DETERMINATION OF SOME METAL LEVELS IN SELECTED IRRIGATED CROPS ALONG THE BANKS OF ROMI RIVER KADUNA. NIGERIA.

BY

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A DISSERTATION SUBMITTED TO THE DEPARTMENTOF PURE AND INDUSTRIAL CHEMISTRY, FACULTY OF SCIENCE, BAYERO UNIVERSITY KANO NIGERIA. IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF A DEGREE IN (M.SC) ANALYTICAL CHEMISTRY

NOVEMBER, 2016

DECLARATION

I hereby declare that this work is the product of my own research efforts undertaken under the supervision of Professor A.A. Audu and has not been presented elsewhere for the award of any degree certificate. All sources have been duly acknowledged.

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CERTIFICATION

This is to certify that this dissertation titled, "Determination of some metal levels in some selected irrigated crops along the banks of Romi River, Kaduna. Nigeria" was conducted by Markus Zarmai Yari (SPS/MCH/00019) under my supervision.

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APPROVAL

This is to certify that this dissertation titled "Determination of some metal levels in some selected irrigated crops along the banks of Romi River Kaduna, Nigeria" has been examined and approved as part of the requirements for the award of the Master of Science (MSc.) Analytical Chemistry in the Department of Pure and Industrial Chemistry Bayero University,Kano, Nigeria

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ACKNOWLEDGEMENT

I want to give God all the glory for His Love and Grace upon my life as He has always been there for me. To my able supervisor, Prof. A.A. Audu I appreciate all that you did to ensure that this work was carried out in accordance with the required standards, sir may Almighty God bless your family.

The management of the department of chemistry, led by the Head of Department Dr. Haruna Musa, lecturers and the Technical staff of the department, I thank you for the encouragement and support throughout the program.

Mr Lucky Endas and my course mates, your support to the success of this work cannot be overemphasized, may God grant you all your heart desires.

My brother and former colleague in the office, Mal, Sabiu Hamza Dalawa and the entire staff of Nigeria Commodity Exchange Kano office your efforts towards the success of this work is acknowledged.

Finally to my lovely wife and children Mrs Hajara M. Yari, John ShekwoYemgbelo, Favour Saitu, Benjamin Shekwonu Mwaza and Peace Salamatu Anyida you were always there for me I really appreciate.

DEDICATION

This work is dedicated to God almighty for His Grace upon my life, and to my late parent Baba Yari Zarmai Bashishi and Mama Jummai Yari Zarmai who taught me to seek for Wisdom and Knowledge of the WORD of God as a pillar to every success.

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ABSTRACT

The concentrations of some heavy metals in crops such as garden egg, okra, maize, tomato, and spinach irrigated with water from Romi River were investigated. Their concentrations were found to be in the magnitude of Cd> Pb>Fe>Cu>Zn, while that of the trace metals were Ca>K>P>Mg>Na in order of magnitude. There was varying levels of significance ($p<0.05$) with increased concentrations of the determined metals. The high lead and cadmium concentrations were above WHO/FAO.2006, limits in the irrigated crops and these may lead to its toxic effects as it cans bio-accumulate in the tissues and muscles of human and domestic animals that feed on these crops. The concentrations of lead were: garden Egg (1.7µg/g), okra (0.7 µg/g), maize (0.8 µg/g), tomato (1.4µg/g), and spinach (2.2 µg/g) compared to the FAO/WHO. 2006 maximum permissible limit of (0.2 µg/g).The concentrations of cadmium was garden egg (1.0µg/g), okra (3.5 µg/g), maize (2.0µg/g), tomato (3,0µg/g), and spinach (3.0µg/g) compared to the WHO/FAO maximum permissible limit of (0.1 µg/g). It is observed that the water from the Romi River used in the irrigation farming is polluted with high concentration of heavy metals hence the consumption of crops cultivated by irrigation along the downstream of Romi River should be discouraged, due to high concentration of cadmium, lead and other toxic substances.

