the Niger Delta region of Southern Nigeria: A survey of antibiogram profiles of its bacterial isolates. *African Journal of Environmental Science and Technology* 2(6): 134–141.

Acevedo-Figueroa, D., Jiménez, B. D. and Rodriguez-Sierra, C. J. 2006. Trace metals in sediments of two estuarine Lagoons from Puerto Rico. *Environmental Pollution* 141: 336–342.

Ademoroti, C. M. A. 1996a. *Environmental Chemistry and Toxicology*. 1st ed. Ibadan: Foludex Press Ltd.

Ademoroti, C. M. A. 1996b. *Standard Methods for Water and Effluents Analysis*. 1st ed. Ibadan: Foludex Press Ltd. 182pp.

Aderinola, O. J., Clarke, E. O., Olarinmoye, O. M., Kusemiju, V. and Anatekhai, M. A. 2009. Heavy metals in surface water, sediments, fish and periwinkles of Lagos Lagoon. *American-Eurasian Journal of Agriculture and Environmental Science* 5(5): 609-617.

Adeyemo, O. K., Adedokun, O. A., Yusuf, R. K. and Adeleye, E. A. 2008. Seasonal changes in physicochemical parameters and nutrient load of river sediments in Ibadan city, Nigeria. *Global NEST Journal* 10(3): 326 – 336.

ADWG (Australian Drinking Water Guideline). 2004. *Australian Drinking Water Guidelines 6 ADWG*. National Water Quality Management Strategy. Published by the National Health and Medical Research Council (NHMRC). Retrieved June 18, 2009, from http://www.nhmrc.gov.au

Agbaire, P. O. and Obi, C. G. 2009. Seasonal variations of some physicochemical properties of river Ethiope water in Abraka, Nigeria. *Journal of Applied Science and Environmental Management* 13.1: 55 – 57.

Agbaire, P. O. and Oyibo, I. P. 2009. Seasonal variation of some physicochemical properties of borehole water in Abraka, Nigeria. *African Journal of Pure and Applied Chemistry* 3.6: 116-118.

Akcay, H., Oguz, A. and Karapire, C. 2003. Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research* 37: 813-822.

Akporido, S. O. 2010. An assessment of water, sediment and soil pollution arising from crude oil spillages in the vicinity of Esi River , Western Niger Delta. A Ph.D. Thesis. Department of Chemistry. University of Ibadan. Xxvi + 387pp.

Alam, M. N., Elahi, F. and Didar-UL-Alam, M. D. 2006. Risk and water quality Assessment overview of river Sitalakhya in Bangladesh. Academic Open Internet Journal 19, ISSN 1311 – 4360 [On-line]. http://www.acadjournal. com.

Alloway, B. J. 1995. *Heavy Metals in Soil*. 2nd ed. United Kingdom: Chapman and Hall.

American Public Health Association (APHA). 1998. *Standard methods for the examination of water and wastewater*. 20th ed. Washington, DC: American Water Works Association and Water Pollution Federation.

Anon. 2007. Pollution causes 40 percent of deaths worldwide, study finds. *Science Daily News*. Retrieved August 20, 2009, from http://www.sciencedaily.com/releases/htm.

ANZECC and ARMCANZ (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand). 2000a. *Australian and New Zealand guidelines for water quality monitoring and reporting*. National Water Quality Management Strategy No. 7. Canberra.

ANZECC and ARMCANZ (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand). 2000b. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*, vols. 1 and 2. National Water Quality Management Strategy. No. 4. Canberra. 678pp.

ANZECC and ARMCANZ (Australian and New Zealand Environment and Conservation Council and Agriculture and Resource Management Council of Australia and New Zealand). 2000c. *Sediment Quality Guidelines*. In: Australian and New Zealand guidelines for fresh and marine water quality. Retrieved June 20, 2009 from http://www.mincos.gov.au/publications/australian_and_new_zealand_guidelines_for_fresh_and_marine_water_quality.

APHA-AWWA-WEF (American Public Health Association, American Water Works Association and Water Environment Federation). 2005. *Standard methods for the*

Examination of Water and Wastewater. 21st ed. Washington, DC: American Water Works Association and Water Environment Federation. 7-15pp.

Appelo, C. A. J. and Postma, D. 2005. *Geochemistry, groundwater and pollution.* 2nd Ed. Rotterdam: Balkema. 558pp.

Arain, M. B., Kazi, T. G., Jamali, M. K., Afridi, H. I., Jalbani, N., Sarfraz, R. A. Baig, J. A., Kandhro, G. A. and Memon, M. A. 2008. Time saving modified BCR sequential extraction procedure for the fraction of Cd, Cr, Cu, Ni, Pb and Zn in sediment samples of polluted lake. *Journal of Hazardous Materials* 160(1): 235-239.

Arain, M.B., Kazi, T. G., Jamali, M. K., Baig, J. A., Afridi, H. I., Jalbani, N. and Sarfraz, R. A. 2009. Comparison of different extraction approaches for heavy metal partitioning in sediment sample. *Pedosphere* 19(4): 476-485**.**

Armah, A. K., Dapaah, G. A. and Wiafi, G. 1999. Water quality studies on two irrigation associated rivers in Southern Ghana. *Journal of Ghana Science Association* 1(2): 100–109.

Asonye, C. C., Okolie, N. P., Okenwa, E. E. and Inwuanyanwu, U. G. 2007. Some physicochemical characteristics and heavy metal profiles of Nigerian rivers, streams and water ways. *African Journal of Biotechnology* 6(5): 617-624.

ASTM (American Standard for Testing Materials). 2001. American Society for Testing and Materials Standards. New York.

Avila-Perez, P., Balcazar, M., Zarazua-Ortega, G., Barcelo-Quintal, B. and Dıaz-Delgado, C. 1999. Heavy metal concentration in water and sediments of a Mexican reservoir. *The Science of the Total Environment* 234: 185-196.

Awofolu, O. R., Du Plessis, R. and Rampedi, I. 2007. Influence of discharged effluent on the quality of surface water utilized for agricultural purposes. *African Journal of Biotechnology* 6(19): 2251-2258.

Azizullah, A., Khattak, M. N. K., Richter, P. and Häder, D. 2011. Water pollution in Pakistan and its impact on public health - A review. *Environment International* 37(2): 479-97.

Baig, J. A., Kazi, T. G., Arain, M. B., Afridi, H. I., Kandhro, G. A., Sarfraz, R. A., Jamal, M. K. and Shah, A. Q. 2009a. Evaluation of arsenic and other physicochemical parameters of surface and ground water of Jamshoro, Pakistan. *Journal of Hazardous Materials* 166: 662–669.

Baig, J. A., Kazi, T. G., Arain, M. B., Shah, A. Q., Sarfraz, R. A., Afridi, H. I., Kandhro, G. A., Jamali, M. K. and Khan, S. 2009b. Arsenic fractionation in sediments of different origins using BCR sequential and single extraction methods. *Journal of Hazardous Materials* 167: 745–751.

Baird, C. 1995. *Environmental Chemistry*. 2nd ed., New York: W. H. Freeman and Co.

Banks, D., Younger, P. L., Arnesen, R.-T., Iversen, E. R. and Banks, S. B. 1997. Mine-water chemistry: The good, the bad and the ugly. *Environmental Geology* 32(3): 157–174.

Bartram, J. and Ballance, R. 1996. A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes. Published on behalf of United Nations Environmental Programme (UNEP) and World Health Organization (WHO), E&FN Spoon Publishers, 172-177, 192-196.

Bartram, J. And Helmer, R. (1996). *Introduction*. In: Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes by J. Bartram and R. Balance (Eds.). Published on behalf of the United Nations Environment Programme and the World Health Organization (UNEP/WHO).

Bassey, D. E. and Udosen, E. D. 2007. Correlation between levels of some heavy metals in plants and sediments from a segment of Calabar River and associated creeks in Cross River state of Nigeria. *Toxicological and Environmental Chemistry* 89(1): 7–14.

Benson, N. U. and Etesin, U. M. 2008. Metal contamination of surface water, sediment and *Tympanotonus fuscatus var. radula* of Iko River and environmental impact due to Utapete gas flare station, Nigeria. *Environmentalist* 28: 195-202.

Bervoets, L., Blust, R. and Verheyen, R. 1996. Uptake of zinc by the midge larvae *Chironomus riparus* at different salinities: Role of speciation, acclimation, and calcium. *Environmental Toxicology and Chemistry* 15: 1423–1428.

Bezuidenhout, C. C., Mthembu, C., Puckree, T. and Lin, J. 2002. Microbiological evaluation of the Mhlathuze River, Kwazulu-Natal (RSA). *Water SA*. 28(3): 281-286.

Bhandari, N. S. and Nayal, K. 2008. Correlation study on physico-chemical parameters and quality assessment of Kosi River water, Uttarakhand. *E-Journal of Chemistry* 5.2: 342-346. Retrieved September 09, 2009, from http://www.e-journals.net.

Bharti, N. and Katyal, D. 2011. Water quality indices used for surface water vulnerability assessment. *International Journal of Environmental Science* 2(1): 154-173.

Bhattacharya, A., Routh, J., Jacks, G., Bhattacharya, P. and Morth, M. 2006. Environmental assessment of abandoned mine tailings in Adak, Vasterbotten District (northern Sweden). *Applied Geochemistry* 21: 1760–1780.

Bodek, I. B., Lyman, W. J., Reehl, W. F. and Rosenblatt, D. H. 1988. *Environmental inorganic chemistry: Properties, processes, and estimation methods*. SETAC Spec. Publ. Ser. New York: Pergamon Press. 158pp.

Bora, C. Jan. 08, 2013. Industrial Water Pollution. Retrieved April 12, 2013, from http://www.buzzle.com/articles/industrial-water-pollution.html.

Boyd, C. E. and Tucker, C. S. 1998. *Pond Aquaculture Water Quality Management.* Boston, Massachusetts. Kluwer Academic Publishers. 700pp.

Bryan, G. W. and Langston, W. J. 1992. Bioavailability, accumulation and effects of heavy metals in sediments with reference to United Kingdom estuaries: a review. *Environmental Pollution* 76: 89-131.

Campbell, P. G. C. 1995. *Interactions between trace metals and aquatic organisms: a critique of the Free-ion Activity Model*. In: A. Tessier, D. R. Turner (Eds.), Metal Speciation and Bioavailability in Aquatic Systems. New York, USA: John Wiley and Sons. 45-102pp.

Campbell, P. G. C., Lewis, A. G., Chapman, P. M., Crowder, A. A., Fletcher, W. K., Imber, B., Luoma, S. N., Stokes, P. M. and Winfrey, M. 1988. *Biologically available metals in sediments*. Ottawa: National Research Council of Canada, Canada Publication, 27694pp.

CCME (Canadian Council of Ministers of Environment). 1999. Canadian water quality guidelines for the protection of aquatic life. Canadian Water Quality Index 1.0. Technical Report, Canadian Environmental Quality Guidelines. Retrieved May 20, 2010, from http://www.ec.gc.ca/ceqgrcqe/English/Html/water_protocol-aquatic_life.cfm.

Cheggour, M., Chafik, A., Fisher, N. S. and Benbrahim, S. 2005. Metal concentration in sediments and clams in four Moroccan estuaries. *Marine Environmental Research*. 59: 119–137.

Cheung, K. C., Poon, B. H. T., Lan, C. Y. and Wong, M. H. 2003. Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China. *Chemosphere* 52: 1431-1440.

Chewonki, 2009. Clean water our precious resource. Retrieved August 16, 2013 from http://chewonki.org/Cleanwater/Cleanwater/water_pollution.asp.

Chhatwal, R. J. 2009. *Environmental Sciences: A Systematic Approach*. New Delhi, UDH Publishers & Distributors (P) Ltd. 368pp.

Chindah, A. C., Braide, S. A. and Sibeudu, O. C. 2004. Distribution of hydrocarbons and heavy metals in sediment and a crustacean (shrimps-*Penaeus notialis*) from the Bonny/New Calabar River Estuary, Niger Delta. *AJEAM-RAGEE* 9: 1 –17.

Cho, Y. G., Lee, C. B. and Choi, M. S. 1999. Geochemistry of surface sediments of the southern and western coast of Korea. *Marine Geology* 159: 111-129.

Cornelisa, G., Poppe, S., Gerven, T. V., Broeck, E. V., Ceulemans, M., Vandecasteele, C. 2008. Geochemical modelling of arsenic and selenium leaching in alkaline water treatment sludge from the production of non-ferrous metals. *Journal of Hazardous Materials* 159: 271–279.

Croxford, S. J., England, A. and Jarvis, A. P. 2004. Application of the PHREEQC geochemical Computer Model during the Design and Operation of UK Mine Water

Treatment Schemes. In: Jarvis, A. P., Dudgeon, B. A. & Younger, P. L.: mine water. 2004 Proceedings of International Mine Water Association Symposium 2, 8 Tab.; Newcastle Upon Tyne (University of Newcastle). 125-134pp.

Davies, O. A. and Abowei, J. F. N. 2009. Sediment quality of lower reaches of Okpoka Creek, Niger Delta, Nigeria. *European Journal of Scientific Research* 26(3): 437-442.

Davies, O. A., Ugwumba, A. A. A. and Abolude, A. S. 2008. Physicochemical quality of Trans-Amadi (Woji) Creek, Port Harcourt, Niger Delta, Nigeria. *Journal of Fish International* 3(3): 91-97.

De Wit, M., Behrendt, H., Bendoricchio, G., Bleuten, W. and van Gaans, P. 2002. The contribution of agriculture to nutrient pollution in three European rivers, with reference to the European Nitrates Directive. European Water Management. Official Publication of the European Water Association (EWA).

Debels, P. Figueroa, R. Urrutia, R. Barra, R. and Niell, X. 2005, Evaluation of water quality in the Chilla'n River (Central Chile) using physicochemical parameters and a modified water quality index. *Environmental Monitoring and Assessment* 110: 301–322.

Denman, K. L., Brasseur, G., Chidthaisong, A., Ciais, P., Cox, P. M., Dickinson, R. E., Hauglustaine, D., Heinze, C., Holland, E., Jacob, D., Lohmann, U., Ramachandran, S., da Silva Dias, P. L, Wofsy S. C. and Zhang, X. 2007. Couplings between Changes in the Climate System and Biogeochemistry. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change.* In: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M. and Miller, H. L. (eds.). Cambridge, United Kingdom and New York, NY, USA, Cambridge University Press.

Department of Petroleum Resources (DPR). 1997. Data on Oil spill incidents. Victoria Island, Lagos.

Di Toro, D. M., Kavvadas, C. D., Mathew, R., Paquin, P. R. and Winfield, R. P. 2001. *The persistence and availability of metals in aquatic environments*. Ontario, Canada, International Council on Metals in the Environment (ICME), 67pp.

Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr, S. M. and Redmond, M. S. 1990. Toxicity of cadmium in sediments: the role of acid volatile sulphide. *Environmental Toxicology and Chemistry* 9: 1487-1502.

Drever, J. I. 1997. *The geochemistry of natural waters: Surface and groundwaters environments*. 3rd ed. Englewood Cliffs, New Jersey-USA: Prentice-Hall. 149pp.

Dulo, S. O. 2008. Determination of some physico-chemical parameters of the Nairobi River, Kenya. *Journal of Applied Sciences and Environmental Management* 12(1): 57-62.

Emoyan, O. O., Ogban, F. E. and Akarah, E. 2006. Evaluation of heavy metals loading of River Ijana in Ekpan – Warri, Nigeria. *Journal of Applied Sciences and Environmental Management* 10(2): 121-127.

Environment Canada. 1981. *Analytical Methods Manual*. Water Quality Branch, Inland Waters Directorate. Ottawa: Environment Canada. 172pp.

Essien, J. P., Antai, S. P. and Olajire, A. A. 2009a. Distribution, seasonal variations and ecotoxicological significance of heavy metals in sediments of Cross River estuary mangrove swamp. *Water, Air and Soil Pollution* 197: 91-105.

Essien, J. P., Essien, V. and Olajire, A. A. 2009b. Heavy metal burdens in patches of asphyxiated swamp areas within the Qua Iboe estuary mangrove ecosystem. *Environmental Research* 109: 690–696.

Ettler, V., Mihaljevic, M., Matura, M., Skalova, M., Sebek, O. and Bezdicka, P. (2008). Temporal variation of trace elements in waters polluted by municipal solid waste landfill leachate. *Bulletin of Environmental Contamination and Toxicology* 80: 274 – 279.

Fan, W. H., Wang, W. -X., Chen, J. S., Li, X. D., Yen, Y. F. 2002. Cu, Ni, and Pb speciation in surface sediments from a contaminated bay of northern China. *Marine Pollution Bulletin* 44: 820–826.

Federal Environmental Protection Agency (FEPA). 1999. *Guidelines and Standards for Environmental Pollution Control in Nigeria.* Decree 58 of 1988, 238pp.

Fergusson, J. E. 1990. *The heavy elements: Chemistry, environmental impact and health effects*. Oxford, Pergamon Press.

Fianko, J. R., Lowor, S. T., Donkor, A. and Yeboah, P. O. 2010. Nutrient chemistry of the Densu River in Ghana. *Environmentalist* 30: 145–152.

Forstner, U. and Wittman, G. T. W. 1983. *Metal Pollution in the Aquatic Environment*. Berlin: Springer-Verlag. 486pp.

Francis, A., Sikoki, F. D. and Ansa, E. J. 2007. Physicochemical parameters of the Andoni River, Niger Delta, Nigeria. *Journal of Fisheries International* 2(1): 27-31.

Gao, X., Chen, S. and Long, A. 2008. Chemical speciation of 12 metals in surface sediments from the northern South China Sea under natural grain size. *Marine Pollution Bulletin 56*: 770–797.

Garrels, R. M. and Christ, C. L. 1965. *Solutions, Minerals and Equilibria.*, New York, Harper & Row. 450pp.

Gasim, M. B., Ismail, B. S., Toriman, E., Mir, S. I. and Chek, T. C. 2007. A physico-chemical assessment of the Bebar River, Pahang, Malaysia. *Global Journal of Environmental Research* 1(1): 07-11.

GESAMP. 1993. *Impact of oil and related chemicals and wastes on the marine environment*. Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP) Reports and Studies No. 50. IMO, London. 180pp.

Gupta, S., Bhatnagar, M. and Jain, R. 2003. Physicochemical characteristics and analysis of Fe and Zn in tube-well water and sewage water of Bikaner City. *Asian Journal of Chemistry* 15: 727.

HACH. 2003. *Water Analysis Handbook*. 4th ed. Vol. 2. Colorado-USA. HACH Chemical Company. 1268pp.

Hacioglu, N. and Dulger, B. 2009. Monthly variation of some physico-chemical and microbiological parameters in Biga Stream (Biga, Canakkale, Turkey). *African Journal of Biotechnology* 8(9): 1929-1937.

Halim, C. E., Short, S. A., Scott, J. A., Amal, R. and Low, G. 2005. Modelling the leaching of Pb, Cd, As, and Cr from cementitous waste using PHREEQC. *Journal of Hazardous Materials* A 125: 45–61.

Harvey, J. K. April 2008. Pollution Sources: Point and Nonpoint. Retrieved May 2013, from http://www.waterencyclopedia.com/Po-Re/Pollution-Sources-Point-and-Nonpoint.html.

Hasan, I., Rajia, S., Kabir, K. A. and Latifa, G. A. 2009. Comparative study on the water quality parameters in two rural and urban rivers emphasizing on the pollution level. *Global Journal of Environmental Research* 3(3): 218-222.

Hashmi, I., Farooq, S. and Qaiser, S. 2009a. Chlorination and water quality monitoring within a public drinking water supply in Rawalpindi Cantt (Westridge and Tench) area, Pakistan. *Environmental Monitoring and Assessment* 158: 393-403.

Hashmi, I., Farooq, S. and Qaiser, S. 2009b. Incidence of faecal contamination within a public drinking water supply in Ratta Amral, Rawalpindi. *Desalination and Water Treatment* 11:124-31.

Hauser, B. A. 2001. *Drinking Water Chemistry: A Laboratory Manual. Turbidity herp II*. Florida, USA: Lewis Publishers, A CRC Press Company. 71pp.

Herschy, R. W. 1999. *Hydrometry. Principles and Practices*. 2nd ed. Chichester: John Wiley and Sons. 376pp.

Horsfall, M. J. and Spiff, A. 2002. Distribution and partitioning of trace metals in sediments of the lower reaches of the New Calabar River, Port-Harcourt, Nigeria. *Environment Monitoring and Assessment* 78: 309-326.

Houghton, J. 2004. *Global Warming: The Complete Briefing.* 3rd ed. A Comprehensive Guide to the Science and Politics of Global Warming. Cambridge: Cambridge University Press. 340pp.

Hutin, Y., Luby, S. and Paquet, C. 2003. A large cholera outbreak in Kano City, Nigeria: the importance of hand washing with soap and the danger of street-vended water. *Journal of Water and Health* 01(1): 45-52.

Ikem, A., Egiebor, O. N. and Nyavor, K. 2003. Trace elements in water, fish and sediment from Tuskegee Lake, Southern USA. *Water, Air, and Soil Pollution* 149: 51-75.

Ip, C. C. M., Li, X., Zhang, G., Wai, O. W. H. and Li, Y. 2007. Trace metal distribution in sediments at Pearl River estuary and the surrounding coastal area of South China. *Environmental Pollution* 147(2): 311-323.

Iwegbue, C. M. A., Nwajei, G. E and Isirimah, N. O. 2006. Characteristic levels of heavy metals in sediments and dredged sediments of a municipal creek in the Niger delta, Nigeria. *Environmentalist* 26: 129-133.

Iwegbue, C. M. A., Nwajei, G. E. and Arimoro, F. O. 2007. Assessment of contamination by heavy metals in sediments of Ase River, Niger Delta, Nigeria. *Research Journal of Environmental Sciences* 1(5): 220-228.

Izoafuo, W. A. I., Chindah, A. C., Braide, S. A. and Iyalla, I. A. 2004. An assessment of sediment quality in the vicinity of marine landing jetties at the Middle Reach of Bonny Estuary, Niger Delta. *Scientia African* 3(2): 1-10.

Jain, C. K. and Sharma, C. K. 2001. Distribution of trace metals in the Hindon River. *Indian Journal of Hydrology* 253: 81-90.

Janssen, C. R., De Schamphelaere, K., Heijerick, D., Muyssen, B., Lock, K., Bossuyt, B., Vangheluwe, M. and Van Sprang, P. 2000. Uncertainties in the environmental risk assessment of metals. *Human and Ecological Risk Assessment* 6: 1003-1018.

Jayaprakash, M., Srinivasalu, S., Jonathan, M. P. and Mohan, V. R. 2005. A baseline study of physico-chemical parameters and trace metals in waters of Ennore Creek, Chennai, India. *Marine Pollution Bulletin* 50: 583-608.

Jenny, E. A. 1986. Chemical species in freshwater and terrestrial systems. In: *The Importance of Chemical Speciation in Environmental Processes.* M. Bernhard, F. E. Brickman, and P. J. Sandler. Eds., Berlin, Springer-Verlag. 121pp.

Jumbe, A. S. and Nandini, N. 2009. Heavy metals analysis and sediment quality values in Urban Lakes. *American Journal of Environmental Sciences* 5(6): 678-687.

Kabata-Pendias, A. and Pendias, H. 2001. *Trace Elements in Soils and Plants*. 3rd edition. Boca Raton, FL: CRC Press. 395pp.

Kannel, P. R., Lee, S., Lee, Y. S., Kanel, S. R., and Khan, S. P. 2007. Application of water quality indices and dissolved oxygen as indicators for river water classification and urban impact assessment. *Environmental Monitoring and Assessment* 132: 93–110.

Karikari, A. Y. and Bosque-Hamilton, E. K. 2004. The water quality of Lake Bosomtwi and its feeder streams. *Journal of Ghana Science Association* 4(1): 117-120.

Karikari, A. Y., Ansa-Asare, O. D. and Ansa-Asare, O. D. 2006. Physicochemical and microbial water quality assessment of Densu River of Ghana. *West Africa Journal Applied Ecol*ogy 10: 87-100.

Kartal S. and Tokalıoğlu, S. 2006. Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data. *Journal of Hazardous Materials* 132.1: 80-89.

Kennish, M. J. 1992. *Ecology of estuaries: anthropogenic effects*. Marine Science Series. USA: CRC Press. 512pp.

Khan, A. A., Paterson, R and Khan, H. 2003. Modification and Application of the CCME WQI for the Communication of Drinking Water Quality Data in Newfoundland and Labrador, Presented at 38th, Central Symposium on Water Quality Research, Canadian Association on Water Quality 10–11 February 2003, Burlington, Canada. 71pp.

Khan, M. A. A. and Khan, Y. S. A. 2003. Trace metals in littorial sediments from North-East coast of the Bay of Bengal along the ship breaking area, Chittagong Bangladesh. *Journal of Biological Sciences* 3(11): 1050-1057.

Khwaja, A. R., Singh, R. and Tandon, S. N. 2000. Monitoring of Ganga water and sediments vis-à-vis tannery pollution at Kanpur (India): a case study. *Environmental Monitoring and Assessment* 68: 19-35.

Kishe, M. A. Machiwa, J. F. 2003. Distribution of heavy metals in sediments of Mwanza Gulf of Lake Victoria, Tanzania. *Environment International* 28: 619-625.

Korfali, S. I. and Davies, B. E. 2004. Speciation of metals in sediment and water in a river underlain by limestone: Role of carbonate species for purification capacity of Rivers. *Advances in Environmental Research* 8: 599–612.

Korfali, S. I. and Jurdi, M. S. 2011. Speciation of metals in bed sediments and waters from Qaraaoun Reservoir, Lebanon. *Environmental Monitoring Assessment* 178: 568-579.

Koukal, B., Dominik, J., Vignati, D., Arpagaus, P., Santiago, S., Ouddane, B. and Benaabidate, L. 2004. Assessment of water quality and toxicity of polluted rivers

Fez and Sebou in the region of Fez (Morocco). *Environmental Pollution* 131:163-172.

Krantz, D. and Kifferstein, B. 1998. Water Pollution and Society. Retrieved May 12, 2008, from http://www.umich.edu/gs265/society/waterpollution.html.