CHAPTER ONE

1.0 Introduction

Life cannot exist without water because it is the major component of all living things. It is important both physiologically and ecologically as it is used for different purposes; irrigation, sand mining, construction, washing of materials, domestic uses, cattle rearing and waste disposal. The discharge of industrial effluents into water bodies such as river is one of the major causes of environmental pollution and deterioration according to Abida Begum (2009). Some industries lack liquids and solid waste regulations and proper disposal facilities and such waste may be infectious, toxic and radioactive (WHO, 2004). Refinery and petrochemical waste generates wastes that are composed of organic and inorganic compounds including heavy metals. Wastewater released by petrochemical industries are characterized by the presence of large quantity of polycyclic and aromatic hydrocarbons, phenols, metal derivatives, surface active substances, sulphides, napthylinic acids and other chemicals (Suleiman, 1995). The content of the effluents have strong toxicological effects on the aquatic environment and to humans. Refinery effluents containing oils when discharged into water body can cause depletion of dissolved oxygen due to transformation of organic components, loss of biodiversity through the increase in amphipod population that is important in food chain (Beeby, 1993). Due to the ineffectiveness of the purification system, effluent may become dangerous leading to the accumulation of toxic products in the receiving water body with potential serious consequences on the ecosystem (Bay *et al*., 2003). In developing countries, there has been much emphasis on the installation of sewage treatment plants where all the industrial effluents are generally discharged. (Narwal *et al*.,1993). The sewage waters may be used as a potential source of irrigation for vegetables and fodder crops. Industrial effluents are a rich source of plant nutrients in soils, therefore soil provide the logical sink for their disposal. But many untreated and contaminated sewage and industrial effluents may have high concentration of several heavy metals such as Cd, Ni, Pb and Cr (Arora *et al*.2009).

The rate at which water is being polluted has affected the traditional relationship of the people with water. There is a palpable fear that rather than being the source of life, these polluted water bodies have become sources of misery, disease and death. The most worrisome aspect of oil pollution is the rise in occurrence of certain ailments that were previously unknown. (Mustapha and Adeboye, 2014)

1.1 Industrial Effluents

With the industrialization of the country a large volume of liquid and solid wastes are generated daily. The quality of these wastes depends upon the nature of the industry and the type of treatment given to these waters before their release from factory premises. The use of agriculture for the disposal of industrial effluents is becoming a widespread practice. Such materials may contain various toxic metals that could accumulate in larger quantities in soils. Also, soil pollution by heavy metals is one of the major environmental problems associated with the application of effluents from industries involved in metal processing (Antil and Narwal, 2008).

1.2 General Environmental Pollutants

Pollutants can come from many different sources and they can pollute air, water and land in a variety of ways. A bulk of environmental pollutants is organic based, but there are also a number of other sources of environmental pollutants.

The Helsinki convention (http://www.helcom.fi) gave a list of some substances called priority groups of harmful substances, which include:-

a) Heavy metals and their compounds

b) Organo halogen compounds

c) Organic compounds of phosphorus and tin

d) Pesticides, such as fungicides, herbicides, insecticides, slimicides and chemicals used for the preservation of food, wood, timber, wood pulp, cellulose, paper, hides and textiles.

e) Oils and hydrocarbons of petroleum origin

f) Nitrogen and phosphorus compounds

g) Radioactive substances, including wastes.