Kumar, A. and Bahadur, Y. 2009. Physicochemical Studies on the Pollution Potential of River Kosi at Rampur (India). *World Journal of Agricultural Sciences* 5(1): 01-04.

Langmuir, D. 1997. *Aqueous Environmental Chemistry*. Upper Saddle River, New Jersey: Prentice-Hall. 600pp.

Lasheen, M. R. and Ammar, N. S. 2009. Speciation of some heavy metals in River Nile sediments, Cairo, Egypt. *Environmentalist* 29: 8-16.

Leotsinidis, M. and Sazakli, E. 2008. Evaluating contamination of dredges and disposal criteria in Greek coastal areas. *Chemosphere* 72: 811-818.

Li, Q. S., Wu, Z. F., Chu, B., Zhang, N., Cai, S. S. and Fang, J. H. 2007. Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. *Environmental Pollution* 149: 158–164.

Li, X. D., Shen, Z. G., Wai, O. W. H. and Li, Y. S. 2001. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. *Marine Pollution Bulletin* 42: 215–223.

Long, E. R. and MacDonald, D. D. 1998. Recommended uses of empirically derived sediment quality guidelines for marine and estuarine ecosystems. *Human and Ecological Risk Assessment* 4: 1019-1039.

Long, E. R., MacDonald, D. D., Smith, S. L. and Calder, F. D. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19: 81-97.

Longe, E. O. and Omole, D. O. 2008. Analysis of pollution status of River Illo, Ota, Nigeria. *Environmentalist* 28: 451-457.

Loska, K. and Wiechula, D. 2003. Application of principal component analysis of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere* 57: 723-733.

Luoma, S.N. 1990. Processing affecting metal concentrations in estuarine and coastal marine sediments. In: *Heavy Metals in the Marine Environment*. P. S. Rainbow and R. W. Furness. Eds. Cleveland, OH: CRC Press.

Luoma, S.N., 1989. Can we determine the biological availability of sediment-bound trace elements? *Hydrobiologia* 176/177: 379-396.

Ma, L. Q. and Rao, G. N. 1997. Chemical fractionation of Cd, Cu, Ni, and Zn in contaminated soils. *Journal of Environmental Quality* 26: 259–264.

MacDonald, D. D., Ingersoll, C. G. and Berger, T. A. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Archives of Environmental Contamination and Toxicology* 39: 20-31.

Maiz, I., Arambarri, I., Garcia, R. and Millan, E. 2000. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedures using factor analysis. *Environmental Pollution* 110: 3-9.

Majumder, M. May 24, 2009. Water quality index calculator. Retrieved June 12, 2012 from http://network.carboncapturejournal.com/profiles/blogs/water-quality-index-calculator/

Markowitz, D. 1999. *What's in Our Water?* A Water Quality Education Project. Environmental Health Sciences Centre. University of Rochester. pp

Mastrandrea, M. and Schneider, S. H. 2007. "Global Warming." Microsoft Student 2008 [DVD]. Redmond, WA: Microsoft Corporation.

McCready, S., Birch, G. F. and Long, E. R. 2006. Metallic and organic contaminants in sediments of Sydney Harbour, Australia and vicinity – A chemical dataset for evaluating sediment quality guidelines. *Environment International* 32: 455-465.

Meybeck, M., Kuusisto, E., Mäkelä, A. and Mälkki, E. (1996). *Water Quality*. In: Water Quality Monitoring - A Practical Guide to the Design and Implementation of Freshwater Quality Studies and Monitoring Programmes by J. Bartram and R. Balance (Eds.). Published on behalf of the United Nations Environment Programme and the World Health Organization (UNEP/WHO).

Miller, G. P. 2001. Surface complexation modelling of arsenic in natural water and sediment systems. A Ph.D. dissertation on geochemistry, Department of Earth and Environmental Science New Mexico Institute of Mining and Technology, Socorro, New Mexico. 216pp.

Morel, F. M. M. and Herring, J. G. 1993. *Principles and Applications of Aquatic Chemistry*. 2nd ed. New York: John Wiley & Sons, Inc. 588pp.

Morrison, G., Fatoki, O. S., Persson, L. and Ekberg, A. 2001. Assessment of the impact of point source pollution from the Keiskammahoek sewage treatment plant on the Keiskamma River – pH, electrical conductivity, oxygen demanding substances (COD) and nutrients. *Water SA* 27(4): 475-480.

Mostafa, A. R., Al-Alimi, A. K. A. and Barakat, A. O. 2009. Metals in surface sediments and marine bivalves of the Hadhramout coastal area, Gulf of Aden, Yemen. *Baseline/Marine Pollution Bulletin* 58: 290-311.

Mudroch, A. and Macknight, S. D. 1994. *Techniques for Aquatic Sediments Sampling*. Boca Raton: Lewis Publishers. 658pp.

Mudroch. A., Azcue, J. M. and Mudroch, P. 1997. *Manual of Physico-chemical Analysis of Aquatic Sediments.* Boca Raton, FL. Lewis Publishers.

Muniz, P., Danulat, E., Yannicelli, B. and Garcia-Alonso, J. 2004. Assessment of contamination by heavy metals and petroleum hydrocarbons in sediments of Montevideo Harbour (Uruguay). *Environment International* 29: 1019-1028.

Muohi, A. W., Onyari, J. M., Omondi, J. G. and Mavuti, K. M. 2003. Heavy metals in sediments from Makupa and Port–Reitz Creek systems: Kenyan Coast. *Environment International* 28: 639-647.

Murdoch, T., Cheo, M. and O'Laughlin, K. 2001. *Stream Keeper Field Guide. Watershed Inventory and Stream Monitoring Methods*. Everett, WA: Adopt-A-Stream Foundation. 258pp.

Mustapha, M. K. 2008. Assessment of the water quality of Oyun Reservoir, Offa, Nigeria, using selected physicochemical parameters. *Turkish Journal of Fisheries and Aquatic Sciences* 8: 309-319.

Naji, A., Ismail, A. and Ismail, A. R. 2010. Chemical speciation and contamination assessment of Zn and Cd by sequential extraction in surface sediment of Klang River, Malaysia. *Microchemical Journal* 95: 285-292.

Nduka, J. K. and Orisakwe, O. E. 2010. Water-quality issues in the Niger Delta of Nigeria: a look at heavy metal levels and some physicochemical properties. *Environmental Science and Pollution Research* 18(2): 237-246.

Nduka, J. K., Orisakwe, O. E. and Ezenweke, L. O. 2008. Some physiological parameters of potable water supply in Warri, Niger Delta area of Nigeria. *Scientific Research and Essay* 3(11): 547-551.

Nemati, K., Abubakar, N. K. and Abas, M. R. 2009. Investigation of heavy metals mobility in shrimp aquaculture sludge—comparison of two sequential extraction procedures. *Microchemical Journal* 91: 227–231.

Nordstrom, D. K. and Munoz, J. L. 1986. *Geochemical thermodynamics*. Palo Alto, CA, Blackwell Scientific Publications. pp477.

NRC (National Research Council). 1989. *Contaminated marine sediments – assessment and remediation*. Washington DC: National Academy Press. 493pp.

NRC (National Research Council). 2000. *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution*. Washington, DC: National Academy Press. Retrieved May 20, 2009, from http://www.nap.edu/catalog /9812.html.

Nriagu, J. O. and Pacyna, J. M. 1988. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. *Nature* 333: 134-140.

Nubi, O. A. and Nubi, A. T. 2010. Pollution assessment of the impact of industrial effluents on the qualities of surface water and sediments of River Ona in Ibadan, Oyo state, Nigeria. *World Review of Science, Technology and Sustainable Development* 7(4): 379-386.

Nwilo, P. C. and Badejo, O. T. 2005. *Impacts and management of oil spill pollution along the Nigerian coastal areas.* Retrieved June 12, 2009, from http://www.fig.net/pub/figpub/pub36/chapters/chapter_8.pdf.

Obiefuna, G. I. and Orazulike, D. M. 2010. Chemical speciation of some metal ions in ground waters of Yola area using geochemical model. *Journal of Applied Science and Environmental Management* 14(2): 65-70.

Obire, O., Tamuno, D. C. and Wemedo, S. A. 2003. Physicochemical quality of Elechi Creek in Port Harcourt. *Journal of Applied Science and Environmental Management* 7(1): 43-49.

Odukuma, L. O. and Okpokwasili, G. C. 1997. Seasonal influences of the organic pollution monitoring of the New Calabar River, Nigeria. *Environmental Monitoring Assessment* 45(1): 43-56.

Oguzie, F. A. and Izevbigie, E.E. 2009. A study of heavy metals concentrations in the sediments upstream of Ikpoba River and reservoir in Benin City, Nigeria. *Bioscience Research Communications* 21(3): 19-127

Ohimain, E. I., Imoobe, T. O and Bawo, D. D. S. 2008. Changes in water physico-chemical properties following the dredging of an oil well access canal in the Niger Delta. *World Journal of Agricultural Sciences* 4(6): 752-758.

Olaifa, F. E. 2006. Hydrocarbon and heavy metal pollution of water and sediments of Cross River and Akwa Ibom coastal waters, Nigeria. *Journal of Environmental Systems* 32(1): 27-36.

Olajire, A. A and Imeokparia, F. E. 2000. Water quality assessment of Osun River: studies on inorganic nutrients. *Environmental Monitoring Assessment* 69: 17-28

Olobaniyi, S. B., Owoyemi, F. B. 2006. Characterization by factor analysis of the chemical facies of ground water in the deltaic plain sands aquifer of Warri, Western Niger Delta, Nigeria. African Journal of Science and Technology 7(1): 73-81.

Omo-Irabor, O. O., Olobaniyi, S. B., Oduyemi, K. and Akunna, J. 2008. Surface and groundwater water quality assessment using multivariate analytical methods: A case study of the Western Niger Delta, Nigeria. *Physics and Chemistry of the Earth* 33: 666-673.

Onianwa, P. C. Ipeaiyeda, A. and Emurotu, J. E. 2001. Water quality of the urban rivers and streams of Ibadan - Nigeria. *Environmental Education and Information* 20(2): 107-120.

Oribhabor, B. J. and Ogbeibu, A. E. 2009. Concentration of heavy metals in a Niger Delta mangrove Creek, Nigeria. *Global Journal of Environmental Sciences* 8(2): 1–8.

Otokunefor, T. V. and Obiukwu, C. O. 2005. Impact of Refinery influent on physic-chemical properties of a water body on Niger Delta. *Journal of Applied Ecology and Environmental Research* 3: 61-72.

Owhonda, N. K., Akinrotimi, O. A., Ansa, E. J., Edun, O. M., Anyanwu, P. E., Okpara, J. Y. and Onunkwo, D. O. 2007. Wet season variation in some physicochemical parameters of brackish water fish ponds and main channels in Buguma, Rivers State, Nigeria. *Journal of Fisheries International* 2((3): 255-259.

Oze, G., Oze, R., Anunuso, C., Ogukwe, C., Nwanjo, H. and Okorie, K. 2006. Heavy metal pollution of fish of Qua-Iboe River estuary: Possible implications for neurotoxicity. *The Internet Journal of Toxicology* 3.1. Retrieved May 20, 2009, from, http://www.ispub.com/journal/the_internet_journal_of_toxicology/volume_3_number_1_55/article_printable/heavy_metal_pollution_of_fish_of_qua_iboe_river_estuary_possible_implications_for_neurotoxicity.html

Pardo, R., Barrado, E., Lourdes, P. and Vega, M. 1990. Determination and speciation of heavy metals in sediments of the Pisuerga River. *Water Research* 24: 373–379.

Parkhurst, D. L. and Appelo., C. A. J. 1999. *User's Guide to PHREEQC (Version 2)- A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations.* Water Resources Investigation Report 99-4259. Denver, Colorado, US Geological Survey.326pp.

Patnaik, K. N. 2005. Studies on environmental pollution of major industries in Paradip Area. A Ph.D. Thesis. Utkal University, Bhubneshwar, (Unpublished).

Prati, L., Pavenello, R. and Pesaria, F. 1971. Assessment of surface water quality by a single index pollution. *Water Research* 741-751.

Pretorious, L. 2000. An investigation into the effect of various levels of sanitation on surface water quality in a typical developing community. *SA Water Bulletin* 26(2): 10-12.

Prieto, A., Zuloaga, O., Usobiaga, A., Bartolome, L., Fernandez, L. A. and Etxeberria, N. 2008. Levels and spatial distribution of inorganic and organic contaminants in sediments along the Bilbao estuary. *Baseline/Marine Pollution Bulletin* 56: 2082-2105.

Pueyo, M., Mateu, J., Rigol, A., Vidal, M., López-Sánchez, J. F. and Rauret, G. 2008. Use of the modified BCR three-step sequential extraction procedure for the study of trace element dynamics in contaminated soils. *Environmental Pollution* 152(2): 330-341.

Puyate, Y. T., Rim-Rukeh, A. and Awatefe, J. K. 2007. Metal pollution assessment and particle size distribution of sediments of Orogodo River, Agbor, Delta State, Nigeria. *Journal of Applied Sciences Research* 3(12): 2056-2061.

Rabadjieva, D., Tepavitcharova, S., Todorov, T., Dassenakis, M., Paraskevopoulou, V. and Petrov, M. 2009. Thermodynamic modelling of inorganic chemical speciation in river waters affected by mine water discharges. *Euro-Asian Journal of Sustainable Energy Development Policy* 3: 15–25.

Ramos, L., Hernandez, L. M. and Gonzalez, M. J. 1994. Sequential fractionation of copper, lead, cadmium and zinc in soils from near Donana National Park. *Journal of Environmental Quality* 23: 50–57.

Rao, C. R. M., Sahuquillo, A. and Sanchez, J. F. L. 2008. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water, Air and Soil Pollution* 189: 291–333.

Rauret, G. R. R. and Lopez Sanchez, J. F. 1989. Optimization of Tessier procedure for metal solid speciation in river sediments. *International Journal of Environmental Analytical Chemistry* 36: 69–83.

Rauret, G., Lopez-Sanchez, J. F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A. and Quevauviller, P. 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *Journal of Environmental Monitoring* 1: 57–61.

Rim-Rukeh, A., Ikhifa, G. O. and Okokoyo, P. A. 2006. Effects of agricultural activities on the water quality of Orogodo River, Agbor Nigeria. *Journal of Applied Sciences and Research* 2(5): 256-259.

Rim-Rukeh, A., Ikhifa, G. O. and Okokoyo, P. A. 2007. Physicochemical characteristics of some waters used for drinking and domestic purposes in the Niger Delta, Nigeria. *Environmental Monitoring Assessment* 128: 475-482.

Roach, A. C. 2005. Assessment of metals in sediments from Lake Macquarie, New South Wales, Australia, using normalisation models and sediment quality guidelines. *Marine Environmental Research* 59: 453-472.

Sahuquillo, A., Lopez-Sanchez, J. F., Rubio, R., Rauret, G., Thomas, R. P., Davidson, C. M. and Ure, A. M. 1999. Use of a certified reference material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Analytica Chimica Acta* 382: 317–327.

Sakai, H., Kojima, Y. and Saito, K. 1986. Distribution of metals in water and sieved sediments in the Toyohira River. *Water Research* 20: 559-567.

Sakan, S. M., DorCevic, D. S., Manojlovic, D. D. and Predrag, P. S. 2009. Assessment of heavy metal pollutants accumulation in the Tisza river sediments. *Journal of Environmental Management* 90: 3382-3390.

Salomons, W. 1995. Environmental impacts of metals derived from mining activities: processes, prediction, and prevention. *Journal of Geochemistry Exploration* 52: 5–23.

Salomons, W. and Forstner, U. 1980. Trace metal analysis on polluted sediments. Part II: evaluation of environmental impact. *Environmental Technology Letters* 1: 506–517.

Salomons, W. and Forstner, U. 1984. *Metals in the Hydrocycle*. New York, Springer-Verlag. 359pp.

Satapathy, D. P., Panigrahi, R. K. 2005. Modelling of high fluoride groundwaters in India using PHREEQC. *International Journal of Advanced Technology in Civil Engineering* 1: 1-7.

Satheeshkumar, P. and Khan, B. A. 2009. Seasonal variations in physicochemical parameters of water and sediment characteristics of Pondicherry Mangroves. *African Journal of Basic & Applied Sciences* 1(1-2): 36-43.

SAWQG (South African Water Quality Guideline). 1996. *South African Water Quality Guideline*. Vol. 8: Field Guide, 1st Ed. Pretoria. Department of Water and Forestry Affairs. pp

Schumacher, B. A. 2002. Methods for the determination of total organic carbon (TOC) in soils and sediments. *Ecological Risk Assessment* 8(6): 1375-1396.

Sharma, R. (2005). Deep-sea impact experiments and their future requirements. *Marine Georesources and Geotechnology* 23(4): 331-338.

Simpson, C. D., Mosi, A. A., Cullen, W. R. and Reimer, K. J. 1996. Composition and distribution of polycyclic aromatic hydrocarbon contamination in superficial marine sediments from Kitimat Harbour, Canada. *Science of Total Environment* 181: 265-278

Simpson, S. L, Batley, G. E., Chariton, A. C., Stauber, J. L., King, C. K., Chapman, J. C., Hyne, R. V., Gale, S. A., Roach, A. C. and Maher, W. A. 2005. *Handbook for Sediment Quality and Assessment*. Bangor, NSW: CSIRO Energy Technology. 520pp.

Sinex, S. A. and Wright, D. A. 1988. Distribution of trace metals in the sediments and biota of Chesapake Bay. *Marine Pollution Bulletin* 19: 425-431.

Singh, K. P., Mohan, D., Singh, V. K. and Malik, M. 2005. Studies on distribution and fractionation of heavy metals in Gomti River sediments—a tributary of the Ganges, India. *Journal of Hydrology* 312: 14-27

Skye, J. 2013. Effects of Water Pollution. Retrieved August 18, 2013 from http://greenliving.lovetoknow.com/

Smith, S. L., MacDonald, D. D., Keenleyside, K. A., Ingersoll, C. G. and Field, J. 1996. A preliminary evaluation of sediment quality assessment values for freshwater ecosystems. *Journal of Great Lakes Research* 22: 624-638.

Sohrabi, T., Ismail, A. and Nabavi, M. B. 2010. Distribution and normalization of some metals in surface sediments from South Caspian Sea. *Bulletin of Environmental Contamination and Toxicology*. DOI 10.1007/s00128-010-0112-z. Published online on October 19, 2010.

SPDC (Shell Petroleum Development Company). 2012. Oil Spill in the Niger Delta – Monthly Data for 2012. Annual Report of Shell Petroleum Development Company. December 2012 Report. Lagos, SPDC. Retrieved July 13, 2013 from http://www.shell.com.ng/environment-society/environment-tpkg/oil-spills.html

Srinivasa-Reddy, M., Basha, S. Joshi, H. V. and Ramachandraiah, G. 2005. Seasonal distribution and contamination levels of total PHCs, PAHs and heavy metals in coastal waters of the Alang-Sosiya ship scrapping yard, Gulf of Cambay, India. *Chemosphere* 61: 1587-1593.

Stumm, W. and Morgan, J. J. 1996. *Aquatic Chemistry*, 3rd ed. New York: John Wiley and Sons, Inc. 1022pp.

Subyani, A. M. 2005. Hydrochemical identification and salinity problem of ground-water in Wadi Yalamlam basin, Western Saudi Arabia. *Journal of Arid Environments* 60: 53–66.

Suthar, S., Nema, A. K., Chabukdhara, M. and Gupta, S. K. 2009. Assessment of metals in water and sediments of Hindon River, India: Impact of industrial and urban discharges. *Journal of Hazardous Materials* 171: 1088-1095.

Suthar, S., Sharma, J., Chabukdhara, M., and Nema, A. K. 2010. Water quality assessment of river Hindon at Ghaziabad, India: Impact of industrial and urban waste water. *Environmental Monitoring and Assessment* 165: 103–112. doi:10.1007/s10661-009-0930-9.

Sutherland, R. A. and Tack, F. M. G. 2003. Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure. *Advances in Environmental Research* 8(1): 37-50.

Sutherland, R. A. and Tack, F. M. G. 2007. Sequential extraction of lead from grain size fractionated river sediments using optimized BCR procedure. *Water, Air, Soil Pollution* 184: 269-284.

Tabata, M., Ghaffar, A., Eto, Y., Nishimoto, J. and Yamamoto, K. 2007. Distribution of heavy metals in interstitial waters and sediments at different sites in Ariake bay, Japan. *E-Water* 5: 1-24.

Templeton, D. M., Ariese, F., Cornelis, R., Danielson, l.-G., Muntau, H., Van Leeuwen, H. P. and Lobinski, R. 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches. *Pure and Applied Chemistry* 72(8): 1453-1470.

Templeton, D. M., Ariese, F., Cornelis, R., Danielsson, L-G., Muntau, H., Van Leeuwen, H. P. and Lobinski, R. 2000. Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches. *Pure and Applied Chemistry* 72: 1453-1470.

Tepavitcharova, S., Todorov, T., Rabadjieva, D., Dassenakis, M. and Paraskevopoulou, V. 2009. Chemical speciation of inorganic pollutants in *river–estuary–sea* water systems. *Environmental Monitoring and Assessment* 149.1-4: 251-260. DOI: 10.1007/s10661-008-0199-4

Tepavitcharova, S., Todorov, T., Dassenakis, M., Paraskevopoulou, V. 2010. Chemical speciation in water influenced by lead-zinc metallurgical industry. *Environmental Monitoring and Assessment* 169: 27-36.

Tepavitcharova, S., Todorov, T., Rabadjieva, D., Dassenakis, M., Paraskevopoulou, V. 2011. Chemical speciation in natural and brine sea waters. *Environmental Monitoring and Assessment* 180: 217-227.

Tepe, Y. and Mutlu, E. 2005. Physicochemical characteristics of Hatay Harbiye Spring Water. *Journal of the Institute of Science and Technology of Dumlupınar University* 6: 77-88.

Tepe, Y., Tűrkmen, A., Mutlu, E. and Atęs, A. 2005. Some physicochemical characteristics of Yarseli Lake, Hatay, Turkey. *Turkish Journal of Fisheries and Aquatic Sciences* 5: 35-42.

Tessier, A. and Turner, D. R. 1995. *Metal Speciation and Bioavailability in Aquatic Systems*. Chichester, Wiley and Sons. 679pp.

Tessier, A., Campbell, P. G. C., Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Analytical Chemistry* 51: 844–851.

Tewari, A., Joshi, H. V., Trivedi, R. H., Sravankumar, V. G., Raghunathan, C., Khambhaty, Y., Kotiwar, O. S. and Mandal, S. K. 2001. Studies on the effect of ship scrapping industry and its associated waste on the biomass production and biodiversity of biota ‘‘in situ’’ condition at Alang. *Marine Pollution Bulletin* 42: 462-469.

Trivedy, R. K. and Goyal, P. K. 1986. Chemical and biological methods for water pollution studies. *Enviro-Media Karad.* 3(3-4): 36-96.

Udosen, E. D. 2000. Variations in oxygen and some related pollution parameters in some streams in Itu area of Nigeria. *Journal of Environmental Sciences* 12(1): 75-80.

Udotong, I. R., John, O. U. M. and Udotong, J. I. R. 2008. Microbiological and physicochemical studies of wetland soils in Eket, Nigeria. Proceedings of World Academy of Science, Engineering and Technology Vol. 34 October 2008, ISSN 2070-3740.

Ugwumba, A. O. and Ugwumba, A. A. 1993. A study of the physicochemical hydrology and plankton of Awuba lake in Ibadan, Nigeria. *Fish Acadbiz Comm.* 1: 26-39.

Ullah, R, Malik, R. N. and Qadir, A. 2009. Assessment of groundwater contamination in an industrial city, Sialkot, Pakistan. *African Journal of Environmental Science and Technology* 3: 429-46.

UN-WWAP (United Nations/World Water Assessment Programme). 2003. *Water for People, Water for Life*. 1st UN World Water Development Report: Paris, New York and Oxford. UNESCO and Berghahn Books. 461pp.

UNEP. 2005. *Regional Seas Marine Litter: An Analytical Overview*. Retrieved March 13, 2009, from http://www.unep.org/regionalseas/marinelitter/publications/docs/anl_oview.pdf.

UNEP. 2009. *Environmental pollution and impacts on public health: Implications of the Dandora municipal dumping site in Nairobi, Kenya*. United Nations Environment Programme.

UNEP/WHO. 1996. *A practical guide to the design and implementation of freshwater quality studies and monitoring programmes*. J. Bartram and R. Balance. Eds. Published on behalf of United Nations Environmental Programme and World Health Organization, E&FN Spoon Publishers, 172-177, 192-196.

UNESCO. 2003. *Water for people, water for life*. The United Nations World Water Development Report; United Nations Educational, Scientific and Cultural Organization (UNESCO) and Berghahn Books. 461pp.

UNESCO/WHO/UNEP. 2001. *Water Quality Assessment: A Guide to Use Biota, Sediment and Water in Environmental Monitoring*. 2nd ed. United Nations Environment Programme. ISBN: 041921590: 10-14.

United Nations. 1992. *Report of the United Nations Conference on Environment and Development*. Resolutions adopted by the Conference. A/CONF.151/26/Rev. 1, vol. 1. United Nations, 3-14 June 1992, Rio de Janeiro.

Ure, A. M., Quevauviller, P. H., Muntau, H. and Griepink, B. 1993. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European communities. *International Journal of Environmental Analytical Chemistry* 51: 135–151.

USAID. 1990. *Strategies for linking water and Sanitation programmes to Child Survival*. Washington D.C.: United States Agency for International Development.

US-EPA. 1991. MINTEQA2, A geochemical assessment data base and test cases for environmental systems: Ver. 3.0 user’s manual. EPA/600/3-91/-21. Athens, GA. Allison, J.,D., D.S. Brown, and K.J. Novo-Gradac.

US-EPA. 2009. *Drinking Water Contaminants*. United States Environmental Protection Agency. Retrieved June 15, 2009 from http://www.epa.gov/safewater/mcl.html#mcls .