1.2.1 Air Pollutants

An air pollutant is any substance in the air that can cause harm to humans or the environment in general. Air pollutants may be natural or man- made, organic or inorganic and may take the form of solid particles; liquid droplets or gases. Six common air pollutants (also known as "criteria pollutants") are normally found all over. They are particle pollution (often referred to as particulate matter), ground-level ozone, carbon monoxide, sulfur oxides, nitrogen oxides, and lead. These pollutants can harm human health and the environment, and cause property damage. Of the six pollutants, particle pollution and ground-level ozone are the most widespread health threats. In America the EPA calls these pollutants "criteria" air pollutants because it regulates them by developing human health-based and/or environmentally based criteria (science-based guidelines) for setting standards. The set of limits based on human health is called primary standards and the secondary standards are the set of limits intended to prevent environmental and property damage. http://www.epa.gov.(2007). Atmospheric particles have numerous effects, such as reduction and distortion of visibility, enhancing atmospheric chemical reactions, hence affecting weather in many ways. They can also get into respiratory tract as such damaging health in many ways. These particles in the atmosphere, which range in size from about one-half millimeter down to molecular dimensions, are made up of a large variety of materials and discrete objects that may consist of either solids or liquid droplets. Particulate matter make up the most visible and obvious form of air pollution. Such particulate pollutants especially within the range of 0.001 to 10μm are commonly suspended in the air near sources of pollution such as the urban atmosphere, industrial plants, highways and power plants (Christopher, 2005). Generally some examples of very small particles of the classes given below include carbon black, silver iodide, combustion nuclei, etc. An example of large particles is cement dust, and that of mist includes raindrops, fog and sulfuric acid mist. Aerosols consist of carbonaceous material, metal oxides and glasses, dissolved ionic species and ionic solids. Asbestos is of concern as an air pollutant, because when inhaled it may cause asbestosis (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs). Substances of this kind remain present in the environment. PCBs (polychlorinated biphenyls) are the best-known example; other compounds of this kind are polychlorinated naphthalene (PCNs), chloroparaffins and brominated flame retardants. The use of PCBs has been gradually banned completely in many countries. It has been found to be more difficult to replace some other chemicals with less hazardous substitutes, the use of brominated flame retardants continues almost unabated for this reason. Aromatic organic particles contain polycyclic aromatic hydrocarbons (Christopher, 2005).

These polycyclicaromatic hydrocarbons (PAH) in atmospheric particles have received a great deal of attention because of the known carcinogenic effects of some of the compounds, e.g. benzo(a)pyrene, acephenanthrylene, benzo(j)fluoranthene and indenol, the whole group of these compounds are commonly known as POPs (persistent organic pollutants). A third category of persistent organic pollutants occur mainly as byproducts of various manufacturing or combustive processes. These include hexachlorobenzene (HCB), polycyclic aromatic hydrocarbons (PAHs) and dioxins. Elevated levels of PAHs are most likely to be encountered in polluted urban atmospheres and in the vicinity of natural fires such as forest, also coal furnace and cigarette smoke may contain some levels of PAHs. To a limited extent many of these compounds can also be formed naturally, but anthropogenic emissions have now declined substantially, thanks to a number of steps that have been taken. Renewable energy resources are in the moment's very good alternative to fossil fuel, but not all of them are environmentally friendly. The use of bio-fuels especially in form of fire wood causes a lot of air pollution, as such cannot be considered as good alternative for fossil fuel except where the emissions are being taken care of. Emissions from Bio-fuels combustion include the following pollutants and some effects they cause (Christopher, 2005):

CO_2 – green house gas

CO – health concerns

NOx – ozone precursor

VOC- health concerns and ozone precursor

1.2.2 Water Pollutants

Water pollutants can be defined as follows: a water pollutant is a substance or effect which adversely alters the environment by changing the growth rate of species in the water, interferes with the food chain, is toxic, or interferes with health, comfort, amenities, or property values of humans and all living in and around the water (http:// journals.tubitak.gov),This definition implies a need to set standards or guidelines in order to indicate that water, whose chemical properties exceed the limits of the standards, may cause a particular environmental alteration or interference. There are many materials that constitute water pollutants such as organic compounds, organic matter, heavy metals, inorganic salts, etc. Organic compound in water is of environmental importance for several reasons: e.g. particular compounds may be toxic in varying degrees to living organisms, including human beings. Aqueous organic matter (OM), in particular the bulk residues of plants and animals or some industrial discharges, can be oxidized by oxygen and other oxidizing agents in water. When released into a water body, the bulk OM degrades, consuming oxygen and leaving the system in oxygen deprived state. The loss of oxygen creates stress on many aquatic organisms including fish. These conditions are frequently observed downstream from points where high OM waste water or industrial water is discharged. These OMs when present in high concentration can create anoxic conditions in water. Humic material (HM) is another form of environmental organic matter pollutant. They constitute half of dissolved organic matter (DOM) in surface water Polyaromatic hydrocarbons, polychlorinated biphenyls, and dioxins are all well known because of their contribution to environmental problems. Residues of pesticides and their metabolic products can also be carried into water. (http:// journals.tubitak.gov).

The pesticides used today in developed countries in agriculture are all degradable to varying degrees. However, locally at least, these agents too may be unintentionally dispersed beyond the fields. Low but not insignificant concentrations of pesticides and pesticide residues sometimes occur in streams draining agricultural areas and also sometimes in groundwater. But generally the dispersal of organic pollutants is less effective in water than in the atmosphere. Owing to their low solubility in water, persistent organic pollutants mainly occur adsorbed to particles, which subsequently settle on the bottom, (Alkyuz and Roberts, 1993).

In the Baltic Sea, which is almost cut off from other seas and oceans, organic pollutants have accumulated in higher concentrations than in most other marine areas. Organic pollutants can seep back into the water from contaminated sea and lake beds many years after emissions themselves have ceased. With time, however, the contaminated layer of sediment will become buried under new sediment. Below are the lists of some elements and compounds that can be found in water as pollutants, most of them metals. Of all environmental issues involving water, contamination by toxic metals is one of the most visible, referred to as heavy metal pollution. Example is the widespread contamination of groundwater in Bangladesh and eastern India by semi-metal arsenic (Singh et al, 2010). Metals exist in the aqueous environment in a variety of forms such as aqua-complexes that are fully protonated or partially deprotonated, as complexes with inorganic ligands such as chloride and carbonate, and as complexes with naturally occurring organic molecules including discrete molecules. Of all the metals that causes environmental pollution, mercury is the most extensively studied, because of the several incidents of poisoning by mercury resulting in chronic illness and death. Perhaps the best known case is that which occurred in Minamata, a Japanese fishing village, during the middle of the twentieth century. During this accident, hundreds of people died from eating fish that contained with more than 100µgg-1 of mercury. The source of the mercury was from waste Hg^{2+} catalyst from polyvinyl chloride manufacture that was discharged into the ocean bay (Allchin, 1999).

Inorganic tin undergoes alkylation's in aquatic environments to form compounds such as monomethyl tin (CH_3Sn^{3+}) and dimethyl tin ($((CH)_2\ Sn^{2+})$). These organotin products are more toxic to aquatic biota than are the original inorganic tin compounds, and toxicity become greater as the number of organic groups increases in the series RnSn (4-n) 6, (n) from1to3,R Stands for groups the number of methyl groups. Another form of metal pollutant is in the form of suspended matter. In some water, metals or some other pollutants exist as suspended particulate materials and not dissolved. These suspended particulates are responsible for the distinct milky appearance of water. (WHO, 1993).

Typical measured properties that can indicate pollution in water include the following; - Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Solids (TS), Suspended Solids (SS), Total phosphorus (TP), Total Nitrogen (TN), Conductivity, Sodium hazard, Alkalinity, (pH) etc. The importance of these parameters can be illustrated using sodium, pH and alkalinity. High sodium ions in water affects the permeability of soil and causes infiltration problems, this is because sodium can replace calcium and magnesium adsorbed on the soil clays and causes dispersion of soil particles. If the soil has calcium and magnesium predominantly adsorbed on the soil exchange complex, the soil will be easily cultivated and will have a permeable and granular structure. But if sodium caused dispersion in the soil, this will results in breakdown of soil aggregates with the results that the soil becomes hard and compact when dry and reduces infiltration rates of water and air into the soil affecting its structure (Anderson et al 1989). As with sodium, pH vs. alkalinity also affects water quality.Alkalinity is a measure of the resistance of water to a reduction in pH when hydrogen ions are added. Any weak acid or base can act as a buffer, e.g. carbonate or carbonic acid. Since pH level of water is very important for the aquatic lives in the water, the alkalinity of the water is therefore very important and should be maintained.

1.2.3 Soil Pollutants

Past and present economic activities have resulted in the pollution of the underlying soil where these activities took place. Apart from direct pollutants on soils, there are many other environmental problems that are associated with soil such as erosion, leaching, acidification, etc.