Vanloon, G. W. and Duffy, S. J. 2000. *Environmental Chemistry: A global Perspective.* New York. Oxford University Press.

Villaescusa-Celaya, J. A., Gutierrez-Galindo, E. A. and Flores-Munoz, G. 2000. Heavy metals in the fine fraction of coastal sediments from Baja California (Mexico) and California (USA). *Environmental Pollution* 108: 453-462.

Violintzis, C., Arditsoglou, A. and Voutsa, D. 2009. Elemental composition of suspended particulate matter and sediments in the coastal environment of Thermaikos Bay, Greece: Delineating the impact of inland waters and wastewaters. *Journal of Hazardous Materials* 166: 1250-1260.

Wade, T. L., Sweet, S. T. and Klein, A. G. 2008. Assessment of sediment contamination in Casco Bay Main, USA. *Environmental Pollution* 152(3): 505-521.

Wakawa, R. J., Uzairu, A., Kagbu, J. A. and Balarabe, M. L. 2008. Impact assessment of effluent discharge on physicochemical parameters and some heavy metal concentrations in surface water of River Challawa, Kano, Nigeria. *African Journal of Pure and Applied Chemistry* 2(10): 100-106.

Wang, W. -X. 2002. Interactions of trace metals and different marine food chains. *Marine Ecology Progress Series* 243: 295-309.

Wang, W. -X. and Fisher, N. S. 1999. Delineating metal accumulation pathways for aquatic invertebrates. *Science of the Total Environment* 237/238: 459–472.

Wang, X. and Qin, Y. 2006. Spatial distribution of metals in urban topsoils of Xuzhou (China): Controlling factors and environmental implications. *Environmental Geology* 49: 905-914.

Warner, D. 1998. *Drinking water supply and environmental sanitation for health*. A paper presented at the International Conference of Water for Sustainable Development, Paris. 149pp.

Wegwu, M. O. and Akininwor, J. O. 2006. Assessment of heavy metal profile of the New Calabar River and its impact on juvenile *Clarias gariepinu*. *Chemistry and Biodiversity* 3(1): 79-87.

WHO/UNICEF. 2000. *Global water supply and sanitation assessment 2000 report*. USA: World Health Organization and United Nations Children's Fund. Retrieved June, 2009, from http://www.who.int/water_sanitation_health/ monitoring/jmp2000.pdf.

WHO. 1996. *Guidelines for Drinking Water Quality. Health Criteria and other Supporting Information*. 2nd ed. vol. 2. Geneva. World Health Organization.

WHO. 2004. *Guidelines for Drinking Water Quality*. 3rd ed. In: Recommendation. Geneva. World Health Organization

WHO. 2008. *Guidelines for Drinking Water Quality*. 3rd ed. Incorporating 1st and 2nd Addenda. Vol.1: Recommendations. Geneva. World Health Organization. 515pp.

WHO. 2010. *Water for Health: WHO guidelines for drinking water*. World Health Organization 2010 World Water Day. Retrieved December 01, 2010, from www.who.int/water_sanitation_health/dwq/gdwq3rev.

Wolfhard, S. and Reinhard, B. 1998. The heterogeneity of runoff and its significance for water quality problems. *Hydrological Sciences Journal-des-sciences Hydrologiques* 43: 103-113.

WSSCC (Water Supply and Sanitation Collaborative Council). 2004. The Campaign: WASH Facts and Figures. Retrieved April 22, 2010 from http://www. wsscc.org/dataweb.cfm?edit_id=292&CFID=13225&CFTOKEN=70205233.

Yu, X., Yan, Y. and Wang, W. 2010. The distribution and speciation of trace metals in surface sediments from the Pearl River Estuary and the Daya Bay, Southern China. *Marine Pollution Bulletin* 60: 1364–1371.

Zhang, T., Ding, L., Ren, H., Guo, Z. and Tan, J. 2010. Thermodynamic modelling of ferric phosphate precipitation for phosphorus removal and recovery from wastewater. *Journal of Hazardous Materials* 176: 444–450.

Zhou, H. and Smith, D. W. 2002. Advanced technologies in water and wastewater treatment. *Journal of Environmental Engineering Science* 1(4): 247 – 264.

Appendix 1. Physicochemical properties of surface water samples from Cross River

Sampling Station/Month	Station code	Temp. °C	pH	Alkalnity (mg/L)	Turbidity (NTU)	TDS (mg/L)	E.C. (µS/cm)	Hardness (mg/L)	DO (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Cl^- (mg/L)	F^- (mg/L)	NH_3-N (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
Jun. 09																		
Okopedi Itu	SC-1	26.6	6.79	20.0	31.8	129	301	23	7.25	29.4	1.31	622	0.15	0.02	2.1	0.02	0.05	10.6
Ayadehe	SC-2	26.7	6.48	15.0	35.6	107	269	31	7.43	31.2	1.44	122	0.01	0.05	3.4	0.03	0.06	11.2
Nwaniba	SC-3	26.6	6.38	13.4	57.0	126	558	298	6.22	22.5	1.09	1325	0.46	0.06	15.2	0.16	0.06	34.5
Oron	SC-4	26.7	6.25	47.6	26.0	290	384	289	6.03	19.3	1.02	1160	0.43	0.13	7.7	0.03	0.04	20.7
James Town	SC-5	26.8	6.77	29.9	30.6	189	270	61	7.15	25.3	0.91	131	0.79	0.01	7.3	0.04	0.03	24.3
Ibaka	SC-6	27.2	6.82	58.7	78.2	487	536	354	5.55	20.1	4.10	1834	0.96	0.02	7.9	0.04	0.03	41.0
July. 09																		
Okopedi Itu	SC-1	26.4	6.69	17.3	27.7	149	363	43	8.19	30.4	1.25	532	0.13	0.04	2.8	0.01	0.04	12.5
Ayadehe	SC-2	26.3	6.42	13.5	45.5	153	311	26	8.44	21.6	1.32	201	0.01	0.05	4.9	0.02	0.05	13.2
Nwaniba	SC-3	26.4	6.41	11.6	51.6	186	634	267	6.42	28.3	0.99	1214	0.43	0.30	28.2	0.18	0.05	37.3
Oron	SC-4	26.7	6.75	39.7	21.0	310	597	234	5.93	17.6	0.89	1275	0.41	0.06	7.3	0.02	0.04	21.2
James Town	SC-5	27.3	6.79	22.6	57.5	265	652	50	7.89	29.5	1.15	390	0.68	0.13	9.6	0.03	0.02	28.8
Ibaka	SC-6	27.2	6.80	52.1	67.7	502	844	430	6.72	27.2	2.96	1567	0.88	0.16	12.6	0.03	0.04	40.0
Aug. 09																		
Okopedi Itu	SC-1	26.4	6.77	21.7	27.3	128	223	37	8.17	30.8	1.30	608	0.11	0.06	3.0	0.01	0.06	20.5
Ayadehe	SC-2	26.3	6.32	14.2	36.9	106	330	29	8.20	22.7	1.34	123	0.01	0.05	4.5	0.01	0.06	16.4
Nwaniba	SC-3	26.4	6.78	13.4	59.8	131	394	329	6.17	27.5	1.05	1305	0.64	0.16	26.2	0.23	0.07	26.7
Oron	SC-4	26.7	6.27	46.4	37.0	292	477	257	5.54	18.2	0.95	1360	0.48	0.06	6.9	0.02	0.04	19.9
James Town	SC-5	27.5	6.81	19.6	19.4	182	553	40	8.06	30.0	1.24	521	0.16	0.18	11.4	0.03	0.02	23.7
Ibaka	SC-6	27.5	6.79	47.5	34.4	495	1016	375	6.86	28.0	2.05	1466	0.08	0.22	14.4	0.03	0.04	40.6
Sept. 09																		
Okopedi Itu	SC-1	26.5	6.75	23.3	25.1	167	286	34	8.14	31.2	1.29	594	0.07	0.07	3.9	0.01	0.08	30.5
Ayadehe	SC-2	26.4	6.56	16.7	42.4	148	359	25	8.91	35.4	1.62	120	0.00	0.15	5.6	0.01	0.06	22.1
Nwaniba	SC-3	26.5	5.99	23.4	53.7	155	528	320	5.92	22.7	1.02	1285	0.82	0.52	34.3	0.06	0.08	43.2
Oron	SC-4	26.8	6.21	50.5	43.8	346	696	286	6.71	27.5	1.14	1434	0.31	0.12	9.5	0.01	0.03	25.5
James Town	SC-5	27.1	6.76	28.5	22.4	212	679	38	7.58	31.6	1.44	623	0.65	0.16	11.3	0.02	0.01	28.9
Ibaka	SC-6	27.1	6.83	31.2	24.2	517	1163	388	6.34	21.8	1.23	1213	0.55	0.21	13.2	0.03	0.03	45.5

Appendix 1 continued

Sampling Station/Month	Station code	Temp. °C	pH	Alkalnity (mg/L)	Turbidity (NTU)	TDS (mg/L)	E.C. (µS/cm)	Hardness (mg/L)	DO (mg/L)	COD (mg/L)	BOD$_5$ (mg/L)	Cl$^-$ (mg/L)	F$^-$ (mg/L)	NH$_3$-N (mg/L)	NO$_3$-N (mg/L)	NO$_2$-N (mg/L)	PO$_4^{3-}$ (mg/L)	SO$_4^{2-}$ (mg/L)
Nov. 09																		
Okopedi Itu	SC-1	28.6	6.83	16.7	13.5	125	279	34	8.24	24.6	1.32	651	0.22	0.02	2.2	0.001	0.01	31.1
Ayadehe	SC-2	28.9	6.24	23.4	31.2	105	286	30	7.96	23.7	1.25	124	0.01	0.05	4.1	0.01	0.05	25.4
Nwaniba	SC-3	29.2	5.98	33.3	51.2	217	640	315	6.92	29.9	1.15	567	0.11	0.59	32.2	0.06	0.04	26.7
Oron	SC-4	29.4	6.54	45.2	28.1	274	625	401	5.15	18.7	0.89	1445	0.54	0.06	6.0	0.01	0.05	33.1
James Town	SC-5	29.6	6.65	16.7	13.5	238	711	31	8.24	30.4	1.32	653	0.22	0.24	13.2	0.03	0.01	28.9
Ibaka	SC-6	29.7	6.48	42.9	61.2	346	1121	320	7.01	28.7	1.15	1365	0.11	0.29	16.2	0.03	0.04	37.2
Dec. 09																		
Okopedi Itu	SC-1	29.5	6.48	21.7	9.7	182	292	45	7.87	34.8	1.75	608	0.11	0.19	3.5	0.02	0.06	31.7
Ayadehe	SC-2	29.7	6.53	14.2	37.4	236	375	42	8.69	26.7	1.98	123	0.01	0.26	5.2	0.02	0.06	32.3
Nwaniba	SC-3	30.6	5.78	23.7	62.7	513	856	329	5.88	27.5	1.54	1305	0.64	0.93	33.0	0.56	0.07	28.7
Oron	SC-4	30.8	6.59	56.4	35.4	347	861	245	8.01	19.2	2.45	1360	0.48	0.52	8.3	0.06	0.04	30.2
James Town	SC-5	29.7	6.63	19.6	8.3	234	802	40	8.36	23.3	2.61	520	0.16	0.72	17.2	0.08	0.02	25.6
Ibaka	SC-6	30.9	6.72	47.5	25.5	384	1419	475	7.13	30.0	1.98	1466	0.08	0.62	16.2	0.07	0.04	38.9
Jan. 10																		
Okopedi Itu	SC-1	30.3	6.65	25.9	11.1	208	283	51	6.99	39.8	2.00	695	0.13	0.22	3.9	0.02	0.07	36.3
Ayadehe	SC-2	30.5	6.70	17.0	42.7	270	367	48	7.01	30.5	2.26	141	0.01	0.30	6.0	0.03	0.07	36.9
Nwaniba	SC-3	31.4	5.93	28.4	71.7	586	867	376	6.72	31.4	1.76	1132	0.73	1.06	37.7	0.64	0.08	32.9
Oron	SC-4	31.6	6.54	67.5	40.5	397	974	280	6.88	21.9	2.80	1244	0.55	0.59	9.5	0.06	0.05	34.6
James Town	SC-5	30.5	6.80	23.5	9.5	267	833	145	7.11	26.6	2.98	595	0.19	0.82	19.7	0.10	0.02	29.3
Ibaka	SC-6	31.7	6.89	56.9	29.1	439	1424	543	8.15	34.2	2.26	1675	0.09	0.71	18.5	0.08	0.05	55.8
Feb. 10																		
Okopedi Itu	SC-1	32.2	6.70	25.4	10.8	199	246	49	8.62	38.1	1.92	666	0.12	0.21	3.8	0.02	0.07	34.7
Ayadehe	SC-2	32.5	6.75	16.6	41.7	258	403	46	9.52	29.2	2.17	135	0.01	0.28	5.7	0.03	0.06	35.4
Nwaniba	SC-3	32.6	5.98	27.5	69.8	562	729	360	6.44	30.1	1.69	1224	0.70	1.02	36.2	0.62	0.08	31.5
Oron	SC-4	32.8	6.74	66.0	39.4	380	617	269	8.77	21.0	2.68	1490	0.53	0.57	9.1	0.06	0.05	33.1
James Town	SC-5	32.8	6.86	23.4	9.2	256	670	44	9.16	25.5	2.86	570	0.18	0.79	18.9	0.10	0.02	28.0
Ibaka	SC-6	32.0	6.95	55.6	28.4	421	806	520	7.81	32.8	2.17	1606	0.09	0.68	17.8	0.07	0.05	43.9

Appendix 1 continued

Sampling Station/Month	Station code	Temp. °C	pH	Alkalnity (mg/L)	Turbidity (NTU)	TDS (mg/L)	E.C. (μS/cm)	Hardness (mg/L)	DO (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Cl^- (mg/L)	F^- (mg/L)	NH_3-N (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
Mar. 10																		
Okopedi Itu	SC-1	33.1	6.73	28.5	11.9	223	282	55	9.64	42.6	2.14	644	0.13	0.23	4.2	0.02	0.08	38.8
Ayadehe	SC-2	33.2	6.78	18.7	21.8	289	403	51	10.64	32.6	2.42	251	0.01	0.32	6.4	0.03	0.07	39.6
Nwaniba	SC-3	32.5	7.10	31.2	21.4	628	565	403	7.20	33.7	1.89	1298	0.23	1.04	40.4	0.69	0.09	35.2
Oron	SC-4	34.5	7.02	74.2	24.3	425	446	300	9.81	23.5	3.00	1365	0.04	0.64	10.2	0.07	0.05	37.0
James Town	SC-5	34.6	6.89	25.8	10.2	287	430	49	10.24	28.5	3.20	637	0.99	0.45	21.1	0.11	0.02	31.4
Ibaka	SC-6	34.8	6.98	62.5	31.2	470	711	582	8.73	36.7	2.42	1795	0.10	0.76	19.9	0.08	0.05	49.0
Apr. 10																		
Okopedi Itu	SC-1	30.7	6.88	42.5	16.6	148	235	38	7.96	31.9	2.09	577	0.34	0.30	2.9	0.03	0.08	34.2
Ayadehe	SC-2	30.8	6.39	39.6	36.9	191	324	35	8.59	24.5	2.23	225	0.26	0.35	4.6	0.03	0.06	34.4
Nwaniba	SC-3	31.2	7.22	54.2	14.7	196	317	38	6.34	28.5	1.70	1182	0.12	0.14	12.8	0.08	0.52	18.0
Oron	SC-4	32.3	7.14	70.5	13.2	207	289	24	8.31	33.7	3.80	1488	0.03	0.65	3.9	0.02	0.58	38.9
James Town	SC-5	32.6	6.06	24.6	13.8	194	424	66	7.91	22.5	2.82	404	0.14	0.73	13.5	0.09	0.05	28.3
Ibaka	SC-6	32.7	6.24	48.5	37.8	307	609	469	6.48	26.2	2.19	1540	0.09	0.61	13.5	0.09	0.06	37.8
May-10																		
Okopedi Itu	SC-1	29.6	6.88	67.5	25.1	129	198	35	8.84	32.1	2.64	344	0.61	0.43	2.7	0.04	0.11	20.4
Ayadehe	SC-2	28.9	6.89	69.0	40.1	165	286	32	9.36	24.8	2.71	204	0.55	0.48	4.5	0.05	0.07	23.2
Nwaniba	SC-3	28.7	6.35	77.2	72.9	345	580	197	6.77	29.1	2.79	989	0.96	0.75	19.8	0.37	0.10	32.3
Oron	SC-4	28.9	6.87	82.8	49.3	245	571	148	7.24	19.7	2.95	7475	0.35	0.65	6.7	0.08	0.06	41.4
James Town	SC-5	28.7	6.42	33.2	21.3	185	558	103	8.64	25.1	3.47	349	0.13	0.85	11.9	0.11	0.08	22.3
Ibaka	SC-6	28.8	6.71	56.8	55.9	276	388	235	6.82	26.3	2.74	1424	0.12	0.69	12.8	0.14	0.08	32.3
Mean±SD		29.3± 2.4	6.62± 0.31	36.1± 19.2	34.2± 18.1	275± 133	553± 280	184± 164	7.61± 1.19	27.7± 5.4	1.94± 0.78	880± 518	0.31± 0.28	0.38± 0.30	12.3± 9.6	0.09± 0.15	0.05± 0.02	30.9± 9.0
Range		26.3–34.8	5.78–7.22	11.6–82.8	8.3–78.2	105–628	198–1424	23–582	5.15–10.64	17.6–42.61	0.89–4.10	120–1834	0.002–0.99	0.01–1.06	2.1–40.4	0.001–0.69	0.01–0.58	10.6–55.8
CV (%)		8.2	4.7	53.2	52.9	48.4	50.6	89	15.6	19.3	40.2	101.4	91.3	78.9	78	165.6	41.5	29.1

Appendix 2. Seasonal variation of physicochemical characteristics of surface from Cross River

Parameters	Okopedi (SC-1)		Ayadehe (SC-2)		Nwaniba (SC-3)		Oron (SC-4)		James Town (SC-5)		Ibaka (SC-6)	
	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS
Temp. °C	27.8±1.8	30.8±1.9	27.8±2.0	30.9±1.9	27.8±2.0	31.0±1.8	28.0±1.9	31.1±1.8	27.9±1.9	31.3±2.0	27.8±2.1	31.4±2.0
pH (range)	6.69–6.88	6.48–6.83	6.32–6.89	6.24–6.78	5.99–7.22	6.78–7.10	6.21–7.14	6.54–7.02	6.06–6.81	6.63–6.89	6.24 – 6.83	6.48–6.98
Alkalinity (mgL^{-1})	32.0±20	23.6±4.6	28.0±22	18.0±3.4	32.2±27	28.8±3.7	56.3±17	61.9±11	26.4±5.0	21.8±3.6	49.1±10	53.1±7.8
Turbidity (NTU)	25.6±5.0	11.4±1.4	39.6±3.8	35.0±8.6	51.6±20	55.4±21	31.7±14	33.5±7.1	27.5±16	10.1±2.0	49.7±21	35.1±15
TDS (mgL^{-1})	142±16	187±38	145±33	232±73	190±81	501±160	282±49	365±58	205±31	256±22	431±110	412±48
E. Cond. (μScm^{-1})	268±61	276±18	313±32	367±48	502±120	731±130	502±150	705±210	523±150	689±160	759±300	1100±330
Hardness (mgL^{-1})	35±7	47±8	30±4	43±8	242±110	357±36	206±100	299±60	60±24	62±47	375±80	488±100
DO (mgL^{-1})	8.1±0.5	8.3±1.0	8.5±0.7	8.8±1.4	6.3±0.3	6.6±0.5	6.6±1.0	7.7±1.8	7.9±0.5	8.6±1.2	6.5±0.5	7.8±0.7
COD (mgL^{-1})	31.0±1.0	36.0±7.0	26.7±5.4	28.5±3.5	26.4±3.0	30.5±2.3	22.7±6.5	20.8±2.0	27.3±3.5	26.8±2.7	24.9±3.2	32.5±3.2
BOD_5 (mgL^{-1})	1.65±0.58	1.83±0.32	1.78±0.57	2.02±0.46	1.44±0.71	1.61±0.28	1.79±1.30	2.36±0.85	1.84±1.10	2.59±0.74	2.25±0.56	2.39±0.73
Chloride (mgL^{-1})	546±100	653±32	166±49	155±54	1220±120	1110±310	1280±100	1380±94	403±170	595±53	1510±200	1580±170
Fluoride (mgL^{-1})	0.24±0.21	0.14±0.04	0.14±0.22	0.01±0.00	0.57±0.30	0.48±0.29	0.34±0.16	0.43±0.22	0.42±0.31	0.35±0.36	0.45±0.41	0.09±0.01
NH_3-N (mgL^{-1})	0.15±0.17	0.17±0.09	0.19±0.18	0.24±0.11	0.32±0.26	0.93±0.20	0.28±0.29	0.48±0.24	0.35±0.35	0.60±0.25	0.32±0.27	0.61±0.19
NO_3^--N (mgL^{-1})	2.9±0.6	3.5±0.8	4.6±0.7	5.5±0.9	22.8±8.2	35.9±3.4	7.0±1.8	8.6±1.6	10.9±2.2	18.0±3.0	12.4±2.3	17.7±1.6
NO_2^--N (mgL^{-1})	0.02±0.01	0.02±0.01	0.03±0.01	0.002±0.01	0.18±0.11	0.51±0.26	0.03±0.03	0.05±0.03	0.05±0.04	0.08±0.03	0.06±0.05	0.07±0.02
PO_4^{3-} ($mg\ L^{-1}$)	0.07±0.02	0.06±0.03	0.06±0.01	0.06±0.01	0.07±0.02	0.07±0.02	0.05±0.01	0.05±0.00	0.04±0.03	0.02±0.00	0.05±0.02	0.05±0.00
SO_4^{2-} (mgL^{-1})	21.5±9.4	34.5±3.2	20.1±8.5	33.9±5.4	32.0±8.8	31.0±3.4	27.9±9.7	33.6±2.5	26.1±2.9	28.6±2.1	39.5±4.3	45.2±7.4

N.D. = not detected; WS = wet season, DS = dry season

Appendix 3: Trace metal concentration (µgL^{-1}) in surface water samples from Cross River

Sampling Station/Month	Station code	Trace metal concentration (in µgL^{-1})						
		Cd	Pb	Cr	Cu	Zn	Ni	Co
Jun. 09								
Okopedi Itu	SC-1	6	7	11	16	94	21	17
Ayadehe	SC-2	13	36	15	19	36	31	25
Nwaniba	SC-3	3	14	5	8	20	11	8
Oron	SC-4	10	24	11	17	30	31	27
James Town	SC-5	21	38	14	20	230	42	35
Ibaka	SC-6	12	41	17	22	70	54	31
Aug. 09								
Okopedi Itu	SC-1	2	12	7	23	165	11	2
Ayadehe	SC-2	4	19	6	37	87	13	28
Nwaniba	SC-3	55	1	19	18	62	5	5
Oron	SC-4	1	2	3	13	39	22	3
James Town	SC-5	14	21	64	62	136	191	91
Ibaka	SC-6	7	14	25	71	98	81	54
Sept. 09								
Okopedi Itu	SC-1	3	17	10	24	247	8	8
Ayadehe	SC-2	11	33	12	35	77	28	33
Nwaniba	SC-3	36	9	15	16	51	12	7
Oron	SC-4	7	16	9	19	43	33	19
James Town	SC-5	22	37	49	70	229	146	39
Ibaka	SC-6	12	34	26	58	105	84	53
Oct. 09								
Okopedi Itu	SC-1	BDL[a]	28	6	40	234	16	21
Ayadehe	SC-2	7	25	11	42	79	22	25
Nwaniba	SC-3	2	14	12	29	77	14	20
Oron	SC-4	34	9	16	21	58	21	13
James Town	SC-5	13	32	29	46	149	93	46
Ibaka	SC-6	24	31	50	83	134	153	80
Nov. 09								
Okopedi Itu	SC-1	BDL[a]	21	8	31	252	17	19
Ayadehe	SC-2	29	38	11	37	74	24	26
Nwaniba	SC-3	18	18	12	21	61	12	13
Oron	SC-4	26	12	12	29	48	26	15
James Town	SC-5	17	53	37	55	181	132	62
Ibaka	SC-6	12	31	36	67	114	112	67
Dec. 09								
Okopedi Itu	SC-1	BDL[a]	16	4	38	204	19	24
Ayadehe	SC-2	8	21	51	29	113	22	31
Nwaniba	SC-3	13	14	7	18	96	9	21
Oron	SC-4	14	12	22	23	331	161	24
James Town	SC-5	12	26	35	44	76	88	51
Ibaka	SC-6	9	23	36	24	171	72	55
Jan. 10								
Okopedi Itu	SC-1	BDL[a]	17	7	28	191	17	15
Ayadehe	SC-2	8	21	34	25	81	21	27
Nwaniba	SC-3	19	11	12	15	65	10	15
Oron	SC-4	11	12	15	18	180	92	19
James Town	SC-5	14	26	34	44	57	86	51
Ibaka	SC-6	9	23	27	31	118	62	45