In any human society bulk solid wastes are produced as by product of normal and fundamental activities of living. These wastes can be as rudimentary as food scraps, ash from fires and excreta from humans and animals, but with industrialization the wastes are more than rudimental both in quantity and variety. The amounts of waste produced by intensive agriculture and modern industry are very alarming. Also in wealthy countries there are so much wastes generated by ordinary citizens in a consumer-oriented urban setting, and related to this are the increasing populations which have led to the rapid expansion of existing urban areas and the development of new ones. As such areas used by industries in the past have often become valuable land for the development of domestic housing in many parts of the world. Therefore many substances, which are well known toxicants or carcinogens from the former industries, are present in relatively high concentrations in the soil in some urban areas. Some of these areas have been sited and tagged as contaminated sites by many environmental activists. So many contaminated sites such as Love Canal, the Picello farm and the Valley of Drums have become so popular (Connell, 2005). In many countries the problem of management of these contaminated sites is of considerable magnitude. For example, in the Netherlands, over 100,000 sites have been identified as being potentially contaminated, with 10,000 sites confirmed as being contaminated. Likewise in Germany, over 50,000 potentially contaminated sites have been identified. In the U.S. there are an estimated 100,000 sites that have been nominated as contaminated, with 10,000 of these designated as priority areas (Connell, 2005). The most common toxic soil pollutants include metals and their compounds, organic chemicals, oils and tars, pesticides, explosive and toxic gases, radioactive materials, biological active materials, combustible materials, asbestos and other hazardous materials. These substances commonly arise from the disposal of industrial and domestic waste products in designated landfills or uncontrolled dumps. Soil contaminants do not fall into a single, or several simple classes of chemicals, but are very diverse in nature and can be harmful to the natural environment or human health. For example, from the metals, lead originating from motor vehicles is a very common soil contaminant in urban areas. Lead can also originate from smelters and mining operations. Lead is no longer used in paint, but the old paints that have already been used before the ban can contribute to lead in the environment. Copper and chromium are also common heavy metal soil pollutants and primarily originate from tanneries and wood-preserving plants. Other heavy metals pollutants include cadmium, arsenic, zinc and mercury; they are mainly due to industrial activities, waste incineration, agricultural activities, combustion of fossil fuels and road traffic. Organic liquids are used as solvents in many industrial processes and Products such as paints, petroleum products, including gasoline, naphtha, toluene, and xylene, they are common solvents too. In addition, chlorohydrocarbons such as dichloroethylene and carbon tetrachloride are commonly used as solvents. Volatile organic compounds (VOC) such as benzene, toluene, xylenes, dichloro-methane, trichloroethane, and trichloroethylene, may occur as soil contaminants in industrialized and commercialized areas, particularly in countries where enforcement of regulations is not very stringent. One of the common sources of these contaminants is leaking underground storage tanks or transport pipes as is common in Nigeria. (Connell, 2005).

Also improperly discarded solvents are also significant sources of soil VOCs. Almost all of the organic substances used in industry and society in general can constitute soil contaminants.

Waste coal tar produced in many places in time past was disposed into wells and pits. Coal tar consists of highly complex mixture of aromatic hydrocarbons, phenols, and PAHs. As a result, many cities contain sites with very high levels of these soil contaminants. Contamination of soil with artificial radionuclide e.g. cesium-137, strontium-90 and some plutonium isotopes also do occur in some areas where they are used in industries (Connell, 2005).

1.3 Heavy Metal Pollution

Definition of a heavy metal

"Heavy metals" are chemical elements with a specific gravity that is at least 5 times the specific gravity of water. The specific gravity of water is 1 at 4°C (39°F). Simply stated, specific gravity is a measure of density of a given amount of a solid substance when it is compared to an equal amount of water. Some well-known toxic metallic elements with a specific gravity that is 5 or more times that of water are arsenic, 5.7; cadmium, 8.65; iron, 7.9; lead, 11.34; and mercury, 13.546 (Lide 1992).

In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, are commonly found naturally in foodstuffs, in fruits and vegetables, and in commercially available multivitamin products. IOSHI (1999).

Diagnostic medical applications include direct injection of gallium during radiological procedures, dosing with chromium in parental nutrition mixtures, and the use of lead as a radiation shield around x-ray equipment. Heavy metals are also common in industrial applications such as in the manufacture of pesticides, batteries, alloys, electroplated metal parts, textile dyes, steel, and so forth. IOSHI (1999).,many of these products are in our homes and actually add to our quality of life when properly used.

What metals are in our water?