Appendix 3 continued

Sampling Station/Month	Station code	Trace metal concentration (in µgL^{-1})						
		Cd	Pb	Cr	Cu	Zn	Ni	Co
Feb-10								
Okopedi Itu	SC-1	6	19	9	17	178	15	14
Ayadehe	SC-2	9	22	16	24	48	19	22
Nwaniba	SC-3	24	8	12	12	33	11	8
Oron	SC-4	7	12	8	14	28	22	14
James Town	SC-5	16	25	32	44	38	89	49
Ibaka	SC-6	10	23	18	37	65	52	34
Mar. 10								
Okopedi Itu	SC-1	5	27	10	24	297	20	28
Ayadehe	SC-2	13	40	15	42	93	34	42
Nwaniba	SC-3	44	11	18	19	62	15	15
Oron	SC-4	8	19	11	23	52	54	23
James Town	SC-5	27	45	59	85	277	77	96
Ibaka	SC-6	15	41	31	70	127	82	64
Apr. 10								
Okopedi Itu	SC-1	BDL[a]	13	12	32	124	8	16
Ayadehe	SC-2	2	12	7	23	65	11	12
Nwaniba	SC-3	4	17	6	37	87	13	28
Oron	SC-4	55	1	19	18	62	5	5
James Town	SC-5	1	2	3	13	39	22	3
Ibaka	SC-6	14	21	64	92	136	191	91
May-10								
Okopedi Itu	SC-1	BDL[a]	13	19	41	87	47	30
Ayadehe	SC-2	30	16	24	42	92	37	34
Nwaniba	SC-3	23	16	21	35	93	57	28
Oron	SC-4	45	33	56	79	181	71	60
James Town	SC-5	37	89	47	66	151	59	62
Ibaka	SC-6	14	31	50	83	134	153	80
Mean±SD[b]		16 ±13	22 ±14	21±16	36±21	112±71	50 ±47	32 ±22
Range		BDL-55	1-89	3-64	8-92	20-331	5-191	2-96
CV[c] (%)		81	64	76	58	63	94	72

[a] BDL = below detection limit; [b] SD = standard deviation; [c] CV = coefficient of variation

Appendix 4. Seasonal variation of trace metal levels (μgL^{-1}) in surface water samples from Cross River

Metals	Okopedi (SC-1)		Ayadehe (SC-2)		Nwaniba (SC-3)		Oron (SC-4)		J.Town (SC-5)		Ibaka (SC-6)	
	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS
Cadmium	4±2 (50.0)	6±1 (16.7)	11±10 (90.9)	13±9 (69.2)	21±22 (14.8)	24±12 (50.0)	25±22 (88.0)	13±8 (61.5)	18±12 (66.7)	17±6 (35.3)	14±6 (42.9)	11±3 (27.3)
Lead	15±7 (46.7)	20±4 (20.0)	24±10 (41.7)	28±10 (35.7)	12±6 (50.0)	12±4 (33.3)	14±13 (92.9)	13±3 (23.1)	37±29 (78.4)	35±13 (37.1)	29±10 (34.5)	28±8 (28.6)
Chromium	11±5 (45.5)	8±2 (25.0)	13±7 (53.8)	25±17 (68.0)	13±7 (53.8)	12±4 (33.3)	19±19 (100)	14±5 (35.7)	34±23 (67.6)	39±11 (28.2)	39±19 (48.7)	30±8 (26.7)
Copper	29±10 (34.5)	28±8 (28.4)	33±10 (30.3)	31±8 (25.8)	24±12 (50.0)	17±4 (23.5)	28±25 89.3	21±6 (28.6)	46±24 (52.2)	54±18 (33.3)	68±25 (36.8)	46±21 (45.7)
Zinc	159±69 (43.4)	224±49 (21.9)	73±20 (27.4)	82±24 (29.3)	65±27 (41.5)	63±22 (34.9)	69±56 (81.2)	128±129 (100.8)	156±71 (45.5)	126±101 (80.2)	113±27 (23.9)	119±38 (31.9)
Nickel	19±15 (78.9)	18±2 (11.1)	24±10 (41.7)	24±6 (25.0)	19±19 (100)	11±2 (18.2)	31±22 (71.0)	71±58 (81.7)	92±65 (70.7)	94±22 (23.4)	119±54 (45.4)	76±23 (30.3)
Cobalt	16±10 (62.5)	20±6 (30.0)	26±8 (30.8)	30±8 (26.7)	16±11 (68.8)	14±5 (35.7)	21±21 (100.0)	19±5 (26.3)	46±29 (63.0)	62±20 (32.3)	65±23 (35.4)	53±14 (26.4)

BDL = Below detection limit; Coefficient of variation (CV, %) in parentheses, WS = wet season, DS = dry season

Appendix 5. Monthly distribution of some physicochemical properties of sediments samples from Cross River

Sampling Station/Month	Station code	Physicochemical parameters						
		pH	E.C. (μScm^{-1})	NO_3-N (mgkg^{-1})	NO_2-N (mgkg^{-1})	PO_4^{3-} (mgkg^{-1})	SO_4^{2-} (mgkg^{-1})	TOC (%)
Jun-09								
Okopedi Itu	SC-1	5.86	1419	212.0	5.64	249.7	200.6	0.94
Ayadehe	SC-2	6.77	2669	220.0	6.40	223.0	211.8	1.75
Nwaniba	SC-3	5.79	2969	94.4	4.62	137.0	357.0	1.53
Oron	SC-4	7.51	3526	375.0	7.44	111.5	64.0	0.87
James Town	SC-5	6.80	1056	90.0	6.40	86.1	133.2	0.83
Ibaka	SC-6	6.82	2877	80.0	6.80	167.9	55.5	0.64
Aug-09								
Okopedi Itu	SC-1	6.69	3245	190.9	5.08	229.1	180.6	0.85
Ayadehe	SC-2	6.42	3931	198.1	5.77	195.2	190.7	1.58
Nwaniba	SC-3	6.41	3244	85.2	4.16	129.7	321.5	1.38
Oron	SC-4	6.75	2775	337.7	6.70	116.4	57.6	0.78
James Town	SC-5	6.79	3944	81.4	5.77	95.8	120.0	0.75
Ibaka	SC-6	6.8	3545	72.7	6.19	152.1	50.0	0.58
Oct-09								
Okopedi Itu	SC-1	6.75	4088	207.9	5.53	190.3	196.7	0.93
Ayadehe	SC-2	6.56	3588	215.7	6.28	214.5	207.7	1.72
Nwaniba	SC-3	5.99	3950	92.5	4.53	138.2	350.0	1.51
Oron	SC-4	6.21	2638	367.7	7.30	130.9	62.8	0.85
James Town	SC-5	6.76	3420	88.6	6.28	82.4	130.6	0.82
Ibaka	SC-6	6.83	4925	79.1	6.74	164.8	54.4	0.63
Dec-09								
Okopedi Itu	SC-1	6.48	3080	266.4	7.09	156.4	252.1	1.19
Ayadehe	SC-2	6.53	3521	276.4	8.05	179.4	266.1	2.2
Nwaniba	SC-3	5.78	3404	118.6	5.80	112.7	448.6	1.92
Oron	SC-4	6.59	8506	471.2	9.35	98.2	80.4	1.09
James Town	SC-5	6.63	4377	113.6	8.05	75.2	167.4	1.05
Ibaka	SC-6	6.72	2498	101.4	8.64	150.3	69.7	0.81
Feb-09								
Okopedi Itu	SC-1	6.70	3184	210.9	5.61	162.4	199.5	0.94
Ayadehe	SC-2	6.75	3894	218.8	6.37	170.9	210.7	1.74
Nwaniba	SC-3	5.98	3750	93.9	4.59	83.6	355.1	1.52
Oron	SC-4	6.74	7133	373.0	7.40	77.6	63.7	0.86
James Town	SC-5	6.86	3842	89.9	6.37	85.5	132.5	0.83
Ibaka	SC-6	6.95	2735	80.3	6.84	137.0	55.2	0.64
Apr-09								
Okopedi Itu	SC-1	6.88	2998	188.7	5.02	194.5	178.5	0.84
Ayadehe	SC-2	6.39	3082	195.8	5.70	204.8	188.5	1.56
Nwaniba	SC-3	7.22	1132	84.0	4.11	128.5	317.7	1.36
Oron	SC-4	7.14	1986	333.8	6.62	118.8	57.0	0.77
James Town	SC-5	6.06	3502	80.5	5.70	112.1	118.6	0.74
Ibaka	SC-6	6.24	1899	71.8	6.12	150.9	49.4	0.57
Mean±SD		6.59± 0.40	3398± 1392	179.4± 109.7	6.25± 1.20	151.6± 39.6	171.0± 107.4	1.10± 0.43
Range		5.78-7.51	1056-8506	71.8-471.2	4.11-9.35	75.2-249.7	49.4-448.6	0.57-2.20
CV (%)		7.4	47.5	64.2	15.9	26.1	66.1	40.3

SD = standard deviation; CV = coefficient of variation; BDL = below detection limit

Appendix 6. Seasonal variation of physicochemical characteristics of sediment samples from Cross River

Trace Metals	Okopedi (SC-1)		Ayadehe (SC-2)		Nwaniba (SC-3)		Oron (SC-4)		J. Town (SC-5)		Ibaka (SC-6)	
	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS
Temp. °C	26.1±0.6	30.1±0.8	26.0±0.6	30.3±0.7	26.2±0.4	30.8±0.8	26.7±0.1	31.1±0.7	27.1±0.3	30.5±0.8	27.2±0.1	31.4±0.6
pH	5.86–6.75	6.48–6.88	6.42–6.77	6.39–6.75	5.79–6.41	5.78–7.22	6.21–7.51	6.59–7.14	6.76–6.80	6.06–6.86	6.80–6.83	6.24–6.95
E.Cond. (μScm^{-1})	2920±1400	3090±93	3400±660	3500±410	3390±510	2760±1400	2980±480	5880±3400	2810±1500	3910±440	3780±1000	2380±430
NO_3^-- N (mgkg^{-1})	204±11	222±40	211±12	230±42	91±5	99±18	360±20	393±71	87±5	95±17	77±4	85±15
NO_2^-- N (mgkg^{-1})	5.4±0.3	5.9±1.1	6.2±0.3	6.7±1.2	4.4±0.2	4.8±0.9	7.2±0.4	7.8±1.4	6.2±0.3	6.7±1.2	6.6±0.3	7.2±1.3
PO_4^{3-} (mgkg^{-1})	223±30	171±21	211±14	185±18	135±5	108±23	120±10	98±21	88±7	91±19	162±8	146±8
SO_4^{2-} (mgkg^{-1})	193±11	210±38	203±11	222±40	343±19	374±67	62±3	67±12	128±7	140±25	53±3	58±11
TOC (%)	0.91±0.05	0.99±0.18	1.68±0.09	1.83±0.33	1.47±0.08	1.60±0.29	0.83±0.05	0.91±0.17	0.80±0.04	0.87±0.16	0.62±0.03	0.67±0.12

WS = wet season, DS = dry season

Appendix 7. Monthly distribution of trace metal concentrations of sediment samples from Cross River

Sampling Station/Month	Station code	Metal concentration (μgg^{-1}) dry weight						
		Cd	Pb	Cr	Cu	Zn	Ni	Co
Jun-09								
Okopedi Itu	SC-1	0.78	53.5	7.5	84.9	113	7.0	6.8
Ayadehe	SC-2	0.59	44.7	11.0	51.3	124	5.5	6.2
Nwaniba	SC-3	0.55	64.4	13.0	63.8	131	6.2	7.9
Oron	SC-4	0.42	59.9	17.5	83.1	129	11.5	9.7
James Town	SC-5	0.04	35.4	15.5	50.1	116	2.9	3.5
Ibaka	SC-6	0.83	82.6	22.0	92.8	139	6.5	6.6
Aug-09								
Okopedi Itu	SC-1	0.68	60.4	8.5	89.1	125	7.8	7.9
Ayadehe	SC-2	0.44	48.8	13.0	53.6	136	6.0	7.2
Nwaniba	SC-3	0.65	70.3	16.0	70.8	133	7.0	9.1
Oron	SC-4	0.46	67.3	20.5	90.8	133	12.0	10.7
James Town	SC-5	0.09	38.9	17.5	54.6	128	3.7	3.7
Ibaka	SC-6	0.87	87.6	25.0	100.7	152	7.0	7.6
Oct-09								
Okopedi Itu	SC-1	0.72	63.2	9.0	73.8	134	7.5	9.0
Ayadehe	SC-2	0.48	55.2	14.5	55.7	139	6.3	9.1
Nwaniba	SC-3	0.51	72.9	17.0	80.8	136	8.1	10.7
Oron	SC-4	0.28	65.8	20.5	84.5	139	8.5	9.2
James Town	SC-5	0.24	50.9	20.5	67.5	141	3.6	4.7
Ibaka	SC-6	0.47	61.7	22.5	79.3	145	4.7	6.2
Dec-09								
Okopedi Itu	SC-1	0.80	66.1	7.5	84.1	130	8.0	8.9
Ayadehe	SC-2	0.49	49.3	14.0	49.9	139	5.9	8.1
Nwaniba	SC-3	0.59	71.8	16.0	74.8	130	7.2	10.2
Oron	SC-4	0.42	72.6	21.0	93.4	135	10.9	11.1
James Town	SC-5	0.07	39.8	18.5	55.4	134	3.3	3.3
Ibaka	SC-6	0.87	84.8	26.0	102.5	155	6.4	8.5
Feb-09								
Okopedi Itu	SC-1	0.66	54.4	6.0	69.2	107	6.6	7.3
Ayadehe	SC-2	0.40	40.6	11.5	41.1	115	4.9	6.7
Nwaniba	SC-3	0.49	59.1	13.0	61.5	107	5.9	8.4
Oron	SC-4	0.35	59.8	17.5	76.9	111	9.0	9.1
James Town	SC-5	0.06	32.7	15.0	45.6	110	2.7	2.8
Ibaka	SC-6	0.72	69.8	21.5	84.4	128	5.3	7.0
Apr-09								
Okopedi Itu	SC-1	0.73	60.3	7.0	76.7	118	7.3	8.1
Ayadehe	SC-2	0.45	45.0	13.0	45.5	127	5.4	7.4
Nwaniba	SC-3	0.54	65.5	14.5	68.2	119	6.6	9.3
Oron	SC-4	0.39	66.2	19.5	85.2	123	9.9	10.1
James Town	SC-5	0.07	36.3	17.0	50.5	122	3.0	3.1
Ibaka	SC-6	0.80	77.3	24.0	93.5	142	5.9	7.8
Mean±SD[a] (n=36)		0.50± 0.24	59.3± 14.2	15.9± 5.3	71.8± 17.3	129± 12	6.6± 2.3	7.6± 2.3
Range		0.04-0.87	32.7-87.6	6.0 -26.0	41.1-102.5	107-155	2.68-11.96	2.8-11.1
CV (%)[b]		48.0	23.9	34.4	24.1	9.3	35.0	29.7

[a] SD = standard deviation; [b] CV = coefficient of variation

Appendix 8. Seasonal variation of trace metal levels (µgg^{-1} dry weight) of sediment samples from Cross River

Trace Metals	Okopedi (SC-1)		Ayadehe (SC-2)		Nwaniba (SC-3)		Oron (SC-4)		J. Town (SC-5)		Ibaka (SC-6)	
	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]
Cd	0.73±0.04	0.73±0.10	0.49±0.07	0.45±0.06	0.56±0.06	0.54±0.07	0.39±0.08	0.39±0.05	0.11±0.09	0.07±0.01	0.74±0.18	0.80±0.11
Pb	59.4±4.1	60.3±8.3	48.4±4.9	45.0±6.2	68.3±4.01	65.5±9.0	64.8±3.3	66.2±9.1	40.4±7.2	36.3±5.0	77.3±11.2	77.3±10.6
Cr	8.0±0.9	6.6±1.1	12.9±1.4	12.8±1.8	15.1±1.8	14.5±2.1	19.5±1.4	19.3±2.5	17.6±2.1	16.8±2.5	23.4±1.4	23.8±3.2
Cu	81.1±7.1	76.7±10.5	51.5±4.4	45.5±6.2	70.9±7.2	68.2±9.4	85.9±3.4	85.2±11.7	55.7±8.1	50.5±6.9	91.6±8.9	93.5±12.8
Zn	123±9	119±16	132±7	127±18	130±8	119±16	131±7	123±17	127±11	122±18	145±6	142±19
Ni	7.4±0.3	7.3±1.0	5.8±0.4	5.4±0.7	7.0±0.8	6.6±0.9	10.5±1.6	9.9±1.4	3.3±0.4	3.0±0.4	6.0±1.0	5.9±0.8
Co	8.0±0.9	8.1±1.1	7.4±1.2	7.4±1.0	9.3±1.2	9.3±1.3	9.9±0.6	10.1±1.4	3.7±0.7	3.1±0.4	7.0±0.8	7.8±1.1

[a] WS = wet season, [b] DS = dry season

Appendix 9. Results of fraction-specific concentrations of trace metals levels of modified BCR protocol for Cross River

Station	Fraction	Metal concentration in µgg^{-1} dry weight						
		Cd	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
SC-1	Exchangeable	0.21	1.5	0.2	13.1	38.8	0.9	1.2
	Reducible	0.28	33.1	3.3	38.6	44.8	3.1	3.3
	Oxidisable	0.27	6.4	2.7	17.1	24.5	1.3	1.4
	Residual	0.09	24.7	1.8	13.9	21.7	2.3	2.3
	Sum of 3 steps + R	0.85	65.7	8.0	82.7	129.8	7.6	8.2
	Pseudo-total	0.80	66.1	7.5	84.1	130.0	8.0	8.9
	% Recovery	106.3	99.4	106.7	98.3	99.8	94.5	92.2
SC-2	Exchangeable	0.13	1.2	0.4	7.4	41.5	0.8	1.1
	Reducible	0.17	25.4	5.7	21.7	48.9	2.4	3.0
	Oxidisable	0.16	4.9	4.6	9.6	26.6	1.1	1.3
	Residual	0.05	19.0	3.1	7.8	23.1	1.8	2.2
	Sum of 3 steps + R	0.51	50.5	13.8	46.5	140.2	6.1	7.6
	Pseudo-total	0.49	49.3	14	49.9	139.3	5.9	8.1
	% Recovery	104.1	102.4	98.7	93.2	100.6	102.0	93.4
SC-3	Exchangeable	0.16	1.6	0.4	12.1	42.1	0.9	1.4
	Reducible	0.21	35.6	6.5	35.2	43.0	2.8	4.0
	Oxidisable	0.19	6.9	5.2	15.6	21.9	1.2	1.8
	Residual	0.06	26.5	3.5	12.7	21.3	2.1	2.9
	Sum of 3 steps + R	0.62	70.6	15.6	75.6	128.3	7.0	10.1
	Pseudo-total	0.59	71.8	16.0	74.8	130.1	7.2	10.2
	% Recovery	105.1	98.3	97.6	101.1	98.6	97.5	98
SC-4	Exchangeable	0.10	5.2	0.6	14.8	36.0	1.4	1.5
	Reducible	0.14	30.7	9.1	43.1	49.1	4.5	4.2
	Oxidisable	0.12	7.5	7.4	19.1	26.1	1.9	1.9
	Residual	0.04	27.3	5.0	15.6	23.3	3.4	3.0
	Sum of 3 steps + R	0.40	70.7	22.1	92.6	134.5	11.2	10.6
	Pseudo-total	0.42	72.6	21	93.4	134.9	10.9	11.1
	% Recovery	95.2	97.4	105.7	99.1	99.7	102.8	94.6
SC-5	Exchangeable	0.02	1.4	0.9	8.5	37.8	0.3	0.5
	Reducible	0.03	19.5	7.1	23.9	45.6	1.3	1.4
	Oxidisable	0.02	5.4	5.6	11.2	24.0	0.6	0.7
	Residual	0.01	13.9	3.5	8.9	22.2	1.2	1.0
	Sum of 3 steps + R	0.08	40.2	17.1	52.5	129.6	3.4	3.6
	Pseudo-total	0.07	39.8	18.5	55.4	134	3.3	3.3
	% Recovery	114.3	101.0	102.7	96.6	99.0	98.2	104.8
SC-6	Exchangeable	0.21	3.7	1.5	16.1	47.5	1.1	1.2
	Reducible	0.27	40.5	9.6	46.8	50.1	2.5	3.4
	Oxidisable	0.26	7.4	7.8	20.7	27.1	1.1	1.5
	Residual	0.10	33.4	5.7	16.9	24.8	1.8	1.5
	Sum of 3 steps + R	0.84	85.0	24.6	100.5	149.5	6.5	7.6
	Pseudo-total	0.87	84.3	26	102.5	155.2	6.4	8.5
	% Recovery	96.6	100.8	98.1	98	96.3	101.1	88.9

Appendix 10. Percentage fractionation of trace metals levels using modified BCR protocol for Cross River

Fraction	Percentage metal concentration						
	SC-1	SC-2	SC-3	SC-4	SC-5	SC-6	**SCR$_T$**
Cd							
Exchangeable	24.7	25.5	25.8	25	25	25	25.2
Reducible	32.9	33.3	33.9	35	37.5	32.1	34.1
Oxidisable	31.8	31.4	30.7	30	25	31	30.0
Residual	10.6	9.8	9.7	10	12.5	11.9	10.8
Pb							
Exchangeable	2.3	2.3	2.3	7.4	3.5	4.4	3.7
Reducible	50.4	50.4	50.4	43.4	48.5	47.7	48.4
Oxidisable	9.7	9.7	9.8	10.6	13.4	8.7	10.3
Residual	37.6	37.6	37.5	38.6	34.6	39.3	37.5
Cr							
Exchangeable	2.6	2.7	2.7	2.8	4.6	5.7	3.7
Reducible	41.4	41.3	41.3	41.2	42.5	41.4	41.0
Oxidisable	33.9	33.4	33.4	33.4	34.5	30.6	33.1
Residual	22.1	22.6	22.6	22.6	18.4	22.3	22.3
Cu							
Exchangeable	15.8	15.9	16	16	15.9	16	16.0
Reducible	46.7	46.7	46.6	46.5	46.5	46.6	46.4
Oxidisable	20.7	20.7	20.6	20.6	20.9	20.6	20.7
Residual	16.8	16.8	16.8	16.9	16.6	16.8	16.8
Zn							
Exchangeable	29.9	29.6	32.8	26.8	29.2	31.8	30.0
Reducible	34.5	34.9	33.5	36.5	35.2	33.5	34.7
Oxidisable	18.9	19.0	17.1	19.4	18.5	18.1	18.5
Residual	16.7	16.5	16.6	17.3	17.1	16.6	16.8
Ni							
Exchangeable	12.5	12.4	12.4	12.3	10.3	16.9	12.7
Reducible	40.4	40.3	40.3	40.4	39.4	38.8	39.5
Oxidisable	17.4	17.4	17.3	17.3	19.7	16.3	17.3
Residual	29.8	29.9	30	30	30.6	28	30.5
Co							
Exchangeable	18.4	14	17.2	12.3	13.1	15.7	14.5
Reducible	37.5	39.9	36.7	38.1	40.9	44.7	40.4
Oxidisable	15.7	17.6	17.6	20.4	18.6	19.8	18.2
Residual	28.4	28.5	28.5	28.6	27.4	19.8	26.9

Appendix 11: Distribution of trace element species in surface water from Cross River using PHREEQC model

	Station SC-1		Station SC-2		Station SC-3		Station SC-4		Station SC-5		Station SC-6	
Metal species	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**
Cd (II)	**$3.56x10^{-8}$**		**$1.07x10^{-7}$**		**$1.87x10^{-7}$**		**$1.78x10^{-7}$**		**$1.51x10^{-7}$**		**$1.07x10^{-7}$**	
$CdCl^+$	$2.93x10^{-8}$	82.3	$8.56x10^{-8}$	80.0	$1.54x10^{-7}$	82.4	$1.43x10^{-7}$	80.3	$1.20x10^{-7}$	79.5	$8.79x10^{-8}$	82.1
$CdCl_2$	$3.62x10^{-9}$	10.2	$4.63x10^{-9}$	4.3	$1.86x10^{-8}$	9.9	$2.52x10^{-8}$	14.2	$6.04x10^{-9}$	4.0	$1.06x10^{-8}$	9.9
Cd^{2+}	$2.64x10^{-9}$	7.4	$1.63x10^{-8}$	15.2	$1.42x10^{-8}$	7.6	$9.46x10^{-9}$	5.3	$2.47x10^{-8}$	16.4	$8.11x10^{-9}$	7.6
$Cd(Cl_3)^-$	$3.64x10^{-11}$	0.1	$1.88x10^{-11}$	0.0	$1.85x10^{-10}$	0.1	$3.83x10^{-10}$	0.2	$2.28x10^{-11}$	0.0	$1.07x10^{-10}$	0.1
$Cd(HCO_3)^+$	$2.73x10^{-11}$	0.1	$1.64x10^{-10}$	0.2	$1.60x10^{-10}$	0.1	$1.87x10^{-10}$	0.1	$2.60x10^{-10}$	0.2	$1.52x10^{-10}$	0.1
$Cd(OH)Cl$	$1.94x10^{-11}$	0.1	$4.18x10^{-11}$	0.0	$2.69x10^{-12}$	0.0	$6.59x10^{-12}$	0.0	$1.50x10^{-11}$	0.0	$1.77x10^{-12}$	0.0
Pb(II)	**$8.22x10^{-8}$**		**$1.21x10^{-7}$**		**$5.80x10^{-8}$**		**$6.77x10^{-8}$**		**$1.35x10^{-7}$**		**$1.35x10^{-7}$**	
Pb^{2+}	$3.46x10^{-8}$	42.1	$6.64x10^{-8}$	54.9	$3.36x10^{-8}$	57.9	$3.25x10^{-8}$	48.0	$9.41x10^{-8}$	69.7	$7.82x10^{-8}$	57.9
$PbCl^+$	$2.20x10^{-8}$	26.8	$2.01x10^{-8}$	16.6	$2.08x10^{-8}$	35.9	$2.80x10^{-8}$	41.4	$2.64x10^{-8}$	19.6	$4.85x10^{-8}$	35.9
$PbCO_3$	$1.82x10^{-8}$	22.1	$2.55x10^{-8}$	21.1	$5.14x10^{-10}$	0.9	$2.29x10^{-9}$	3.4	$9.68x10^{-9}$	7.2	$2.30x10^{-9}$	1.7
$PbOH^+$	$4.85x10^{-9}$	5.9	$7.54x10^{-9}$	6.2	$1.25x10^{-10}$	0.2	$3.05x10^{-10}$	0.5	$2.73x10^{-9}$	2.0	$3.38x10^{-10}$	0.3
$PbCl_2$	$2.39x10^{-9}$	2.9	$9.56x10^{-10}$	0.8	$2.22x10^{-9}$	3.8	$4.35x10^{-9}$	6.4	$1.17x10^{-9}$	0.9	$5.19x10^{-9}$	3.8
$Pb(NO_3)^+$	$7.61x10^{-11}$	0.1	$2.71x10^{-10}$	0.2	$6.64x10^{-10}$	1.1	$1.58x10^{-10}$	0.2	$1.09x10^{-9}$	0.8	$7.96x10^{-10}$	0.6
$Pb(Cl_3)^-$	$4.43x10^{-11}$	0.1	$7.16x10^{-12}$	0.0	$4.06x10^{-11}$	0.1	$1.21x10^{-10}$	0.2	$8.10x10^{-12}$	0.0	$9.45x10^{-11}$	0.1

Appendix 11: Distribution of trace element species in surface water from Cross River contd.