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentrations. Heavy metals are natural components of the Earth's crust. They cannot be degraded or destroyed.(Bubb J.M. and Lester, J.N. 1991). The density of heavy metals is usually more than 5.0 g/cm3. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), lead (Pb), Copper (Cu), Zinc (Zn),Cobalt (Co), Nickel (Ni), and Iron (Fe). These metals are classified in to three categories: toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am, etc.) (Volesky,1990; Bishop, 2002). To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination (e.g. lead pipes), high ambient air concentrations near emission sources, or intake via the food chain. (Lenntech, 2011).

Among all the pollutants, heavy metals are most dangerous as these are non –biodegradable and persist in the environment. These enter into the water resources through both natural and anthropogenic activities. More attention is being given to the potential health hazards posed by heavy metals. Toxic metals cause toxicity to organisms even at part per million (ppm) level of concentration. Heavy metals are natural components of the earth's crust. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some of these heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. (Ferner, 2001).However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain. Heavy metals are dangerous because these tend to bio-accumulate. Bioaccumulation means an increase in the concentration of a chemical in an organism over time, compared to its concentration in the environment. Compounds accumulate in living systems when these are taken up and are stored faster than they are broken down (metabolized) or excreted. Heavy metals may enter a water supply through industrial or wastes releasing heavy metals into streams, lakes, rivers, and groundwater. Unlike organic pollutants, heavy metals, being non-biodegradable pose different kind of challenges for remediation. A well known environmental disaster associated with heavy metals is the Minamata disease caused by mercury pollution in Japan. (Volesky, 1990; Bishop, 2002).

a) Sources of Heavy Metal Pollution

Heavy metal pollution mainly arises from the effluents of industrial units where irrigation with effluents released from paper mills and fertilizer factories add various alkalies, ammonia, cyanides and heavy metals into water resources (Singh, et al 2010). The waste water from the dyes and pigment industries, film and photography, galvanometry, metal cleaning, electroplating, leather and mining industries contains considerable amounts of heavy metal ions.

b) Common industrial units releasing heavy metals into water bodies.

The characteristics of the waste stream from industries are so toxic and corrosive due to the presence of heavy metals like:

i) Chromium from Chrome plating, petroleum refining, electroplating industry, leather tanning, textile manufacturing and pulp process units. Chromium exists in hexavalent and trivalent forms.

ii) Nickel may be released into water bodies through galvanization, paint, powder batteries processing units, metal refining and super phosphate fertilizers.

iii) Lead is most times released through petrol based materials, pesticides, leaded gasoline, mobile batteries, electroplating, plastic, metal refining and several industrial emissions.

iv) Zinc from Rubber industries, paints, dyes, wood preservatives and ointments.

v) Cadmium from Batteries, electroplating industries, phosphate fertilizers, detergents, refined petroleum products, paint pigments, pesticides, galvanized pipes, plastics, polyvinyl and copper refineries.

vi) Iron from metal refining, engine parts.

vii) Aluminium Industries preparing insulated wiring, ceramics, automotive parts, aluminum phosphate and pesticides.

viii) Automobile exhaust, industrial dust, wood preservatives and dyes.

Others are Mercury, electric/light bulb, wood preservatives, leather tanning, ointments, thermometers, adhesives and paints. (Ferner, 2001).

1.3.1 Metal Health Risks

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, mercury and arsenic. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Heavy metals have been used by humans for thousands of years. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years. Many individuals in Europe already exceed these exposure levels and the margin is very narrow for large groups. Therefore, measures should be taken to reduce heavy metal exposure in the general population in order to minimize the risk of adverse health effects. The general population is primarily exposed to mercury via food, fish being a major source of methyl mercury exposure, and dental amalgam (Jarup, 2003).

Lead

Lead accounts for most of the cases of pediatric heavy metal poisoning (Roberts 1999). It is a very soft metal and was used in pipes, drains, and soldering materials for many years. Millions of homes built before 1940 still contain lead (e.g., in painted surfaces), leading to chronic exposure from weathering, flaking, chalking, and dust. Every year, industry produces about 2.5 million tons of lead throughout the world. Most of this lead is used for batteries.

Target organs are the bones, brain, blood, kidneys, and thyroid gland, gastrointestinal tract, joints and reproductive system, and acute or chronic damage to the nervous system, anemia, headache, fatigue, weight loss, cognitive dysfunction and decreased coordination, memory loss, nerve conductions. The central nervous system is most sensitive to the effects of lead. (Roberts 1999).

Copper

Copper at very high levels is toxic and can cause vomiting, diarrhea, loss of strength or, for serious exposure, cirrhosis of the liver. Water turns blue-green in color as the corroded copper comes off the inside of the pipes and appears in the water as a precipitate. This reaction only occurs in a small percentage of cases. Biliary obstruction (inability to excrete excess copper), liver disease, renal dysfunction, fibromyalgia symptoms, muscle and joint pains, depression, chronic fatigue symptoms, irritability, tumor, anemia, learning disabilities and behavioral disorders, stuttering, insomnia, niacin deficiency, leukemia, high-blood pressure. Zinc Nausea and vomiting. (Roberts, 1999)

Cadmium

Cadmium is a byproduct of the mining and smelting of lead and zinc. It is used in nickel-cadmium batteries, PVC plastics, and paint pigments. It occurs mostly in association with zinc and gets into water from corrosion of zinc-coated ("galvanized") pipes and fittings.

Target organs are the liver, placenta, kidneys, lungs, brain, and bones. Hypertension or high blood pressure, dulled sense of smell, anemia, joint soreness, hair loss, dry scaly skin, loss of appetite, decreased production of T-cells and, therefore, a weakened immune system, kidney diseases and liver damage, emphysema, cancer and shortened lifespan.(Roberts, 1999)

Aluminium

Although aluminium is not a heavy metal (specific gravity of 2.55-2.80), it makes up about 8% of the surface of the earth and is the third most abundant element. It is readily available for human ingestion through drinking water.

Studies began to emerge about 20 years ago suggesting that aluminium might have a possible connection with developing Alzheimer's disease when researchers found what they considered to be significant amounts of aluminum in the brain tissue of Alzheimer's patients. Although aluminum was also found in the brain tissue of people who did not have Alzheimer's disease, recommendations to avoid sources of aluminum received widespread public attention. (Lenntech, 2011).As a result, many organizations and individuals reached a level of concern that prompted them to dispose of all their aluminum cookware and storage containers and to become wary of other possible sources of aluminum, such as soda cans, personal care products, and even their drinking water.

However, the World Health Organization (WHO, 1998) concluded that, although there were studies that demonstrate a positive relationship between aluminum in drinking water and Alzheimer's disease, the WHO had reservations about a causal relationship because the studies did not account for total aluminum intake from all possible sources.

Although there is no conclusive evidence for or against aluminum as a primary cause for Alzheimer's disease, most researchers agree that it is an important factor in the dementia component and most certainly deserves continuing research efforts. Therefore, at this time, reducing exposure to aluminum is a personal decision. (WHO, 1998)

Target organs for aluminum are the central nervous system, kidney, and digestive system. Gastrointestinal disturbance, fatigue, headache, poor calcium metabolism, decreased liver and kidney function, forgetfulness, speech disturbances and memory loss, weak and aching muscles, seizures, vertigo and loss of balance

Arsenic

Arsenic is the most common cause of acute heavy metal poisoning in adults. Arsenic is released into the environment by the smelting process of copper, zinc, and lead, as well as by the manufacturing of chemicals and glasses. Arsine gas is a common by-product produced by the manufacturing of pesticides that contain arsenic. Arsenic may be also be found in water supplies worldwide, leading to exposure of shellfish, cod, and haddock. Other sources are paints, rat poisoning, fungicides, and wood preservatives. (Ferner, 2001).

Target organs and possible signs are the blood, kidneys, and central nervous, digestive, and skin systems, Headache, confusion, drowsiness, convulsions, changes in fingernail pigmentation, vomiting, diarrhea, bloody urine, muscle cramps, convulsions, gastrointestinal upsets and coma.

Iron

Iron is a heavy metal of concern, particularly because ingesting dietary iron supplements may acutely poison young children. Ingestion accounts for most of the toxic effects of iron because iron is absorbed rapidly in the gastrointestinal tract. The corrosive nature of iron seems to further increase the absorption. It can cause a rusty red or brown stain on fixtures or laundry and/or cause your water to develop a metallic taste.(Lenntech, 2011).

Target organs are the liver, cardiovascular system, and kidneys.