	Station SC-1		**Station SC-2**		**Station SC-3**		**Station SC-4**		**Station SC-5**		**Station SC-6**	
Metal species	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%
Ni (II)	**$3.07x10^{-7}$**		**$3.92x10^{-7}$**		**$2.56x10^{-7}$**		**$8.03x10^{-7}$**		**$1.69x10^{-6}$**		**$1.71x10^{-6}$**	
Ni^{2+}	$3.02x10^{-7}$	98.4	$3.85x10^{-7}$	98.2	$2.51x10^{-7}$	98.0	$7.90x10^{-7}$	98.4	$1.65x10^{-6}$	97.6	$1.67x10^{-6}$	97.7
$NiSO_4$	$4.08x10^{-9}$	1.3	$6.89x10^{-9}$	1.8	$3.83x10^{-9}$	1.5	$9.84x10^{-9}$	1.2	$3.08x10^{-8}$	1.8	$3.42x10^{-8}$	2.0
$NiCl^{+}$	$7.33x10^{-10}$	0.2	$4.37x10^{-10}$	0.1	$5.95x10^{-10}$	0.2	$2.64x10^{-9}$	0.3	$1.74x10^{-9}$	0.1	$3.97x10^{-9}$	0.2
$Ni(NO_3)^{+}$	$1.02x10^{-10}$	0.0	$2.37x10^{-10}$	0.1	$7.60x10^{-10}$	0.3	$5.94x10^{-10}$	0.1	$2.89x10^{-9}$	0.2	$2.61x10^{-9}$	0.2
Cu(1)	**$2.67x10^{-7}$**		**$1.17x10^{-7}$**		**$2.42x10^{-7}$**		**$3.44x10^{-7}$**		**$2.34x10^{-7}$**		**$6.86x10^{-7}$**	
$Cu(Cl_2)^{-}$	$2.01x10^{-7}$	75.3	$9.73x10^{-8}$	83.2	$1.82x10^{-7}$	75.2	$2.29x10^{-7}$	66.6	$1.94x10^{-7}$	82.9	$5.18x10^{-7}$	75.5
$Cu(Cl_3)^{2-}$	$6.34x10^{-8}$	23.7	$1.13x10^{-8}$	9.7	$5.68x10^{-8}$	23.5	$1.14x10^{-7}$	33.1	$2.09x10^{-8}$	8.9	$1.60x10^{-7}$	23.3
Cu^{+}	$2.93x10^{-9}$	1.1	$8.00x10^{-9}$	6.8	$2.75x10^{-9}$	1.1	$1.56x10^{-9}$	0.5	$1.87x10^{-8}$	8.0	$7.85x10^{-9}$	1.1
Cu (II)	**$1.90x10^{-7}$**		**$3.87x10^{-7}$**		**$7.34x10^{-8}$**		**$5.03x10^{-8}$**		**$5.37x10^{-7}$**		**$2.12x10^{-7}$**	
$CuCO_3$	$8.83x10^{-8}$	46.5	$1.56x10^{-7}$	40.3	$2.42x10^{-9}$	3.3	$6.72x10^{-9}$	13.4	$9.63x10^{-8}$	17.9	$1.30x10^{-8}$	6.1
Cu^{2+}	$6.88x10^{-8}$	36.2	$1.69x10^{-7}$	43.7	$6.47x10^{-8}$	88.1	$3.85x10^{-8}$	76.5	$3.89x10^{-7}$	72.4	$1.80x10^{-7}$	84.9
$CuOH^{+}$	$2.54x10^{-8}$	13.4	$4.98x10^{-8}$	12.9	$6.34x10^{-10}$	0.9	$9.64x10^{-10}$	1.9	$2.93x10^{-8}$	5.5	$2.05x10^{-9}$	1.0
$CuCl^{+}$	$4.15x10^{-9}$	2.2	$4.77x10^{-9}$	1.2	$3.80x10^{-9}$	5.2	$3.18x10^{-9}$	6.3	$1.02x10^{-8}$	1.9	$1.06x10^{-8}$	5.0
$CuSO_4$	$1.53x10^{-9}$	0.8	$5.00x10^{-9}$	1.3	$1.63x10^{-9}$	2.2	$7.91x10^{-10}$	1.6	$1.19x10^{-8}$	2.2	$6.08x10^{-9}$	2.9
$Cu(PO_4)^{-}$	$9.74x10^{-10}$	0.5	$1.61x10^{-9}$	0.4	$2.20x10^{-12}$	0.0	$6.84x10^{-12}$	0.0	$1.52x10^{-10}$	0.0		

Appendix 11. Distribution of trace element species in surface water from Cross River contd.

	Station SC-1		**Station SC-2**		**Station SC-3**		**Station SC-4**		**Station SC-5**		**Station SC-6**	
Metal species	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**	**conc. (M)**	**%**
Zn (II)	**3.26x10^{-6}**		**1.15x10^{-6}**		**9.65x10^{-7}**		**1.46x10^{-6}**		**2.11x10^{-6}**		**1.75x10^{-6}**	
Zn^{2+}	2.97x10^{-6}	91.1	1.07x10^{-6}	93.0	8.91x10^{-7}	92.3	1.31x10^{-6}	89.7	1.99x10^{-6}	94.3	1.59x10^{-6}	90.9
$ZnCl^{+}$	1.37x10^{-7}	4.2	2.31x10^{-8}	2.0	4.05x10^{-8}	4.2	8.54x10^{-8}	5.8	4.06x10^{-8}	1.9	7.50x10^{-8}	4.3
$ZnSO_4$	6.56x10^{-8}	2.0	3.13x10^{-8}	2.7	2.23x10^{-8}	2.3	2.70x10^{-8}	1.8	6.07x10^{-8}	2.9	5.39x10^{-8}	3.1
$ZnOH^{+}$	3.07x10^{-8}	0.9	8.83x10^{-9}	0.8	2.49x10^{-10}	0.0	9.57x10^{-10}	0.1	4.32x10^{-9}	0.2	5.41x10^{-10}	0.0
$Zn(HCO_3)^{+}$	2.74x10^{-8}	0.8	9.51x10^{-9}	0.8	8.99x10^{-9}	0.9	2.36x10^{-8}	1.6	1.86x10^{-8}	0.9	2.70x10^{-8}	1.5
$Zn(OH)Cl$	1.71x10^{-8}	0.5	2.16x10^{-9}	0.2	1.34x10^{-10}	0.0	7.32x10^{-10}	0.1	9.50x10^{-10}	0.0	2.76x10^{-10}	0.0
$ZnCl_2$	4.24x10^{-9}	0.1	3.13x10^{-10}	0.0	1.23x10^{-9}	0.1	3.73x10^{-9}	0.3	5.08x10^{-10}	0.0	2.24x10^{-9}	0.1
Co (II)	**3.06x10^{-7}**		**4.58x10^{-7}**		**2.55x10^{-7}**		**3.40x10^{-7}**		**8.83x10^{-7}**		**9.86x10^{-7}**	
Co^{2+}	2.07x10^{-7}	67.6	3.82x10^{-7}	83.4	2.46x10^{-7}	96.5	3.25x10^{-7}	95.6	8.67x10^{-7}	98.2	9.54x10^{-7}	96.8
$H(CoO_2)^{-}$	9.21x10^{-8}	30.1	7.00x10^{-8}	15.3	2.10x10^{-12}	0.0	5.15x10^{-11}	0.0	2.65x10^{-9}	0.3	1.27x10^{-11}	0.0
$CoCl^{+}$	6.93x10^{-9}	2.3	6.00x10^{-9}	1.3	8.06x10^{-9}	3.2	1.50x10^{-8}	4.4	1.26x10^{-8}	1.4	3.12x10^{-8}	3.2
$Co(NO_3)^{+}$	4.40x10^{-11}	0.0	1.49x10^{-10}	0.0	4.71x10^{-10}	0.2	1.54x10^{-10}	0.0	9.58x10^{-10}	0.1	9.41x10^{-10}	0.1
$CoSO_4$	2.23x10^{-11}	0.0	5.47x10^{-11}	0.0	3.01x10^{-11}	0.0	3.23x10^{-11}	0.0	1.29x10^{-10}	0.0	1.56x10^{-10}	0.0
Cr (III)	**7.77x10^{-8}**		**1.55x10^{-7}**		**1.04x10^{-7}**		**1.38x10^{-7}**		**3.11x10^{-7}**		**2.94x10^{-7}**	
$Cr(OH)_2^{+}$	6.95x10^{-8}	89.4	1.38x10^{-7}	89.0	2.67x10^{-8}	25.7	6.57x10^{-8}	47.6	2.28x10^{-7}	73.3	8.46x10^{-8}	28.8
$Cr(OH)^{2+}$	5.03x10^{-9}	6.5	1.23x10^{-8}	7.9	7.25x10^{-8}	69.7	7.07x10^{-8}	51.2	7.95x10^{-8}	25.6	1.98x10^{-7}	67.3
$Cr(OH)_3$	3.17x10^{-9}	4.1	4.71x10^{-9}	3.0	3.25x10^{-11}	0.0	2.11x10^{-10}	0.2	1.99x10^{-9}	0.6	1.20x10^{-10}	0.0
Cr^{3+}	7.98x10^{-12}	0.0	2.42x10^{-11}	0.0	4.33x10^{-9}	4.2	1.65x10^{-9}	1.2	6.10x10^{-10}	0.2	1.02x10^{-8}	3.5
$CrCl^{2+}$			1.58x10^{-13}	0.0	5.82x10^{-11}	0.1	3.12x10^{-11}	0.0	3.69x10^{-12}	0.0	1.37x10^{-10}	0.0

Appendix 12: Physicochemical characteristics of surface water quality from Qua Iboe River

Sampling Station/Month	Station Code	Temp. °C	pH	Alkalnity (mg/L)	Turbidity (NTU)	TDS (mg/L)	E.C. (μS/cm)	Hardness (mg/L)	DO (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Cl^- (mg/L)	F^- (mg/L)	NH_3-N (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
Jun. 09																		
Iwuokpom 1	SQ-I	25.1	7.11	68.3	45.3	871	1645	26	5.17	22.9	2.33	989	0.99	0.01	2.4	0.02	0.07	10.3
Iwuokpom 2	SQ-2	25.3	7.02	80.3	30.2	1181	2222	26	5.76	19.1	2.05	1159	1.02	0.01	2.9	0.03	0.03	10.5
Iwuochang	SQ-3	25.9	6.79	40.2	57.8	464	929	21	4.58	20.2	2.12	1064	0.08	0.07	5.4	0.08	0.04	13.4
Eketai	SQ-4	25.9	6.61	18.2	30.1	173	346	272	6.34	19.3	2.19	172	0.00	0.04	5.0	0.04	0.12	34.2
Atabong	SQ-5	26.1	6.68	20.4	78.6	242	484	852	4.75	16.2	1.89	289	0.02	0.08	9.4	0.15	0.08	46.3
Marina	SQ-6	26.2	6.79	22.2	54.3	205	410	761	5.54	14.4	1.71	434	0.10	0.06	7.2	0.06	0.08	44.5
Jul-09																		
Iwuokpom 1	SQ-I	25.8	7.01	66.6	38.4	598	1404	21	5.29	24.2	2.42	1074	0.95	0.05	3.5	0.02	0.04	26.2
Iwuokpom 2	SQ-2	26.0	6.92	78.6	31.6	804	1886	21	6.34	18.9	2.34	1331	0.99	0.08	4.5	0.03	0.05	14.4
Iwuochang	SQ-3	26.6	6.69	38.4	59.4	329	838	18	3.92	17.3	1.99	416	0.13	0.24	4.2	0.08	0.08	31.9
Eketai	SQ-4	26.6	6.59	16.5	41.6	129	328	224	5.43	23.4	2.63	293	0.06	0.37	3.2	0.10	0.08	36.6
Atabong	SQ-5	26.7	6.58	18.9	60.3	238	606	702	4.94	18.2	2.39	454	0.07	0.50	12.2	0.15	0.09	39.6
Marina	SQ-6	26.8	6.73	20.4	55.8	158	404	626	5.75	17.5	2.41	368	0.15	0.26	4.3	0.09	0.09	38.3
August 09																		
Iwuokpom 1	SQ-I	26.3	7.11	66.7	33.5	618	1454	27	5.88	25.4	2.48	1095	1.03	0.49	1.3	0.01	0.08	32.7
Iwuokpom 2	SQ-2	26.2	6.97	78.7	46.7	822	1902	27	5.16	19.9	2.45	1345	0.99	0.53	1.3	0.02	0.05	28.1
Iwuochang	SQ-3	26.6	7.21	38.6	54.5	318	811	23	4.38	18.1	2.39	659	0.13	0.75	1.5	0.04	0.05	27.6
Eketai	SQ-4	26.6	6.49	16.6	32.7	113	288	295	6.26	25.2	2.53	201	0.05	0.95	2.8	0.08	0.10	32.6
Atabong	SQ-5	26.7	6.97	18.7	75.2	262	667	776	4.82	17.9	2.26	378	0.07	1.13	4.5	0.10	0.09	36.2
Marina	SQ-6	26.8	6.58	20.6	50.9	178	453	827	5.02	18.2	2.41	245	0.15	0.79	2.1	0.05	0.10	37.7
Sept. 09																		
Iwuokpom 1	SQ-I	26.3	7.11	68.3	36.8	654	1668	56	6.17	26.5	2.82	1307	0.92	0.05	2.4	0.03	0.11	28.7
Iwuokpom 2	SQ-2	26.5	7.02	80.3	30.2	922	2198	36	5.71	22.7	2.73	1559	0.95	0.08	2.9	0.04	0.04	28.4
Iwuochang	SQ-3	27.1	6.79	40.2	47.8	572	1460	21	4.58	16.8	2.32	664	0.18	0.24	7.4	0.13	0.02	29.0
Eketai	SQ-4	27.2	6.59	18.3	30.0	127	324	372	6.34	25.9	3.07	247	0.11	0.37	7.0	0.12	0.12	39.2
Atabong	SQ-5	26.8	6.68	32.5	68.6	275	701	699	5.75	18.4	2.79	318	0.12	0.50	11.3	0.15	0.09	42.9
Marina	SQ-6	26.9	6.79	22.2	54.2	179	456	797	5.54	17.8	2.81	263	0.20	0.26	7.2	0.12	0.11	43.3

Appendix 12 continued

Sampling Station/Month	Station code	Temp. °C	pH	Alkalinity (mg/L)	Turbidity (NTU)	TDS (mg/L)	E. C. (µS/cm)	Hardness (mg/L)	DO (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Cl^- (mg/L)	F^- (mg/L)	NH_3-N (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
Oct. 09																		
Iwuokpom 1	SQ-I	25.8	7.22	82.6	65.8	881	2383	25	4.56	21.9	2.25	1452	1.07	0.02	3.2	0.01	0.05	11.5
Iwuokpom 2	SQ-2	26.5	7.02	98.6	42.5	1300	3180	27	6.43	25.3	2.81	1536	1.03	0.51	1.3	0.01	0.06	32.1
Iwuochang	SQ-3	29.4	7.32	43.1	71.2	922	1604	30	6.94	27.7	1.25	1678	1.1	0.11	1.8	0.1	0.1	42.1
Eketai	SQ-4	30.5	6.87	24.0	61.7	924	420	256	7.96	30.9	3.58	1715	1.11	0.7	2.1	0.11	0.12	51.2
Atabong	SQ-5	30.0	6.82	42.2	71.4	284	802	677	6.23	30.3	3.88	2422	1.21	0.6	6.4	0.09	0.11	54.7
Marina	SQ-6	29.4	6.84	28.0	76.6	248	550	810	7.68	30.1	4.05	1876	1.13	0.54	2.1	0.1	0.12	47.8
Nov. 09																		
Iwuokpom 1	SQ-I	29.1	7.21	70.0	44.2	617	1573	30	6.63	26.4	1.29	1139	1.01	0.09	1.4	0.06	0.13	33.7
Iwuokpom 2	SQ-2	29.3	7.12	82.0	28.4	862	2120	30	6.65	20.1	1.32	1485	1.05	0.14	1.7	0.06	0.08	33.1
Iwuochang	SQ-3	29.6	6.89	42.0	51.2	340	866	25	6.22	21.2	1.62	712	0.15	0.42	4.0	0.10	0.08	32.6
Eketai	SQ-4	28.9	6.49	20.0	25.4	134	343	320	6.11	28.3	1.15	259	0.07	0.69	4.4	0.13	0.15	32.6
Atabong	SQ-5	29.3	6.78	22.0	53.8	293	748	1003	4.93	19.3	2.89	416	0.08	0.92	7.5	0.17	0.13	36.2
Marina	SQ-6	29.4	6.88	24.0	42.6	214	545	895	5.61	20.0	1.14	310	0.17	0.47	4.3	0.11	0.15	37.7
Dec. 09																		
Iwuokpom 1	SQ-I	29.7	7.26	75.0	32.6	626	1597	26	8.14	28.2	3.07	1272	1.02	0.69	1.5	0.08	0.15	47.0
Iwuokpom 2	SQ-2	30.2	7.19	77.0	31.3	869	2137	23	8.24	22.1	2.96	1317	1.01	0.46	3.3	0.08	0.09	46.2
Iwuochang	SQ-3	30.4	7.21	43.6	48.5	350	894	23	8.91	20.2	2.91	759	0.15	0.75	4.0	0.10	0.08	44.7
Eketai	SQ-4	31.7	6.64	16.6	27.7	155	395	295	6.92	27.3	3.71	240	0.07	0.95	4.5	0.13	0.15	44.1
Atabong	SQ-5	32.1	6.88	28.8	68.9	286	728	777	5.15	21.3	3.01	648	0.14	0.71	14.4	0.21	0.13	39.5
Marina	SQ-6	32.1	6.54	19.7	44.8	224	572	760	6.71	20.4	3.23	340	0.19	0.68	6.8	0.13	0.14	42.2
Jan. 10																		
Iwuokpom 1	SQ-I	31.3	7.12	109.0	39.1	623	1588	19	8.68	24.4	3.27	1797	1.09	0.64	1.4	0.08	0.14	43.9
Iwuokpom 2	SQ-2	31.6	7.09	121.0	37.5	854	2168	17	8.78	19.1	3.15	1832	1.08	0.66	3.0	0.07	0.09	43.1
Iwuochang	SQ-3	32.2	6.77	126.0	74.1	894	2286	19	6.82	26.8	3.81	2144	1.18	0.43	1.9	0.10	0.12	52.8
Eketai	SQ-4	32.4	6.98	98.0	58.2	371	946	17	5.32	17.5	3.10	966	0.16	0.70	3.8	0.10	0.08	41.7
Atabong	SQ-5	32.8	6.52	56.8	82.6	274	698	527	5.49	18.4	3.21	648	0.15	0.67	7.1	0.20	0.12	36.8
Marina	SQ-6	32.1	6.83	44.5	53.7	223	569	56	7.15	17.7	3.44	356	0.20	0.64	6.4	0.12	0.13	39.3

Appendix 12 continued

Sampling Station/Month	Station code	Temp. °C	pH	Alkalnity (mg/L)	Turbidity (NTU)	TDS (mg/L)	E.C. (µS/cm)	Hardness (mg/L)	DO (mg/L)	COD (mg/L)	BOD_5 (mg/L)	Cl^- (mg/L)	F^- (mg/L)	NH_3-N (mg/L)	NO_3-N (mg/L)	NO_2-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)
Feb. 10																		
Iwuokpom 1	SQ-I	32.1	7.19	96.8	37.7	726	1851	23	8.85	27.6	3.33	1351	1.11	0.7	1.5	0.07	0.13	44.9
Iwuokpom 2	SQ-2	32.5	7.14	104.2	36.2	838	2136	21	8.95	21.7	3.21	1850	1.10	0.59	3.3	0.06	0.08	47.5
Iwuochang	SQ-3	33.1	6.95	74.5	56.1	374	955	21	7.48	19.8	3.16	734	0.16	0.76	4.1	0.09	0.07	45.4
Eketai	SQ-4	32.8	6.64	31.3	32.1	186	474	171	7.71	26.7	4.03	254	0.08	0.96	4.5	0.11	0.14	44.8
Atabong	SQ-5	32.4	6.71	45.1	79.7	302	771	439	5.62	20.8	3.27	648	0.15	0.73	11.3	0.19	0.12	40.1
Marina	SQ-6	33.7	6.68	33.7	51.8	235	600	429	7.29	20.1	3.51	470	0.21	0.69	6.9	0.11	0.13	42.8
Mar. 10																		
Iwuokpom 1	SQ-I	33.3	7.20	99.8	40.4	744	1897	22	8.32	24.3	3.47	859	1.16	0.71	1.5	0.08	0.14	40.7
Iwuokpom 2	SQ-2	33.7	7.16	118.5	38.8	714	1821	20	9.33	21.4	3.35	939	1.15	0.66	3.3	0.07	0.09	40.1
Iwuochang	SQ-3	34.4	7.09	90.8	60.1	517	1319	20	6.74	19.6	3.29	812	0.17	0.77	4.1	0.10	0.08	38.7
Eketai	SQ-4	33.2	6.69	39.1	34.3	175	447	106	8.11	26.5	4.20	460	0.08	0.97	4.6	0.12	0.15	38.2
Atabong	SQ-5	34.2	6.65	53.6	85.4	298	759	261	5.83	20.7	3.41	590	0.15	0.73	9.7	0.21	0.13	34.2
Marina	SQ-6	34.6	6.81	41.2	55.5	241	615	255	7.60	19.9	3.65	260	0.22	0.70	7.0	0.12	0.14	36.5
Apr. 10																		
Iwuokpom 1	SQ-I	30.8	7.34	90.8	46.3	739	1885	26	7.29	24.2	3.13	926	1.16	0.39	2.1	0.05	0.11	34.5
Iwuokpom 2	SQ-2	30.9	7.27	107.4	37.3	664	1692	24	8.15	20.7	2.91	855	1.17	0.36	3.4	0.05	0.07	27.3
Iwuochang	SQ-3	32.6	7.11	70.8	63.7	329	838	22	6.11	20.4	2.92	527	0.13	0.45	5.2	0.10	0.07	29.9
Eketai	SQ-4	31.9	6.82	31.0	34.8	154	392	204	7.81	23.4	3.45	451	0.05	0.55	5.2	0.09	0.15	39.1
Atabong	SQ-5	33.1	6.60	40.0	54.8	214	545	602	5.71	18.9	2.86	402	0.09	0.44	10.3	0.19	0.11	43.5
Marina	SQ-6	32.8	6.73	34.2	59.3	173	441	122	7.10	17.6	2.91	287	0.17	0.41	7.7	0.10	0.12	50.3
May-10																		
Iwuokpom 1	SQ-I	28.3	7.23	79.5	45.8	528	1346	26	6.23	23.6	2.73	835	1.07	0.20	2.2	0.04	0.09	22.4
Iwuokpom 2	SQ-2	28.6	7.14	93.8	33.8	631	1610	25	6.95	19.9	2.48	998	1.10	0.19	3.1	0.04	0.06	18.9
Iwuochang	SQ-3	29.3	6.95	55.5	60.7	326	832	22	5.34	20.3	2.52	546	0.10	0.26	5.3	0.09	0.05	21.6
Eketai	SQ-4	28.9	6.71	24.6	32.4	158	402	238	7.07	21.4	2.82	316	0.02	0.30	5.1	0.06	0.13	36.6
Atabong	SQ-5	29.6	6.64	30.2	66.7	223	569	727	5.23	17.5	2.37	690	0.05	0.26	9.8	0.17	0.09	44.9
Marina	SQ-6	29.5	6.76	28.2	56.8	190	483	441	6.32	16.1	2.31	384	0.13	0.23	7.5	0.08	0.10	47.4
Mean± SD		29.6± 2.8	6.91± 0.24	61.3± 35.1	50.5± 15.8	495± 315	1210± 737	222± 291	6.42± 0.94	21.9± 1.6	2.77± 0.71	860± 140	0.53± 0.04	0.46± 0.26	4.6± 1.0	0.09± 0.03	0.10± 0.02	36.2± 6.6
Range (n = 72)		25.1-34.6	6.49-7.34	16.5-132.2	25.4-85.4	113-1300	288-3180	17-1003	3.92-9.33	14.4-30.9	0.89-4.20	172-2420	0.003-1.21	0.01-1.13	1.25-14.36	0.01–0.21	0.02-0.15	10.3-54.7

SD = standard deviation

Appendix 13. Seasonal variation of physicochemical characteristics of surface water samples from Qua Iboe River system

Parameters	Iwuokpom 1 (SQ-1)		Iwuokpom 2 (SQ-2)		Iwuoachang (SQ-3)		Eketai (SQ-4)		Atabong (SQ-5)		Marina (SQ-6)	
	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS
Temp. °C	27.1±2.1	31.1±1.7	27.3±2.1	31.5±1.8	28.0±2.5	32.0±2.0	27.9±2.2	31.5±1.7	28.2±2.1	32.4±2.1	28.2±1.7	32.4±2.0
pH (range)	7–01–7.34	7.12–7.26	6.92–7.27	7.09–7.19	6.69–7.21	6.89–7.21	6.49–6.82	6.49–6.69	6.58–6.97	6.52–6.88	6.58–6.79	6.54–6.88
Alkalinity (mgL^{-1})	73.4±9.8	90.1±17	86.5±12	100.5±20	47.3±13	69.8±26	20.9±5.8	30.0±12	26.8±8.8	41.3±15	24.6±5.5	32.6±11
Turbidity (NTU)	41.0±5.5	38.8±4.2	35.0±6.3	34.4±4.4	57.3±5.6	54.8±4.8	33.6±4.3	30.5±3.8	67.4±8.9	74.1±13	55.2±2.8	49.7±5.7
TDS (mgL^{-1})	668±120	667±62	837±200	827±64	390±110	390±72	142±23	169±24	242±23	291±11	180±16	228±11
E. Cond. (μScm^{-1})	1570±200	1700±160	1920±250	2080±140	951±252	996±180	347±43	430±61	595±80	741±29	441±30	580±28
Hardness (mgL^{-1})	30±13	24±4	27±5	22±5	21±2	21±3	268±61	210±93	726±84	601±290	596±270	479±350
DO (mgL^{-1})	6.0±0.8	8.1±0.9	6.4±1.1	8.4±1.1	4.8±0.8	6.9±1.4	6.5±0.8	7.3±0.8	5.2±0.4	5.4±0.4	5.9±0.7	6.9±0.8
COD (mgL^{-1})	24.5±1.3	26.2±1.8	20.2±1.4	20.9±1.2	18.9±1.6	19.7±1.4	23.1±2.4	26.5±1.8	17.9±0.9	20.1±1.2	16.9±1.4	19.6±1.1
BOD_5 (mgL^{-1})	2.65±0.30	2.89±0.90	2.49±0.30	2.80±0.84	2.38±0.33	2.82±0.68	2.78±0.44	3.41±1.30	2.43±0.36	2.76±1.10	2.43±0.43	2.99±1.1
Chloride (mgL^{-1})	1040±160	1280±340	1210±260	1590±380	646±230	797±100	280±100	307±190	422±140	590±100	330±76	347±78
Fluoride (mgL^{-1})	1.02±0.09	1.08±0.06	1.04±0.08	1.08±0.05	0.13±0.03	0.15±0.01	0.05±0.04	0.08±0.00	0.07±0.04	0.13±0.028	0.15±0.03	0.20±0.02
NH_3-N (mgL^{-1})	0.20±0.20	0.57±0.27	0.21±0.20	0.50±0.22	0.34±0.24	0.68±0.15	0.43±0.30	0.89±0.12	0.49±0.36	0.75±0.1.0	0.33±0.25	0.64±0.10
NO_3^--N (mgL^{-1})	2.28±0.71	1.43±0.06	3.01±1.01	2.92±0.70	4.84±1.93	4.02±0.15	4.69±1.52	4.42±0.16	9.58±2.71	10.00±2.97	6.01±2.27	6.27±1.15
NO_2^--N (mgL^{-1})	0.03±0.01	0.07±0.01	0.03±0.01	0.07±0.01	0.09±0.03	0.11±0.01	0.08±0.03	0.12±0.01	0.15±0.03	0.20±0.02	0.08±0.025	0.12±0.01
PO_4^{3-} (mg/L)	0.08±0.03	0.14±0.01	0.05±0.01	0.09±0.00	0.05±0.02	0.08±0.00	0.12±0.02	0.15±0.01	0.09±0.01	0.13±0.01	0.10±0.014	0.14±0.01
SO_4^{2-} (mgL^{-1})	25.8±8.8	42.0±5.2	21.3±7.8	42.0±5.7	25.6±6.9	40.6±5.2	36.4±2.6	40.2±5.0	42.2±3.7	37.4±2.4	43.6±5.0	39.7±2.7

BDL = Below detection limit; WS = wet season, DS = dry season`

Appendix 14: Results of trace metal levels (μgL^{-1}) in surface water from Qua Iboe River

Sampling Station/Month	Station code	Trace metal concentration (in μgL^{-1})						
		Cd	Pb	Cr	Cu	Zn	Ni	Co
Jun-09								
Iwuokpom 1	SQ-I	BDL[a]	23	12	32	124	8	19
Iwuokpom 2	SQ-2	2	12	7	23	65	11	12
Iwuochang	SQ-3	55	1	19	18	62	5	5
Eketai	SQ-4	1	2	3	13	39	22	3
Atabong	SQ-5	14	21	64	92	136	191	91
Marina	SQ-6	7	14	25	71	98	81	54
Jul-09								
Iwuokpom 1	SQ-I	2	17	8	28	88	15	24
Iwuokpom 2	SQ-2	1	13	8	17	76	9	18
Iwuochang	SQ-3	75	6	26	14	59	7	6
Eketai	SQ-4	2	1	4	9	36	3	4
Atabong	SQ-5	82	32	76	132	168	128	88
Marina	SQ-6	44	18	32	65	124	87	67
Sept. 09								
Iwuokpom 1	SQ-I	1	13	11	34	73	17	25
Iwuokpom 2	SQ-2	1	11	9	21	84	11	21
Iwuochang	SQ-3	55	8	22	18	62	8	5
Eketai	SQ-4	3	1	5	11	34	2	3
Atabong	SQ-5	65	41	65	82	173	131	51
Marina	SQ-6	33	20	24	55	135	75	62
Oct. 09								
Iwuokpom 1	SQ-I	2	23	15	48	132	25	37
Iwuokpom 2	SQ-2	1	18	13	29	123	15	32
Iwuochang	SQ-3	121	11	37	24	93	12	8
Eketai	SQ-4	4	2	7	15	54	4	5
Atabong	SQ-5	113	56	109	164	263	196	107
Marina	SQ-6	59	29	43	92	211	124	99
Nov. 09								
Iwuokpom 1	SQ-I	3	21	13	32	234	22	43
Iwuokpom 2	SQ-2	3	15	18	29	98	12	26
Iwuochang	SQ-3	76	14	34	34	87	9	8
Eketai	SQ-4	6	8	8	17	65	8	5
Atabong	SQ-5	84	67	87	224	174	136	122
Marina	SQ-6	56	23	56	78	187	178	87
Dec. 09								
Iwuokpom 1	SQ-I	4	31	22	61	279	35	62
Iwuokpom 2	SQ-2	4	23	25	46	165	21	42
Iwuochang	SQ-3	118	20	51	47	135	15	12
Eketai	SQ-4	8	8	112	26	91	9	7
Atabong	SQ-5	135	98	138	278	315	242	157
Marina	SQ-6	81	39	73	121	293	230	135

Appendix 14 continued

Sampling Station/Month	Station code	Trace metal concentration (in µgL^{-1})						
		Cd	Pb	Cr	Cu	Zn	Ni	Co
Jan. 09								
Iwuokpom 1	SQ-I	4	32	20	56	258	33	57
Iwuokpom 2	SQ-2	3	22	22	42	154	19	40
Iwuochang	SQ-3	126	18	49	42	126	14	11
Eketai	SQ-4	7	7	51	23	84	8	7
Atabong	SQ-5	133	88	134	266	301	230	154
Marina	SQ-6	70	36	69	116	276	213	128
Feb. 09								
Iwuokpom 1	SQ-I	4	33	22	62	282	36	62
Iwuokpom 2	SQ-2	3	24	24	46	321	21	44
Iwuochang	SQ-3	138	21	53	46	137	15	12
Eketai	SQ-4	8	8	56	25	92	9	8
Atabong	SQ-5	145	97	146	291	329	251	169
Marina	SQ-6	83	41	75	127	302	23	140
Mar-09								
Iwuokpom 1	SQ-I	5	38	27	76	346	43	77
Iwuokpom 2	SQ-2	15	29	31	57	205	26	52
Iwuochang	SQ-3	146	25	63	58	167	19	15
Eketai	SQ-4	10	35	139	32	113	11	9
Atabong	SQ-5	167	220	171	345	391	311	195
Marina	SQ-6	100	48	91	150	363	285	167
Apr. 09								
Iwuokpom 1	SQ-I	3	27	19	53	240	30	53
Iwuokpom 2	SQ-2	7	20	22	40	142	18	36
Iwuochang	SQ-3	102	17	44	40	116	13	15
Eketai	SQ-4	7	7	96	22	78	8	14
Atabong	SQ-5	116	84	119	240	271	208	135
Marina	SQ-6	70	34	63	104	252	198	114
May-09								
Iwuokpom 1	SQ-I	3	43	16	44	202	25	44
Iwuokpom 2	SQ-2	4	17	18	33	118	15	30
Iwuochang	SQ-3	87	14	37	35	97	11	100
Eketai	SQ-4	6	42	82	18	65	7	8
Atabong	SQ-5	97	70	99	199	225	173	112
Marina	SQ-6	58	28	52	87	210	165	96
Mean±SD[b]		41± 49	31±30	45± 39	70±71	163± 89	62±82	55±48
Range		BDL–167	1–220	3–171	9–345	34–391	2–311	3–195
CV (%)[a]		120	97	87	101	55	132	87

[a] BDL = below detection limit; [b] SD = standard deviation; [c] CV = coefficient of variation

Appendix 15. Seasonal variation of trace metal levels (μgL^{-1}) in surface water samples from Qua Iboe River

Sampling station	Station code			Mean metal concentration						
				Cd	Pb	Cr	Cu	Zn	Ni	Co
Iwuokpom 1	SQ-1	Wet season	Mean±SD	2±1	24±10	14±4	40±10	143±65	20±8	34±13
		Dry season	CV (%)	50.0	41.7	28.6	25.0	45.5	40.0	38.2
		Wet season	Mean±SD	4±1	31±6	21±5	57±16	280±42	34±8	60±12
		Dry season	CV (%)	25.0	19.4	23.8	28.1	15.0	23.5	20.0
Iwuokpom 2	SQ-2	Wet season	Mean±SD	3±2	15±4	13±6	27±8	101±31	13±3	25±9
		Dry season	CV (%)	66.7	26.7	46.2	29.6	30.7	23.1	36.0
		Wet season	Mean±SD	6±5	23±5	24±5	44±10	197±94	20±5	41±9
		Dry season	CV (%)	83.3	21.7	20.8	22.7	43.9	25.0	22.0
Iwuochang	SQ-3	Wet season	Mean±SD	83±26	10±6	31±10	25±10	82±24	9±3	23±38
		Dry season	CV (%)	31.3	60.0	32.3	40.0	29.3	33.3	165.2
		Wet season	Mean±SD	121±27	20±4	50±10	45±9	130±29	14±4	12±3
		Dry season	CV (%)	22.3	20.0	20.0	20.0	22.3	28.6	25.0
Eketai	SQ-4	Wet season	Mean±SD	4±2	9±16	33±44	15±5	51±18	8±7	6±4
		Dry season	CV (%)	50.0	177.8	133.3	33.3	35.3	87.5	66.7
		Wet season	Mean±SD	8±1	13±12	73±52	25±5	89±17	9±1	7±1
		Dry season	CV (%)	12.5	92.3	71.2	20.0	19.1	11.1	14.3
Atabong	SQ-5	Wet season	Mean±SD	81±38	51±24	89±24	152±62	206±55	171±34	97±24
		Dry season	CV (%)	46.9	47.1	27.0	40.8	26.7	19.9	28.9
		Wet season	Mean±SD	133±30	114±61	135±31	281±44	302±79	234±63	159±26
		Dry season	CV (%)	22.6	53.5	23.0	15.7	26.2	26.9	16.4
Marina	SQ-6	Wet season	Mean±SD	45±23	24±8	40±16	79±18	172±61	122±50	82±24
		Dry season	CV (%)	51.1	33.3	40.0	22.8	35.5	41.0	29.3
		Wet season	Mean±SD	78±16	037±9	73±13	118±26	284±63	226±39	131±29
		Dry season	CV (%)	20.5	24.3	17.8	22.0	22.2	17.3	22.1

CV (%) = coefficient of variation; SD = standard deviation

Appendix16. Monthly distribution of some physicochemical properties of sediments from Qua Iboe River

Sampling station/Month	Physicochemical parameters							
	pH	E.C. (μScm^{-1})	NO_3^- ($mgkg^{-1}$)	NO_2^- ($mgkg^{-1}$)	PO_4^{3-} ($mgkg^{-1}$)	SO_4^{2-} ($mgkg^{-1}$)	TOC (%)	TOM (%)
Iwuokpom1 (SQ-1)								
Jul-09	7.56	1400	137.5	3.20	102.7	180.9	1.22	2.10
Sep-09	8.06	1402	137.5	5.21	271.4	215.4	0.69	1.19
Nov-09	8.11	1405	137.5	7.20	440.0	249.8	0.16	0.28
Jan-10	7.22	6512	161.8	7.31	418.5	273.6	0.50	0.86
Mar-10	6.67	7201	173.3	8.08	471.2	297.4	0.46	0.79
May-10	7.27	11944	149.7	7.23	329.2	261.7	0.33	0.57
Iwuokpom 2 (SQ-2)								
Jul-09	7.55	13000	225.0	4.00	45.4	177.6	0.32	0.55
Sep-09	6.65	13220	168.8	6.00	93.1	366.3	1.28	2.21
Nov-09	6.59	13440	112.5	8.00	140.8	555.0	2.24	3.86
Jan-10	7.12	15682	165.5	8.24	137.6	541.9	2.07	3.57
Mar-10	6.56	16229	160.4	9.09	153.8	605.8	2.34	4.03
May-10	6.86	19414	139.2	8.12	139.2	548.5	2.15	3.71
Iwuochang (SQ-3)								
Jul-09	7.40	14300	156.5	3.78	33.6	167.8	1.10	1.90
Sep-09	7.68	9880	184.5	5.49	232.4	208.8	1.12	1.93
Nov-09	7.95	5460	212.5	7.20	431.2	249.8	1.14	1.97
Jan-10	6.99	9023	233.5	7.46	390.3	269.7	1.33	2.29
Mar-10	6.92	9765	218.4	8.22	444.7	294.1	1.43	2.47
May-10	7.47	9655	223.0	7.33	410.2	259.7	1.24	2.14
Eketai (SQ-4)								
Jul-09	6.69	11200	162.5	3.00	27.8	183.2	0.72	1.24
Sep-09	6.86	6310	168.8	4.30	71.1	230.5	0.64	1.10
Nov-09	6.61	1420	175.0	5.60	114.4	277.8	0.55	0.95
Jan-10	7.15	4547	202.2	5.82	109.1	299.0	0.72	1.24
Mar-10	7.12	4798	199.8	6.41	122.7	326.2	0.76	1.31
May-10	6.88	3978	188.6	5.71	111.8	288.4	0.64	1.10
Atabong (SQ-5)								
Jul-09	7.11	11048	171.4	3.70	84.9	175.6	1.04	1.79
Sep-09	6.95	11712	147.6	5.05	148.8	189.0	0.61	1.05
Nov-09	6.78	12376	123.5	6.40	212.6	202.4	0.17	0.29
Jan-10	7.04	14169	159.5	6.73	212.6	230.2	0.46	0.79
Mar-10	7.02	14228	158.4	7.39	236.2	248.1	0.43	0.74
May-10	6.91	17696	141.5	6.57	212.6	216.3	0.32	0.55
Marina (SQ-6)								
Jul-09	7.24	7208	145.2	3.20	45.4	188.7	0.82	1.41
Sep-09	7.18	6994	144.6	4.50	121.8	156.0	0.47	0.81
Nov-09	7.02	6780	144.0	5.80	198.2	123.3	0.11	0.19
Jan-10	7.12	8102	169.8	6.06	188.2	164.3	0.34	0.59
Mar-10	7.03	9178	171.5	6.66	211.9	171.2	0.32	0.55
May-10	7.07	9921	156.9	5.93	193.2	143.8	0.23	0.40
Mean±SD (n = 36)	7.12± 0.39	9461± 4731	167.4± 29.5	6.11± 1.62	203.0± 131.4	264.9± 120.3	0.85± 0.61	1.46± 1.05
Range	6.56–8.11	1400–19414	112.5–233.5	3.00–9.09	27.84–471.2	123.3–605.8	0.11–2.34	0.19–4.03
CV (%)	5.5	50.0	17.6	26.5	64.7	45.4	71.8	71.9

Appendix 17. Seasonal variation of physicochemical characteristics of sediment samples from Qua Iboe River

Parameters	Iwuokpom 1 (SQ-1)		Iwuokpom 2 (SQ-2)		Iwuoachang (SQ-3)		Eketai (SQ-4)		Atabong (SQ-5)		Marina (SQ-6)	
	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS	WS	DS
Temp. ^{o}C	28.0±1.9	31.1±2.0	28.2±1.9	31.2±2.1	28.2±2.0	31.2±2.1	28.1±2.1	31.3±2.1	28.1±2.0	32.0±2.4	28.3±2.1	31.8±2.3
pH	7.27–8.06	6.67–8.11	6.65–7.55	6.56–7.12	7.40–7.68	6.92–7.95	6.69–6.88	6.61–7.15	6.91–7.11	6.78–7.04	7.07–7.24	7.02–7.12
E.Cond. (µScm^{-1})	4920±6100	5040±3200	15200±3600	15100±1500	11300±2619	8080±2300	7160±3700	3590±1900	13500±3700	13600±1100	8040±1600	8020±1200
NO_3^- (mgkg^{-1})	142±7	158±18	178±44	146±29	188±33	222±11	173±14	192±15	154±16	147±21	149±7	162±15
NO_2^- (mgkg^{-1})	5.2±2.0	7.5±0.5	6.0±2.2	8.4±0.6	5.5±1.8	7.6±0.5	4.3±1.4	5.9±0.4	5.1±1.4	6.8±0.5	4.5±1.4	6.2±0.4
PO_4^{3-} (mgkg^{-1})	234±118	443±27	93±47	144±9	225±188	422±28	70±42	115±7	149±64	221±14	120±74	199±12
SO_4^{2-} (mgkg^{-1})	219±41	274±24	364±186	568±34	212±46	271±22	234±53	301±24	194±21	227±23	163±23	153±26
TOC (%)	0.75±0.45	0.37±0.19	1.35±0.92	2.22±0.14	1.15±0.08	1.30±0.15	0.67±0.05	0.68±0.11	0.66±0.36	0.35±0.16	0.51±0.30	0.26±0.13
TOM (%)	1.23±0.68	0.64±0.32	2.16±1.58	3.82±0.23	1.98±0.14	2.24±0.25	1.16±0.07	1.17±0.19	1.13±0.62	0.61±0.28	0.87±0.51	0.44±0.22

WS = wet season, DS = dry season

Appendix 18. Monthly distribution of trace metals concentration of sediments from Qua Iboe River

Sampling Station/Month	Metal concentration (μgg^{-1}) dry weight						
	Cd	Pb	Cr	Cu	Zn	Ni	Co
Iwuokpom 1 (SQ-1)							
Jul-09	0.78	16.1	8.0	77.0	123	7.7	8.8
Sep-09	0.82	22.9	7.0	81.6	133	8.1	9.3
Nov-09	0.62	16.0	8.0	59.6	133	6.1	7.0
Jan-10	2.10	12.4	35.5	34.3	122	5.3	6.4
Mar-10	1.26	8.6	26.0	24.3	128	3.7	8.7
May-10	1.77	11.1	32.5	30.8	140	4.8	8.0
Iwuokpom 2 (SQ-2)							
Jul-09	0.43	11.1	14.0	45.4	131	5.6	7.7
Sep-09	0.45	16.5	14.5	48.1	141	5.9	8.5
Nov-09	0.34	11.6	11.0	35.1	139	4.5	7.3
Jan-10	1.65	11.9	16.0	25.2	142	3.4	5.4
Mar-10	0.99	8.2	12.0	18.8	135	2.4	7.2
May-10	1.39	10.6	14.5	23.2	99	3.0	6.6
Iwuochang (SQ-3)							
Jul-09	0.71	12.2	12.5	62.8	119	4.1	4.8
Sep-09	0.77	17.4	12.5	66.6	129	4.3	5.1
Nov-09	0.54	12.2	10.0	48.6	110	3.2	3.8
Jan-10	2.66	11.3	5.0	37.0	108	2.7	0.9
Mar-10	1.60	7.8	6.0	26.8	113	1.9	0.8
May-10	2.24	10.1	6.0	35.6	106	2.4	0.9
Eketai (SQ-4)							
Jul-09	2.06	16.1	37.0	53.2	104	6.1	9.0
Sep-09	2.16	22.9	38.5	56.4	113	6.4	9.5
Nov-09	1.62	16.0	29.0	41.2	119	4.8	7.1
Jan-10	1.34	16.3	22.5	42.1	99	4.5	4.4
Mar-10	0.82	11.5	17.0	30.2	103	3.2	3.1
May-10	1.14	14.6	21.0	38.1	87	4.0	3.9
Atabong (SQ-5)							
Jul-09	3.20	23.1	49.0	67.2	144	13.6	8.8
Sep-09	3.45	33.2	51.0	71.3	158	14.2	11.2
Nov-09	2.42	22.6	38.5	52.1	149	10.7	8.4
Jan-10	3.56	14.5	44.0	55.4	127	6.2	4.5
Mar-10	2.14	10.0	32.5	41.2	129	4.3	3.3
May-10	3.00	12.9	40.5	50.8	125	5.5	4.1
Marina (SQ-6)							
Jul-09	1.95	9.4	18.5	52.6	127	3.9	3.1
Sep-09	2.04	13.4	18.5	55.7	137	2.4	3.2
Nov-09	1.53	9.4	15.5	40.7	126	4.7	2.5
Jan-10	1.44	2.6	10.5	39.0	86	1.3	2.6
Mar-10	0.86	1.9	8.0	27.4	94	0.9	1.2
May-10	1.21	2.4	9.5	35.0	98	1.2	2.0
Mean±SD[a]	1.59± 0.87	13.4± 6.2	20.9± 13.5	45.3± 15.8	121 ±17	4.9± 3.0	5.5± 2.9
Range	0.34 – 3.56	1.9 – 33.2	5.0 – 51.0	18.8 – 81.6	86 – 158	0.91 – 14.2	0.7 – 11.2
CV (%)[b]	54.7	46.6	64.4	35.0	14.5	61.0	52.5

[a] SD = standard deviation; [b] CV = coefficient of variation

Appendix 19. Seasonal variation of trace metal levels (µgg^{-1} dry weight) in sediments samples from Qua Iboe River

Trace Metals	Iwuokpom 1 (SQ-1)		Iwuokpom 2 (SQ-2)		Iwuoachang (SQ-3)		Eketai (SQ-4)		Atabong (SQ-5)		Marina (SQ-6)	
	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]	WS[a]	DS[b]
Cadmium	1.12±0.56	1.33±0.74	0.76±0.55	0.99±0.66	1.24±0.87	1.60±1.06	1.79±0.56	1.26±0.41	3.22±0.23	2.71±0.75	1.73±0.46	1.28±0.36
Lead	16.7±6.0	12.4±3.7	12.7±3.3	10.6±2.0	13.2±3.8	10.5±2.3	17.9±4.4	14.6±2.7	23.1±10.1	15.7±6.4	8.4±5.6	4.6±4.2
Chromium	15.8±14.4	23.2±14.0	14.3± 0.3	13.0±2.7	10.3±3.8	7.0±2.7	32.2±9.7	22.8±6.0	46.8±5.6	38.3±5.8	15.5±5.2	11.3±3.8
Copper	63.2±28.1	39.4±18.2	38.9±13.7	26.4±8.2	55.0±16.9	37.5±10.9	49.2±9.8	37.8±6.6	63.1±10.8	49.6±7.4	47.8±11.2	35.7±7.2
Zinc	132±9	128±6	124±22	138±3	118±11	110±2.3	101±13	107±10	142±17	135±11	121±20	102±22
Nickel	6.9±1.8	5.1±1.2	4.9±1.6	3.4±1.0	3.6±1.0	2.6±0.7	5.5±1.3	4.2±0.9	11.1±4.8	7.1±3.2	2.5±1.4	2.3±2.1
Cobalt	8.7±0.7	7.4±1.2	7.6±1.0	6.7±1.1	3.6±2.4	1.8±1.7	7.5±3.1	4.8±2.1	8.1±3.6	5.4±2.7	2.7±0.7	2.1±0.8

[a] WS = Wet season, [b] DS = dry season

Appendix 20. Results of fraction-specific concentrations of trace metals in sediments from Qua Iboe River using modified BCR protocol

Station	**Fraction**	Metal concentration in μgg^{-1} dry weight						
		Cd	**Pb**	**Cr**	**Cu**	**Zn**	**Ni**	**Co**
SQ-1	Exchangeable	0.45	0.3	0.9	5.0	38.9	0.6	0.9
	Reducible	0.73	6.2	13.7	14.7	39.8	2.1	2.6
	Oxidisable	0.60	1.2	11.3	6.5	20.2	0.9	1.2
	Residual	0.26	4.6	7.4	5.3	19.7	1.5	1.9
	Sum of 3 steps + R	2.04	12.2	33.2	31.5	119	5.1	6.5
	Pseudo-total	2.10	12.4	35.5	34.3	121.7	5.3	6.4
	% Recovery	97.1	98.6	93.6	91.7	97.5	96.3	101.6
SQ-2	Exchangeable	0.43	0.4	0.6	3.9	47.1	0.4	0.8
	Reducible	0.56	4.7	5.9	11.4	48.1	1.3	2.1
	Oxidisable	0.53	1.2	4.8	5.0	24.5	0.6	1.0
	Residual	0.16	3.3	3.7	4.1	23.9	1.0	1.5
	Sum of 3 steps + R	1.68	9.7	15.1	24.4	143.5	3.3	5.4
	Pseudo-total	1.65	11.9	16	25.2	141.6	3.4	5.4
	% Recovery	102	81.1	94.1	96.8	101.3	95.9	98.9
SQ-3	Exchangeable	0.49	0.6	0.4	4.5	32.3	0.3	0.1
	Reducible	0.96	5.0	1.9	17.3	36.4	1.1	0.5
	Oxidisable	0.83	1.0	1.7	7.5	20.5	0.5	0.2
	Residual	0.33	3.8	1.4	6.5	16.4	0.8	0.3
	Sum of 3 steps + R	2.61	10.4	5.3	35.7	105.6	2.7	1.1
	Pseudo-total	2.66	11.3	5.1	37.0	108.1	2.7	0.9
	% Recovery	98.1	92.1	103.9	96.3	97.7	99.3	123
SQ-4	Exchangeable	0.30	1.1	1.1	7.2	31.1	0.5	0.7
	Reducible	0.58	6.7	7.7	17.7	35	1.7	1.6
	Oxidisable	0.39	1.6	6.2	8.6	19.7	0.8	0.9
	Residual	0.13	6.0	5.4	6.3	15.7	1.3	1.2
	Sum of 3 steps + R	1.40	15.4	20.4	39.8	102	4.3	4.5
	Pseudo-total	1.34	16.3	22.5	42.1	98.9	4.5	4.4
	% Recovery	104.5	94.5	90.7	94.5	103	96.4	103
SQ-5	Exchangeable	0.97	0.5	1.9	10.2	38.6	0.5	0.6
	Reducible	1.35	6.9	17.5	25	43.3	2.4	1.9
	Oxidisable	0.83	1.9	14.3	12.1	22.7	1.1	0.9
	Residual	0.45	4.9	7.6	8.8	20.9	1.7	1.3
	Sum of 3 steps + R	3.6	14.2	41.3	56.2	125.5	5.6	4.6
	Pseudo-total	3.56	14.5	44.0	55.4	127.4	6.2	4.5
	% Recovery	101.0	97.8	93.9	101.4	98.5	91.1	101.5
SQ-6	Exchangeable	0.32	0.4	0.6	6.5	25.2	0.2	0.4
	Reducible	0.41	5.1	4.1	18.8	29.2	0.5	1.2
	Oxidisable	0.39	1.4	3.0	8.3	16.2	0.2	0.5
	Residual	0.15	3.6	2.2	6.8	14.0	0.3	0.4
	Sum of 3 steps + R	1.26	10.4	9.8	40.4	84.6	1.2	2.5
	Pseudo-total	1.44	12.6	10.5	39.5	86.4	1.3	2.6
	% Recovery	87.5	82.4	93.7	102.3	97.9	91.5	96.1

Appendix 21. Percentage fractionation of trace metals in sediments from Qua Iboe River using modified BCR protocol

Fraction	Percentage metal concentration						
	SQ-1	SQ-2	SQ-3	SQ-4	SQ-5	SQ-6	SQRT
Cd							
Exchangeable	22.1	25.6	18.8	21.4	26.9	25.4	23.4
Reducible	35.8	33.3	36.8	41.4	37.5	32.5	36.2
Oxidisable	29.4	31.6	31.8	27.9	23.1	31	29.1
Residual	12.8	9.5	12.6	9.3	12.5	11.9	11.4
Pb							
Exchangeable	2.3	4.0	5.3	7.3	3.5	3.5	4.3
Reducible	50.3	48.7	48.3	43.4	48.5	48.5	48.0
Oxidisable	9.7	12.9	9.8	10.6	13.5	13.4	11.7
Residual	37.6	34.5	36.7	38.6	34.6	34.6	36.1
Cr							
Exchangeable	2.6	4.2	7.0	5.4	4.6	5.7	4.9
Reducible	41.4	39.4	35.5	37.8	42.5	41.4	39.7
Oxidisable	33.9	31.6	31.9	30.4	34.5	30.6	32.2
Residual	22.1	24.8	25.7	26.4	18.4	22.4	23.3
Cu							
Exchangeable	15.8	15.9	12.5	18.2	18.2	16.0	16.1
Reducible	46.7	46.7	48.4	44.5	44.5	46.6	46.2
Oxidisable	20.7	20.7	20.9	21.6	21.6	20.6	21.0
Residual	16.8	16.8	18.2	15.7	15.7	16.8	16.7
Zn							
Exchangeable	32.8	32.8	30.6	30.6	30.8	29.8	31.2
Reducible	33.5	33.5	34.5	34.5	34.5	34.5	34.2
Oxidisable	17.0	17.1	19.4	19.4	18.1	19.1	18.4
Residual	16.6	16.6	15.5	15.5	16.7	16.6	16.3
Ni							
Exchangeable	12.5	12.3	12.2	12.3	9.4	17.7	12.7
Reducible	40.5	40.2	40.4	40.2	42.4	40.3	40.7
Oxidisable	17.3	17.5	17.4	17.4	18.6	13.5	17.0
Residual	29.8	30.1	30.0	30.1	29.6	28.6	29.7
Co							
Exchangeable	14.1	14.1	11.7	16.4	13.2	16.7	14.4
Reducible	39.9	39.8	41.4	35.6	40.8	47.6	40.9
Oxidisable	17.6	17.7	20.7	20.4	18.7	18.3	18.9
Residual	28.4	28.4	26.1	27.6	27.3	17.5	25.9

Appendix 22: Distribution of aqueous chemical species in surface water from Qua Iboe River using PHREEQC model

Metal species	Station SQ-1		Station SQ-2		Station SQ-3		Station SQ-4		Station SQ-5		Station SQ-6	
	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%
Cd (II)	**2.67x10^{-8}**		**3.56x10^{-8}**		**8.90x10^{-7}**		**5.34x10^{-8}**		**9.35x10^{-7}**		**5.34x10^{-7}**	
Cd(OH)Cl	1.57x10^{-8}	58.8	2.18x10^{-8}	61.2	4.57x10^{-7}	51.3	7.63x10^{-13}	0.0	6.23x10^{-12}	0.0	3.41x10^{-12}	0.0
$CdCl^+$	4.78x10^{-9}	17.9	4.90x10^{-9}	13.8	2.10x10^{-7}	23.6	3.94x10^{-8}	73.8	7.44x10^{-7}	79.6	4.04x10^{-7}	75.7
$Cd(OH)_2$	3.62x10^{-9}	13.6	5.95x10^{-9}	16.7	1.07x10^{-7}	12.0	3.63x10^{-18}	0.0	7.83x10^{-18}	0.0	6.18x10^{-18}	0.0
$CdOH^+$	1.45x10^{-9}	5.4	1.76x10^{-9}	4.9	6.48x10^{-8}	7.3	2.47x10^{-13}	0.0	1.23x10^{-12}	0.0	9.65x10^{-13}	0.0
$CdCl_2$	5.19x10^{-10}	1.9	6.09x10^{-10}	1.7	1.49x10^{-8}	1.7	1.22x10^{-9}	2.3	3.80x10^{-8}	4.1	1.44x10^{-8}	2.7
Cd^{2+}	4.85x10^{-10}	1.8	4.42x10^{-10}	1.2	3.14x10^{-8}	3.5	1.27x10^{-8}	23.8	1.51x10^{-7}	16.1	1.14x10^{-7}	21.3
$Cd(OH)_3^-$			5.57x10^{-11}	0.2	4.60x10^{-10}	0.1	1.31x10^{-25}	0.0	1.27x10^{-25}	0.0	9.78x10^{-28}	0.0
$Cd(HCO_3)^+$					6.70x10^{-11}	0.0	1.47x10^{-10}	0.3	2.19x10^{-9}	0.2	1.48x10^{-9}	0.3
Pb(II)	**1.31x10^{-7}**		**9.18x10^{-8}**		**6.76x10^{-8}**		**5.31x10^{-8}**		**3.82x10^{-7}**		**1.45x10^{-7}**	
$Pb(OH)_2$	7.66x10^{-8}	58.7	4.85x10^{-8}	52.8	4.40x10^{-8}	65.1	2.23x10^{-14}	0.0	2.67x10^{-14}	0.0	1.13x10^{-14}	0.0
$Pb(OH)_3^-$	4.65x10^{-8}	35.6	4.04x10^{-8}	44.0	1.69x10^{-8}	25.0	7.15x10^{-20}	0.0	3.84x10^{-20}	0.0	1.60x10^{-20}	0.0
$PbOH^+$	4.15x10^{-9}	3.2	1.94x10^{-9}	2.1	3.60x10^{-9}	5.3	2.05x10^{-10}	0.4	5.65x10^{-10}	0.1	2.38x10^{-10}	0.2
$PbCO_3$	2.66x10^{-9}	2.0	8.28x10^{-10}	0.9	2.66x10^{-9}	3.9	7.72x10^{-10}	1.5	2.77x10^{-9}	0.7	1.02x10^{-9}	0.7
$Pb(CO_3)_2^{2-}$	6.19x10^{-10}	0.5	1.82x10^{-10}	0.2	4.10x10^{-10}	0.6	4.43x10^{-15}	0.0	1.00x10^{-14}	0.0	2.97x10^{-15}	0.0
$PbCl^+$	5.83x10^{-12}	0.0	1.30x10^{-12}	0.0	2.82x10^{-12}	0.0	7.86x10^{-9}	14.8	8.26x10^{-8}	21.6	2.41x10^{-8}	16.6
Pb^{2+}	3.28x10^{-12}	0.0	2.05x10^{-12}	0.0	7.32x10^{-12}	0.0	4.39x10^{-8}	82.7	2.90x10^{-7}	75.9	1.18x10^{-7}	81.4
$PbCl_2$							2.16x10^{-10}	0.4	3.73x10^{-9}	1.0	7.59x10^{-10}	0.5
$Pb(NO_3)^+$							1.76x10^{-10}	0.3	2.31x10^{-9}	0.6	6.24x10^{-10}	0.4

Appendix 22: Distribution of aqueous chemical species in surface water from Qua Iboe River contd.

Metal species	Station SQ-1		Station SQ-2		Station SQ-3		Station SQ-4		Station SQ-5		Station SQ-6	
	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%
Ni (II)	**$4.44x10^{-7}$**		**$2.73x10^{-7}$**		**$2.06x10^{-7}$**		**$1.36x10^{-7}$**		**$3.41x10^{-6}$**		**$2.88x10^{-6}$**	
$Ni(OH)_2$	$2.66x10^{-7}$	59.9	$1.46x10^{-7}$	53.5	$1.35x10^{-7}$	65.5	$8.55x10^{-17}$	0.0	$3.90x10^{-16}$	0.0	$3.40x10^{-16}$	0.0
$Ni(OH)_3^-$	$1.62x10^{-7}$	36.5	$1.22x10^{-7}$	44.7	$5.18x10^{-8}$	25.1	$2.74x10^{-22}$	0.0	$5.61x10^{-22}$	0.0	$4.80x10^{-22}$	0.0
Ni^{2+}	$1.57x10^{-8}$	3.5	$4.75x10^{-9}$	1.7	$1.75x10^{-8}$	8.5	$1.32x10^{-7}$	97.1	$3.32x10^{-6}$	97.4	$2.79x10^{-6}$	96.9
$NiSO_4$	$2.65x10^{-10}$	0.1	$7.00x10^{-11}$	0.0	$3.44x10^{-10}$	0.2	$3.93x10^{-9}$	2.9	$8.96x10^{-8}$	2.6	$8.74x10^{-8}$	3.0
$NiCl^+$	$3.37x10^{-11}$	0.0	$1.16x10^{-11}$	0.0	$2.56x10^{-11}$	0.0	$8.91x10^{-11}$	0.1	$3.57x10^{-9}$	0.1	$2.14x10^{-9}$	0.1
$NiNO_3^+$							$8.00x10^{-11}$	0.1	$4.00x10^{-9}$	0.1	$2.22x10^{-9}$	0.1
Cu (I)	**$4.33x10^{-11}$**		**$2.44x10^{-11}$**		**$3.93x10^{-11}$**		**$5.60x10^{-8}$**		**$1.22x10^{-6}$**		**$3.54x10^{-7}$**	
$CuCl_2^-$	$3.35x10^{-11}$	77.4	$1.82x10^{-11}$	74.6	$3.25x10^{-11}$	82.7	$4.24x10^{-8}$	75.7	$1.01x10^{-6}$	82.8	$2.79x10^{-7}$	78.8
$CuCl_3^{2-}$	$9.13x10^{-12}$	21.1	$5.86x10^{-12}$	24.0	$5.26x10^{-12}$	13.4	$2.62x10^{-9}$	4.7	$1.11x10^{-7}$	9.1	$2.02x10^{-8}$	5.7
Cu^+	$6.35x10^{-13}$	1.5	$2.61x10^{-13}$	1.1	$1.52x10^{-12}$	3.9	$1.11x10^{-8}$	19.8	$9.42x10^{-8}$	7.7	$5.49x10^{-8}$	15.5
Cu (2)	**$7.56x10^{-7}$**		**$5.52x10^{-7}$**		**$5.36x10^{-7}$**		**$2.43x10^{-7}$**		**$2.09x10^{-6}$**		**$1.17x10^{-6}$**	
$CuCO_3(OH)_2^{2-}$	$6.58x10^{-7}$	87.0	$4.67x10^{-7}$	84.6	$4.36x10^{-7}$	81.3	$9.13x10^{-18}$	0.0	$9.19x10^{-18}$	0.0	$4.33x10^{-18}$	0.0
CuO_2^{2-}	$4.10x10^{-8}$	5.4	$5.92x10^{-8}$	10.7	$1.56x10^{-8}$	2.9	$5.72x10^{-25}$	0.0	$1.92x10^{-25}$	0.0	$1.05x10^{-25}$	0.0
$CuOH^+$	$2.75x10^{-8}$	3.6	$1.52x10^{-8}$	2.8	$4.13x10^{-8}$	7.7	$2.61x10^{-9}$	1.1	$9.63x10^{-9}$	0.5	$5.58x10^{-9}$	0.5
$CuCO_3$	$1.64x10^{-8}$	2.2	$6.04x10^{-9}$	1.1	$2.84x10^{-8}$	5.3	$9.14x10^{-9}$	3.8	$4.38x10^{-8}$	2.1	$2.21x10^{-8}$	1.9
$Cu(CO_3)_2^{-2}$	$9.70x10^{-9}$	1.3	$3.38x10^{-9}$	0.6	$1.15x10^{-8}$	2.1	$1.34x10^{-13}$	0.0	$4.04x10^{-13}$	0.0	$1.65x10^{-13}$	0.0
$CuPO_4^-$	$3.47x10^{-9}$	0.5	$1.12x10^{-9}$	0.2	$3.51x10^{-9}$	0.7	$1.15x10^{-11}$	0.0	$1.53x10^{-11}$	0.0	$9.57x10^{-12}$	0.0
Cu^{2+}	$1.47x10^{-11}$	0.0	$6.09x10^{-12}$	0.0	$3.22x10^{-11}$	0.0	$2.17x10^{-7}$	89.3	$1.90x10^{-6}$	90.9	$1.07x10^{-6}$	91.5
$CuCl^+$	$7.83x10^{-13}$	0.0	$3.67x10^{-13}$	0.0	$1.16x10^{-12}$	0.0	$3.60x10^{-9}$	1.5	$5.03x10^{-8}$	2.4	$2.02x10^{-8}$	1.7
$CuSO_4$							$1.06x10^{-8}$	4.4	$8.45x10^{-8}$	4.0	$5.50x10^{-8}$	4.7

Appendix 22: Distribution of aqueous chemical species in surface water from Qua Iboe River contd.

Metal species	**Station SQ-1**		**Station SQ-2**		**Station SQ-3**		**Station SQ-4**		**Station SQ-5**		**Station SQ-6**	
	conc. (M)	%	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%	**conc. (M)**	%
Cr (VI)	**$1.46x10^{-7}$**		**$1.55x10^{-7}$**		**$3.44x10^{-7}$**		**$9.09x10^{-24}$**		**$2.12x10^{-25}$**		**$1.06x10^{-25}$**	
CrO_4^{2-}	$1.46x10^{-7}$	100.0	$1.55x10^{-7}$	100.0	$3.44x10^{-7}$	100.0	$8.95x10^{-25}$	9.8	$1.03x10^{-26}$	4.9	$1.01x10^{-25}$	95.3
$HCrO_4^-$	$6.27x10^{-12}$	0.0	$4.76x10^{-12}$	0.0	$2.46x10^{-11}$	0.0	$8.19x10^{-24}$	90.1	$2.02x10^{-25}$	95.3	$4.90x10^{-27}$	4.6
Cr (III)	**$4.50x10^{-18}$**		**$1.12x10^{-18}$**		**$3.95x10^{-17}$**		**$4.40x10^{-7}$**		**$9.50x10^{-7}$**		**$4.75x10^{-7}$**	
$Cr(OH)_4^-$	$4.32x10^{-18}$	96.0	$1.08x10^{-18}$	96.4	$3.70x10^{-17}$	93.7	$2.30x10^{-14}$	0.0	$4.63x10^{-15}$	0.0	$2.37x10^{-15}$	0.0
$Cr(OH)_3$	$1.81x10^{-19}$	4.0	$3.30x10^{-20}$	2.9	$2.45x10^{-18}$	6.2	$1.82x10^{-10}$	0.0	$8.18x10^{-11}$	0.0	$4.26x10^{-11}$	0.0
$Cr(OH)_2^+$	$7.87x10^{-22}$	0.0	$1.06x10^{-22}$	0.0	$1.61x10^{-20}$	0.0	$1.34x10^{-7}$	30.5	$1.39x10^{-7}$	14.6	$7.21x10^{-8}$	15.2
$CrOH^{2+}$	-	-	-	-	-	-	$2.91x10^{-7}$	66.1	$7.22x10^{-7}$	76.0	$3.62x10^{-7}$	76.2
Cr^{3+}	-	-	-	-	-	-	$1.38x10^{-8}$	3.1	$8.26x10^{-8}$	8.7	$3.99x10^{-8}$	8.4
$Cr_2(OH)_2^{4+}$	-	-	-	-	-	-	$1.35x10^{-10}$	0.0	$9.48x10^{-10}$	0.1	$2.16x10^{-10}$	0.0
$Cr_3(OH)_4^{5+}$	-	-	-	-	-	-	$1.33x10^{-10}$	0.0	$1.11x10^{-9}$	0.1	$1.19x10^{-10}$	0.0
Zn (II)	**$3.14x10^{-6}$**		**$2.16x10^{-6}$**		**$1.59x10^{-6}$**		**$1.04x10^{-6}$**		**$3.83x10^{-6}$**		**$3.41x10^{-6}$**	
$Zn(OH)_2$	$2.62x10^{-6}$	83.4	$1.70x10^{-6}$	78.7	$1.40x10^{-6}$	88.1	$2.88x10^{-13}$	0.0	$1.91x10^{-13}$	0.0		
$Zn(OH)_3^-$	$4.87x10^{-7}$	15.5	$4.35x10^{-7}$	20.1	$1.65x10^{-7}$	10.4	$2.82x10^{-19}$	0.0	$8.44x10^{-20}$	0.0	$7.65x10^{-20}$	0.0
$ZnOH^+$	$1.78x10^{-8}$	0.6	$8.76x10^{-9}$	0.4	$1.54x10^{-8}$	1.0	$3.48x10^{-10}$	0.0	$5.57x10^{-10}$	0.0	$5.12x10^{-10}$	0.0
Zn(OH)Cl	$8.62x10^{-9}$	0.3	$4.73x10^{-9}$	0.2	$4.54x10^{-9}$	0.3	$4.57x10^{-11}$	0.0	$1.15x10^{-10}$	0.0	$7.38x10^{-11}$	0.0
$Zn(OH)_4^{2-}$	$6.54x10^{-9}$	0.2	$8.18x10^{-9}$	0.4	$1.34x10^{-9}$	0.1	$1.79x10^{-26}$	0.0	$2.50x10^{-27}$	0.0	$2.16x10^{-27}$	0.0
Zn^{2+}	$3.35x10^{-10}$	0.0	$1.20x10^{-10}$	0.0	$3.96x10^{-10}$	0.0	$9.69x10^{-7}$	93.2	$3.54x10^{-6}$	92.4	$3.16x10^{-6}$	92.7
$ZnCl^+$	$1.38x10^{-11}$	0.0	$5.70x10^{-12}$	0.0	$1.16x10^{-11}$	0.0	$1.29x10^{-8}$	1.2	$7.76x10^{-8}$	2.0	$4.94x10^{-8}$	1.4
$ZnSO_4$	$9.28x10^{-12}$	0.0	$2.92x10^{-12}$	0.0	$1.30x10^{-11}$	0.0	$4.77x10^{-8}$	4.6	$1.60x10^{-7}$	4.2	$1.65x10^{-7}$	4.8
$ZnHCO_3^+$					$7.65x10^{-13}$	0.0	$1.00x10^{-8}$	1.0	$4.66x10^{-8}$	1.2	$3.71x10^{-8}$	1.1
$ZnCl_2$					$2.02x10^{-13}$	0.0	$9.87x10^{-11}$	0.0	$9.68x10^{-10}$	0.0	$4.29x10^{-10}$	0.0

Appendix 22: Distribution of aqueous chemical species in surface water from Qua Iboe River contd.

Metal species	Station SQ-1		Station SQ-2		Station SQ-3		Station SQ-4		Station SQ-5		Station SQ-6	
	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%	conc. (M)	%
Co (II)	**$7.82x10^{-7}$**		**$5.44x10^{-7}$**		**$3.06x10^{-7}$**		**$1.19x10^{-7}$**		**$2.14x10^{-6}$**		**$1.77x10^{-6}$**	
$HCoO_2^-$	$7.82x10^{-7}$	100.0	$5.44x10^{-7}$	100.0	$3.06x10^{-7}$	100.0	$1.36x10^{-12}$	0.0	$1.97x10^{-12}$	0.0	$1.66x10^{-12}$	0.0
Co^{2+}							$1.18x10^{-7}$	99.2	$2.11x10^{-6}$	98.6	$1.75x10^{-6}$	98.9
$CoCl^+$							$1.09x10^{-9}$	0.9	$3.11x10^{-8}$	1.5	$1.84x10^{-8}$	1.0
$CoNO_3^+$							$4.49x10^{-11}$	0.0	$1.60x10^{-9}$	0.1	$8.76x10^{-10}$	0.0

DEDICATION

This work is dedicated to

my beloved children: Confidence, Shalom and Beulah

for their understanding and cooperation throughout the period of this research.

ABSTRACT

Cross River (CR) and Qua Iboe River (QIR) in Akwa Ibom State are prone to pollution from diverse sources including urbanisation and agricultural activities. The state and national agencies are exploiting the river banks for establishing industrial and recreational parks. Due to scarcity of data on the pollution and human exposure risks of these rivers, there is need to establish their pollution status. This work was aimed at determining the physicochemical characteristics, metal speciation in surface water and sediments and saturation indices on these rivers.

Surface water and sediment samples were collected monthly between June 2009 and May 2010 from six stations with high human activities along CR (Okopedi, Ayadehe, Nwaniba, Oron, James-Town, Ibaka) and QIR (Iwuokpom1, Iwuokpom2, Iwuochang, Eketai, Atabong, Marina). Sampling was done by compositing three grab samples from each station giving a total of 144 each of water and sediment samples. Selected pollution parameters and trace metal concentrations were determined using APHA methods. A thermodynamic model, pH-Redox-Equilibrium-Computer programming language-Interactive (PHREEQCI), was employed to determine some metal species and saturation indices of associated mineral phases in water samples. The relationship between metal speciation in water with sediment in terms of bioavailability was evaluated using the European Union Binding Corporate Rules reference method. Data were analysed using coefficient of variation and Pearson correlation at $p = 0.05$.

The concentrations (mgL^{-1}) of alkalinity (36.1±19.2, 61.3±35.1), dissolved oxygen (7.6±1.2, 6.4±0.9), nitrate (12.3±9.6, 4.6±2.9), chloride (880±520, 860±140), phosphate (0.05±0.02, 0.10±0.02) and sulphate (30.9±9.0, 36.2±6.6) in the rivers (Cross, Qua Iboe) respectively were obtained. The concentrations (mgL^{-1}) of Cd (0.02±0.01, 0.04±0.05), Pb (0.02±0.01, 0.03±0.03), and Ni (0.05±0.05, 0.06±0.08) in water exceeded the WHO limits while those of Cr (0.02±0.02, 0.04±0.03), Cu (0.04±0.02, 0.07±0.07) and Zn (0.11±0.07, 0.20±0.09) were below the limits. Metal variability in water for Cross River was higher for Cd (81.3%) and Ni (94.0%). There were strong correlations for Cr/Co (r=0.9), Cu/Co (r=0.9) and Ni/Co (r=0.8) indicating point source of metal pollution. The dominant metal species for the rivers were the free hydrated species of Co^{2+}(97.0, 97.7%); Cu^{2+}(82.8, 70.2%); Ni^{2+}(98.1, 97.6%); Pb^{2+}(60.0, 62.0%); $CdCl^+$(82.2, 82.3%) and $CrOH^{2+}$(53.1, 58.7%). The concentrations ($\mu g g^{-1}$) of Cd, Pb, Ni, Cr, Cu, Zn and Co in sediments of Cross and Qua Iboe Rivers correspondingly were 0.50±0.24, 1.59±0.87; 59.3±14.2, 13.4±6.2; 6.60±2.3, 4.9±3.0; 15.9±5.3, 20.9±14.0; 71.8±17.3, 45.3±16; 129±12, 122±18; 7.60±2.3, 5.5±3.0. The non-residual sediment fraction of Cd, Pb and Cu in Cross and Qua Iboe Rivers were 89.3 and 88.7%, 62.4 and 64.0%, and 83.1 and 83.3% respectively. Saturation indices showed supersaturation for $CdCr_2O_4$, $CuCr_2O_4$, $PbHPO_4$ and Pb-pyromorphite minerals. There was a dominance of bioavailable fractions bound to Fe/Mn-oxide and organic/sulphide components. Comparison with PHREEQCI data showed higher metal bioavailability in water than in the sediments.

The metal pollution levels in the two rivers may be due to anthropogenic activities in the rivers. The occurrence of bioavailable metals suggests potential health risk from metal toxicities.

Keywords: Saturation Index, River Pollution, Thermodynamic Modelling, Trace Metal Speciation.

Word count: 480

ACKNOWLEDGEMENTS

I owe my deepest gratitude to my supervisor and mentor, Prof. P. C. Onianwa, for his enthusiasm, inspiration, encouragement, motivation, support and love which kept me focused despite the odds throughout the period of this work.

My gratitude goes to the Head of Department of Chemistry, Prof. A. A. Adesomoju and the entire staff members of the Department for giving me the platform to carry out this study. I wish to mention Prof. O. Osibanjo, Dr. A. Ipeaiyeda, Dr. I. A. Oladosu, Dr. N. O. Obi-Egbedi, Prof. J. A. Babalola, Dr. L. Nwokocha, Dr. O. Adewuyi, Dr. Effiong Etim and Dr. Gilbert Adie whose contributions - counsel and encouragements kept me through the path. I remain greatly indebted to all of you.

I am forever thankful to my colleagues at the University of Uyo, Uyo for their friendship, support and numerous contributions, and for creating a cordial working environment. I would not fail to thank Dr. B. O. Ekpo, Department of Chemistry, University of Calabar and David L. Parkhurst of U.S. Geological Survey, Colorado, U.S.A., who provided information, insight and assistance on the PHREEQC model. I thankfully acknowledge the contributions of Prof. A. P. Udoh, Bassey Antia, Imaobong Udousoro, Eno Moses, Joseph Essien, Saviour Umoren, Atim Johnson, Godwin Ebong, Ime Obot, Jude Emurotu, Tessy Onwordi, Omolara Ojezele, Nsuhoridem Akpan, Iniobong Ante, Elsie Udoh, Ukpono Antia and many others.

I'd not fail to acknowledge the contributions of Mr Ini Obot, Agronomy laboratory; University of Uyo and Dr. Usoro M. Etesin, Analytical/Environmental Laboratory, UC-RUSAL ALSCON Coy., Ikot Abasi, (presently in Akwa Ibom State University) who allowed me use the facilities and equipment in their laboratories.

I am deeply grateful to my Pastor, Dr. Sylvanus Ukafia, for his motivational, inspirational and provoking thoughts which kept me through the difficult and very challenging times of this programme.

Without the support of my wife, Margaret and my children, Confidence, Shalom, and Beulah, I would never have succeeded. Although they often had to endure my absence, they infrequently complained. I am forever indebted to my brothers: Emmanuel, John and Mfoniso and sisters, Enobong, Mary and Dorothy for giving me the opportunities and experiences that have made me who I am today. They selflessly encouraged me to explore new directions in life and seek my own destiny, in spite of their challenging financial moments. This journey would not have been possible if not for these men and women, and I remain very grateful to them all.

Finally, my utmost appreciation is given to GOD ALMIGHTY for his benevolence and guidance through the rough roads and deadly incidences witnessed on the highways. HE has been my guide in all my ways, my present help in times of need.
To Him be all the glory!

GOD BLESS YOU ALL.

CERTIFICATION

I certify that this work was carried out under my supervision by **UMOREN, INI UDOFIA** in the Department of Chemistry, University of Ibadan, Nigeria.

Supervisor

Percy Chuks Onianwa

B. Sc. (Hons.), M. Sc., Ph. D (Ibadan)
Professor of Analytical/Environmental Chemistry,
Department of Chemistry
University of Ibadan, Ibadan, Nigeria

TABLE OF CONTENTS

Page

Title Page - i
Dedication - ii
Abstract - iii
Acknowledgement - v
Certification - vii
Table of contents - viii
List of tables - xvi
List of figures - xix
List of appendices - xxi
List of abbreviations and acronyms - xxiii

CHAPTER ONE: INTRODUCTION

1.1 Environmental pollution - 1
1.2 Types of environmental pollution - 2
1.3 Global water pollution - 2
1.4 Surface water pollution - 4
1.5 Sources of surface water pollution - 5
1.5.1 Domestic sewage - 8
1.5.2 Industrial effluents - 8
1.5.3 Agricultural wastes - 9
1.5.4 Fossil fuel - 9
1.5.5 Municipal wastes - 9
1.5.6 Radioactive substances - 9
1.5.7 Oil spills - 10
1.6 Impacts of water pollution - 13
1.7 Water quality assessment - 15
1.7.1 Water quality index - 17
1.8 Chemical speciation of metals in sediments and surface water - 18
1.9 Statement of the problem and justification of the study - 21
1.10 Aims of the study - 23

CHAPTER TWO: LITERATURE REVIEW

2.1 Water quality - 24

Page
2.1.1 Some water quality parameters - - - - - - 24
2.2 Surface water pollution of some Nigerian rivers - - - 25
2.3 Surface water quality of some other rivers around the world - - 28
2.4 Heavy metals pollution of surface water and sediments - - - 30
2.4.1 Heavy metals pollution of some Nigerian rivers - - - 32
2.4.2 Heavy metals pollution of some rivers around the world - - 33
2.5 Sediment quality: Heavy metals and other physicochemical parameters - - - - - - - - 34
2.6 Speciation of metals in s by sequential extraction - - - 39
2.7 Metal speciation of water using geochemical model - - - 44
2.7.1 Theory and applications of PHREEQC model - - - - 46
2.7.2 Distribution of aqueous species - - - - - 49
2.7.3 The saturation index calculations - - - - - 49

CHAPTER THREE: MATERIALS AND METHOD

3.1 Design of study - - - - - - - - 54
3.2 Description of the study area - - - - - - 56
3.3. Sampling and sample pre-treatment - - - - - 59
3.3.1 Collection of surface water samples - - - - - 59
3.3.2 Sampling of bottom sediment - - - - - - 62
3.4. Analysis of water samples - - - - - - 62
3.4.1 Determination of physicochemical parameters - - - 62
3.4.1.1 Determination of temperature - - - - - - 62
3.4.1.2 Determination of pH (Electrometric method) - - - 63
3.4.1.3 Determination of total alkalinity (Titration method) - - - 63
3.4.1.4 Determination of turbidity - - - - - - 64
3.4.1.5 Determination of total dissolved solids (TDS) - - - - 65
3.4.1.6 Determination of electrical conductivity (EC) - - - - 65
3.4.1.7 Determination of total hardness - - - - - - 65
3.4.1.8 Determination of dissolved oxygen - - - - - 66
3.4.1.9 Determination of chemical oxygen demand - - - - 67
3.4.1.10 Determination of biochemical oxygen demand - - - - 69
3.4.1.11 Determination of chloride (Mohr method) - - - - 70
3.4.1.12 Determination of fluoride - - - - - - 71

Page

3.4.1.13 Determination of ammonia - - - - - - 72
3.4.1.14 Determination of nitrate - - - - - - - 73
3.4.1.15 Determination of nitrite - - - - - - 74
3.4.1.16 Determination of phosphates - - - - - - 76
3.4.1.17 Determination of sulphate - - - - - - 78
3.4.1.18 Determination of trace metals in surface water - - - - 79
3.4.2 Preparation of sediment samples for physicochemical analysis - 81
3.4.2.1 Digestion of sediment samples for determination of nutrient - - 81
3.4.2.2 Digestion of bottom sediment samples for trace metal analysis - 83
3.4.3 Analyses of bottom sediment samples - - - - - 83
3.4.3.1 Determination of pH - - - - - - - 83
3.4.3.2 Determination of nitrate - - - - - - 83
3.4.3.3 Determination of nitrite - - - - - - - 83
3.4.3.4 Determination of phosphate - - - - - - 83
3.4.3.5 Determination of sulphate - - - - - - 84
3.4.3.6 Total organic carbon (TOC) and total organic matter (TOM) - - 84
3.4.3.7 Particle size analysis of sediment samples - - - - 85
3.4.3.8 Determination of metals in sediment samples - - - 85
3.5 Speciation of metals in sediments - - - - - 85
3.6 Speciation of metal ions in surface waters using PHREEQCI model - 87
3.6.1. Computational thermodynamic modelling - - - - 87
3.6.2 Calculation of metal species and saturation indices - - - 88
3.7 Quality control and quality assurance - - - - 88

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Surface water quality characteristics of Cross River system - - 96
4.1.1 Temperature - - - - - - - - 96
4.1.2 pH - - - - - - - - - - 96
4.1.3 Total alkalinity - - - - - - - - 98
4.1.4 Turbidity - - - - - - - - - 98
4.1.5 Total dissolved solids (TDS) - - - - - - 99
4.1.6 Electrical conductivity - - - - - - - 99
4.1.7 Total hardness - - - - - - - - 99
4.1.8 Dissolved oxygen (DO) - - - - - - - 100

Page

4.1.9 Chemical oxygen demand (COD) - 100
4.1.10 Biochemical oxygen demand (BOD) - 101
4.1.11 Chloride - 101
4.1.12 Fluoride - 102
4.1.13 Ammonia - 102
4.1.14 Nitrate - 102
4.1.15 Nitrite - 103
4.1.16 Phosphate - 103
4.1.17 Sulphate - 103
4.1.18 Pearson correlation analysis of physicochemical parameters - 104
4.2 Trace metals levels in surface water of Cross River - 104
4.2.1 Cadmium - 104
4.2.2 Lead - 104
4.2.3 Chromium - 107
4.2.4 Copper - 107
4.2.5 Zinc - 107
4.2.6 Nickel - 108
4.2.7 Cobalt - 108
4.3 Sediment quality for Cross River - 108
4.3.1 pH - 111
4.3.2 Electrical conductivity - 111
4.3.3 Nitrate and nitrite - 111
4.3.4 Phosphates - 111
4.3.5 Sulphate - 111
4.3.6 Total organic carbon (TOC) - 111
4.3.7 Particle size distribution - 112
4.4 Trace metals in sediments from Cross River - 112
4.4.1 Cadmium - 112
4.4.2 Lead - 114
4.4.3 Chromium - 114
4.4.4 Copper - 114
4.4.5 Zinc - 115
4.4.6 Nickel - 115
4.4.7 Cobalt - 115
4.4.8 Correlation analysis of sediment metals - 115

Page
4.5 Evaluation of solution status of metals in sediments - 117
4.5.1 Enrichment factor (EF) analysis - 117
4.5.2 Sediment quality guidelines - 117
4.6 Speciation of trace metals in sediments - 121
4.6.1 Speciation of cadmium - 123
4.6.2 Speciation of lead - 123
4.6.3 Speciation of chromium - 125
4.6.4 Speciation of copper - 125
4.6.5 Speciation of zinc - 125
4.6.6 Speciation of nickel - 127
4.6.7 Speciation of cobalt - 127
4.7 Assessment of trace metals contamination in sediment fractions - 131
4.8 Chemical speciation of metals in surface water using PHREEQCI model - 132
4.8.1 Speciation of cadmium - 133
4.8.2 Speciation of lead - 135
4.8.3 Speciation of chromium - 135
4.8.4 Speciation of copper - 137
4.8.5 Speciation of zinc - 137
4.8.6 Speciation of nickel - 139
4.8.7 Speciation of cobalt - 139
4.9 Calculation of saturation indices - 139
4.10 Surface water quality of Qua Iboe River - 143
4.10.1 Temperature - 143
4.10.2 pH - 143
4.10.3 Total alkalinity - 143
4.10.4 Turbidity - 143
4.10.5 Total dissolved solids (TDS) - 145
4.10.6 Electrical conductivity - 145
4.10.7 Total hardness - 145
4.10.8 Dissolved oxygen (DO) - 145
4.10.9 Chemical oxygen demand (COD) - 146
4.10.10 Biochemical oxygen demand (BOD) - 146
4.10.11 Chloride - 146
4.10.12 Fluoride - 146

Page

4.10.13 Ammonia - - - - - - - - 147
4.10.14 Nitrate - - - - - - - - - 147
4.10.15 Nitrite - - - - - - - - 147
4.10.16 Phosphate - - - - - - - - - 147
4.10.17 Sulphate - - - - - - - - - 148
4.10.18 Pearson correlation analysis of physicochemical parameters - - 148
4.11 Trace metals levels in surface water of Qua Iboe River - - 148
4.11.1 Cadmium - - - - - - - - 148
4.11.2 Lead - - - - - - - - 151
4.11.3 Chromium - - - - - - - - 151
4.11.4 Copper - - - - - - - - 151
4.11.5 Zinc - - - - - - - - 152
4.11.6 Nickel - - - - - - - - 152
4.11.7 Cobalt - - - - - - - - 152
4.12 Sediment quality of Qua Iboe River system - - - - 153
4.12.1 pH - - - - - - - - - 153
4.12.2 Electrical Conductivity - - - - - - - 153
4.12.3 Nitrate and Nitrite - - - - - - - 153
4.12.4 Phosphates - - - - - - - - 156
4.12.5 Sulphate - - - - - - - - 156
4.12.6 Total organic carbon (TOC) - - - - - - 156
4.12.7 Particle size distribution - - - - - - - 156
4.13 Trace metals concentration in sediments of Qua Iboe River - - 157
4.13.1 Cadmium - - - - - - - - - 157
4.13.2 Lead - - - - - - - - - 157
4.13.3 Chromium - - - - - - - - 157
4.13.4 Copper - - - - - - - - - 159
4.13.5 Zinc - - - - - - - - - 159
4.13.6 Nickel - - - - - - - - - 159
4.13.7 Cobalt - - - - - - - - - 159
4.13.8 Correlation analysis of sediment metals - - - - - 160
4.14 Evaluation of pollution status of Qua Iboe River - - - 160
4.14.1 Enrichment factor (EF) analysis - - - - - - 160
4.14.2 Comparison of sediment quality with other sediment quality guidelines - - - - - - - 160

Page

4.15 Speciation of trace metals in sediments of Qua Iboe River - - 164
4.15.1 Speciation of cadmium - - - - - - - 164
4.15.2 Speciation of lead - - - - - - - 167
4.15.3 Speciation of chromium - - - - - - 167
4.15.4 Speciation of copper - - - - - - - 167
4.15.5 Speciation of zinc - - - - - - - 169
4.15.6 Speciation of nickel - - - - - - - 169
4.15.7 Speciation of cobalt - - - - - - - 169
4.16 Assessment of trace metal contamination in sediment fractions - 172
4.17 Chemical speciation of metals in surface water of Qua Iboe River using PHREEQCI model - - - - - 172
4.17.1 Speciation of cadmium - - - - - - - 175
4.17.2 Speciation of lead - - - - - - - 175
4.17.3 Speciation of chromium - - - - - - 177
4.17.4 Speciation of copper - - - - - - - 177
4.17.5 Speciation of zinc - - - - - - - 179
4.17.6 Speciation of nickel - - - - - - - 179
4.17.7 Speciation of cobalt - - - - - - - 182
4.18 Calculation of saturation indices - - - - - 182
4.19 Comparison of water quality status of Cross and Qua Iboe River with other rivers - - - - - 184
4.19.1 Physicochemical characteristics - - - - - - 184
4.19.2 Metals in surface water - - - - - - 187
4.19.3 Metals in bottom sediments of Cross and Qua Iboe River systems - 190
4.20 Speciation modelling in surface water of Cross and Qua Iboe River using PHREEQC model - - - - 192
4.2.1 Saturation Indices for Cross River and Qua Iboe River System - 194

CHAPTER FIVE: SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions - - - - - - 195
5.1.1 Physicochemical characteristics of Cross River and Qua Iboe River - 195
5.1.2 Metal Levels in surface water and sediment of Cross River - - 195
5.1.3 Chemical speciation of metals in sediments from Cross River and Qua Iboe River - - - - - - - 196

Page

5.1.4 Speciation modelling in Surface water of Cross River and Qua Iboe River - - - - - - - 196

5.1.5 Saturation indices for Cross River and Qua Iboe River - - 197

5.2 Recommendations - - - - - - - 197

References - - - - - - - - - - 198

Appendices - - - - - - - - - 220

LIST OF TABLES

Page

Table 1.1. Sources and methods of water pollution - - - - 6
Table 1.2. Annual report of oil spills between 1976 and 1996 in Nigeria - - 11
Table 1.3. Parameters used in the classification of water quality - - - 19
Table 2.1. Chemical reagents and analytical conditions for the Tessier, optimized and modified BCR sequential extraction procedure - 42
Table 2.2. Values of constants for use in the Debye-Hückel equation at 1 atmosphere pressure - - - - - 48
Table 3.1. Sampling stations and human activity near the sampling locations from Cross River system - - - - - 58
Table 3.2. Sampling stations and human activity near the sampling stations for Qua Iboe River - - - - - - 61
Table 3.3. Operating conditions for the atomic absorption spectrophotometer s - 81
Table 3.4. Some thermodynamic data used for speciation calculations for T = 298.15 K - - - - - - 89
Table 3.5. Results of recovery study of Cd in sediment samples - - - - 92
Table 3.6. Results of recovery study of Pb in sediment samples - - - 93
Table 3.7. Results of recovery study of Cu in sediment samples - - - - 94
Table 3.8. Results of recovery study of Zn in sediment samples - - - 95
Table 4.1. Physicochemical properties of surface water samples from Cross River - - - - - - - 97
Table 4.2. Pearson correlation coefficient (r) of physicochemical properties in Cross River system - - - - - 105
Table 4.3. Trace metal concentrations (μgL^{-1}) of surface water samples from Cross River - - - - - - 106
Table 4.4. Pearson correlation coefficient (r) of trace metals in surface water from Cross River system - - - - 109
Table 4.5. Physicochemical properties of bottom sediment samples from Cross River - - - - - - 110
Table 4.6. Trace metal concentrations (μgg^{-1} dry weight) of sediment samples from Cross River system - - - - 113

Page

Table 4.7. Pearson correlation coefficients for trace metals in sediments of the Cross River - - - - - 116
Table 4.8. Enrichment factor values, EF (%) for metals in sediments from Cross River system - - - - - - 118
Table 4.9. Comparison of sediment metal concentrations (μgg^{-1} dry weight) in Cross River with sediment quality guidelines (SQGs) - - 121
Table 4.10. Fractionation of trace metal levels (with standard deviation and % fractionation in parenthesis) of modified BCR protocol for Cross River - - - - - - - - 123
Table 4.11. Individual and global contamination factors of trace metals in sediments from Cross River system - - - - - 132
Table 4.12. Solution composition of water quality parameters in Cross River - 133
Table 4.13 Saturation Indices of some mineral phases in Cross River system - 142
Table 4.14. Mean levels of physicochemical properties of surface water samples from Qua Iboe River - - - - - - 144
Table 4.15. Pearson correlation coefficient(R) of physicochemical properties of Qua Iboe River - - - 149
Table 4.16. Mean trace metal concentrations (μgL^{-1}) of surface water samples from Qua Iboe River - - - - - - 150
Table 4.17. Pearson correlation coefficient (R) of trace metals in surface water from Qua Iboe River system - - - - 154
Table 4.18. Physicochemical properties of bottom sediments from Qua Iboe River - - - - - - - - 155
Table 4.19. Mean trace metal concentration (μgg^{-1} dry weight) of sediment samples from Qua Iboe River - - - - - - 158
Table 4.20. Pearson correlation coefficient (r) of trace metals in sediments from Qua Iboe River system - - 161
Table 4.21. Enrichment factor values, EF (%) for sediment-metals from Qua Iboe River - - - - - - - 162
Table 4.22. Comparison of sediments metals levels (μgg^{-1} dry wt.) for Qua Iboe River system with sediment quality guidelines (SQGs) - - 163

Page

Table 4.23. Fractionation of trace metal levels (% fractionation in parenthesis) of modified BCR protocol for Qua Iboe River - - - - 165

Table 4.24. Individual and global contamination factors of trace metals in sediments from Qua Iboe River system - - - - 173

Table 4.25. Solution composition (molL^{-1}) of water quality parameters in Qua Iboe River - - - - - 174

Table 4.26. Saturation Indices of some mineral phases in Qua Iboe River system - - - - - - 183

Table 4.27. Comparison of water quality parameters with some rivers in Niger Delta and other parts of the world - - - - 185

Table 4.28. Comparison of metal concentrations in surface water with some Rivers in Nigeria and other parts of the world - - -188

Table 4.29. Comparison of results with WHO guideline for drinking-water and Canadian Water Quality Guidelines for fresh water - - 189

Table 4.30. Comparison of results of sediment metals of Cross and Qua Iboe River with other rivers in the Niger Delta and other parts of the world - - - - - - - 191

LIST OF FIGURES

Page

Fig. 1.1 Oil spill statistics in Nigeria showing number and volume of spills between 2006 and 2012 - - - - - - 12

Fig. 3.1 Map of study area showing sampling stations along Cross River - 57

Fig. 3.2 Map of study area showing sampling stations along Qua Iboe River - 60

Fig. 4.1. Speciation of Cd (i) and Pb (ii) in sediments of Cross River - - 124

Fig. 4.2. Speciation of Cr (i) and Cu (ii) in sediments of Cross River - - 126

Fig. 4.3. Speciation of Zn (i) and Ni (ii) in sediments of Cross River - - 128

Fig. 4.4. Speciation of Co in sediments of Cross River - - - - 129

Fig. 4.5. Distribution of Cd (II) (i) and Pb (II) (ii) species in Cross River surface water - - - - - - 134

Fig. 4.6. Distribution of Cr (III) (i) and Cu (I) (ii) species in Cross River surface water - - - - - - 136

Fig. 4.7. Distribution of Cu (II) (ii) and Zn (II) (ii) species in Cross River surface water - - - - - - 138

Fig. 4.8. Distribution of Ni (II) (i) and Co (II) (ii) species in Cross River surface water - - - - - - 140

Fig. 4.9. Speciation of Cd (i) and Pb (ii) in sediments of Qua Iboe River - - - - - - - 166

Fig. 4.10. Speciation of Cr (i) and Cu (ii) in sediments of Qua Iboe River - - - - - - - 168

Fig. 4.11. Speciation of Zn (i) and Ni (ii) in sediments of Qua Iboe River - - - - - - - 170

Fig. 4.12. Speciation of Co (i) in sediments of Qua Iboe River - - - 171

Fig. 4.13. Distribution of Cd (II) (a) and Pb (II) (b) species in Qua Iboe River surface water - - - - - - 176

Fig. 4.14. Distribution of Cr (III)/Cr (VI) (a) and Cu (I) (b) species in surface water of Qua Iboe River - - - - - 178

Fig. 4.15. Distribution of Cu (II) (a) and Zn (II) (b) species in surface water of Qua Iboe River - - - - - 180

Fig. 4.16. Distribution of Ni (II) (a) and Co (II) (b) species in surface water of Qua Iboe River - - - - - 181

LIST OF APPENDICES

Page

Appendix 1. Physicochemical properties of surface water samples from Cross River - - - - - - 220

Appendix 2. Seasonal variation of physicochemical characteristics of surface from Cross River - - - - - - 223

Appendix 3: Trace metal concentration (μgL^{-1}) in surface water samples from Cross River - - - - - - - 224

Appendix 4. Seasonal variation of trace metal levels (μgL^{-1}) in surface water samples from Cross River - - - - - 226

Appendix 5. Monthly distribution of some physicochemical properties of sediments samples from Cross River - - - - - 227

Appendix 6. Seasonal variation of physicochemical characteristics of sediment samples from Cross River - - - - 228

Appendix 7. Monthly distribution of trace metal concentrations of sediment samples from Cross River - - - - 229

Appendix 8. Seasonal variation of trace metal levels (μgg^{-1} dry wt.) of sediment samples from Cross River - - - - 230

Appendix 9. Results of fraction-specific concentrations of trace metals levels of modified BCR protocol for Cross River - - 231

Appendix 10. Percentage fractionation of trace metals levels using modified BCR protocol for Cross River - - - - 232

Appendix 11: Distribution of trace element species in surface water from Cross River using PHREEQC model - - - - 233

Appendix 12: Physicochemical characteristics of surface water quality from Qua Iboe River - - - - - 235

Appendix 13. Seasonal variation of physicochemical characteristics of surface water samples from Qua Iboe River system - - 239

Appendix 14: Results of trace metal levels (μgL^{-1}) in surface water from Qua Iboe River - - - - - - 240

Appendix 15. Seasonal variation of trace metal levels (μgL^{-1}) in surface water samples from Qua Iboe River - - - - - 242

Page

Appendix16. Monthly distribution of some physicochemical properties of sediments from Qua Iboe River - - - - - 243
Appendix 17. Seasonal variation of physicochemical characteristics of sediments samples from Qua Iboe River - - - - 244
Appendix 18. Monthly distribution of trace metals concentration of sediments from Qua Iboe River - - - - - 245
Appendix 19. Seasonal variation of trace metal levels (μgg^{-1} dry weight) in sediments samples from Qua Iboe River - - - - 246
Appendix 20. Results of fraction-specific concentrations of trace metals in sediments from Qua Iboe River using modified BCR protocol - 247
Appendix 21. Percentage fractionation of trace metals in sediments from Qua Iboe River using modified BCR protocol - - - 248
Appendix 22: Distribution of aqueous chemical species in surface water from Qua Iboe River using PHREEQC model - - 249

LIST OF ABBREVIATIONS AND ACRONYMS

ADWG	-	Australian Drinking Water Guidelines
ANZECC	-	Australian and New Zealand Environment and Conservation Council
ARMCANZ	-	Agriculture and Resource Management Council of Australia and New Zealand
ASTM	-	American Society for Testing and Materials
BOD	-	Biological Oxygen Demand
CCME	-	Canadian Council of Ministers of the Environment
COD	-	Chemical Oxygen Demand
CR	-	Cross River
CV	-	Coefficient of Variation
DO	-	Dissolved Oxygen
EC	-	Electrical Conductivity
EF	-	Enrichment Factor
ERL	-	Effects Range Low
ERM	-	Effects Range Median
FDEP	-	Florida Department of Environmental Protection
FEPA	-	Federal Environmental Protection Agency
GESAMP	-	Joint Group of Experts of Scientific Aspects of Marine Environmental Pollution
IG	-	Interim Guideline
ISQG	-	Interim Sediment Quality Guideline
LEL	-	Lowest Effect Level
LLNL	-	Lawrence Livermore National Laboratory
LOEL	-	Lowest-Observed-Effect Level
MHMRC	-	National Health and Medical Research Council
NIS	-	Nigerian Industrial Standards
NOAA	-	National Oceanographic and Atmospheric Administration
NRC	-	National Research Council
NRDC	-	Natural Resources Defence Council
OSRMA	-	Official, Standardised and Recommended Methods of Analysis

PEL	-	Probable Effect Level
PHREEQCI	-	pH-Redox-Equilibrium-Computer Programming Language Interactive
QIR	-	Qua Iboe River
SEL	-	Severe Effect Level
SON	-	Standards Organization of Nigeria
SQG	-	Sediment Quality Guideline
TDS	-	Total Dissolved Solids
TEL	-	Threshold Effect Level
TOC	-	Total Organic Carbon
TOM	-	Total Organic Matter
UNEP	-	United Nations Environment Programme
UNESCO	-	United Nations Educational
USAID	-	United States Agency for International Development
USEPA	-	United States Environment Protection Agency
USGS	-	United States Geological Survey
WHO	-	World Health Organization
WQI	-	Water Quality Index