Mercury

Mercury is generated naturally in the environment from the degassing of the earth's crust, from volcanic emissions. It exists in three forms: elemental mercury and organic and inorganic mercury. Atmospheric mercury is dispersed across the globe by winds and returns to the earth in rainfall, accumulating in aquatic food chains and fish in lakes. Mercury compounds were added to paint as a fungicide until 1990.

These compounds are now banned; however, old paint supplies and surfaces painted with these old supplies still exist. Mercury continues to be used in thermometers, thermostats, and dental amalgam. Certain bacteria are able to transform it into methyl mercury, which is concentrated in the food chain and can cause malformations. (Ferner, 2001).Target organs are the brain and kidneys.

1.3.2 Removal of heavy metals

Several physico-chemical methods like chemical precipitation, electrodialysis, ion-exchange, ultra-filtration, reverse osmosis etc. are commonly employed for stripping toxic heavy metals from waste waters (Mehta and Gaur, 2008).

Some of these methods include:

a) Reverse Osmosis

It is a process in which heavy metals are separated through a semi-permeable membrane at a pressure greater than osmotic pressure caused by the dissolved solids in wastewater. The disadvantage of this method is that it is expensive (Ozaki *et al*., 2002).

b) Electro dialysis

In this process, the ionic components (heavy metals) are separated through the use of semi-permeable ion-selective membranes. Application of an electric potential between the two electrodes causes the migration of cations and anions towards respective electrodes. Because of the alternate spacing of cation and anion permeable membranes, cells of concentrated and dilute salts are formed. The disadvantage is the formation of metal hydroxides, which clog the membrane and thus cost involved is high (Mohammadi *et al*., 2008).

c) Ultra filtration

This is a pressure driven membrane operation that uses porous membranes for the removal of heavy metals.Ultra filtration (UF) membranes provide an efficient, compact way to treat industrial wastewater to make it pure enough for discharge or recycling. Machining processes produce large volumes of sludge containing heavy metals. Without treatment, this sludge must be hauled away and the wastewater cannot be reused.

UF technology separates and concentrates insoluble metals, reducing the heavy metals in wastewater to low enough levels to allow discharge of the wastewater. (www.kochmembrane.com) .

The main disadvantage of this process is the generation of sludge.

d) Ion-exchange

In this process, metal ions from dilute solutions are exchanged with ions held by electrostatic forces on the exchange resin. The disadvantages include high cost and partial removal of certain ions.

e) Chemical Precipitation

Precipitation of metals is achieved by the addition of coagulants such as alum, lime, iron salts and other organic polymers. The large amount of sludge produced during the process is the main disadvantage.

f) Phytoremediation

Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. The disadvantages include the long time for removal of metals and the regeneration of the plant for further bio sorption is difficult. The above stated methods are effective for removal of metals from water with high concentration of metals while for low concentrations (ppm level) of metals these techniques are not very fruitful. These methods also have other several disadvantages such as incomplete metal removal, limited tolerance to pH change, expensive equipment and monitoring system requirements, high reagent or energy requirements and generation of toxic sludge or other waste products that require disposal (Ahalya et al 2003). Further, these techniques may be ineffective or extremely expensive when metal concentration in waste water is in the range 1-100 ppm (Mehta and Gaur, 2008).

There is growing evidence that climate change is occurring and having so much effect on the world environmental conditions. One need only to listen to the news on the television or in the radio and one can clearly see that climate change is already a global problem, For example, on the 15.09.2007, Euro News, National Snow and Ice Data Center (NSIDC) reported that the arctic ice record is low since 30years; millions of cubic meters have melted. According to this news, arctic ice may completely disappear by 2040 if it continued to melt at the present rate. Climate change and other environmental challenges impact every corner and community on the planet (NSIDC report 2007). Our generation is witnessing the early stirrings of extreme weather events, melting ice and other climatic manifestations. Long-lived greenhouse gases like carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are in the increase. It is advisable to have analytical instruments in the plants for process monitoring and pollution control, such types of emissions cannot be discharged into the environment, but rather retreated to reduce the greenhouse gases. The Intergovernmental Panel on Climate Change (IPCC) in its 4th report gave a very comprehensive report on the state of the art as regard climate change (Solomon, et al 2007). The ICPC reported that, the concentration of atmospheric CO_2 has increased from a pre-industrial value of about 280ppm to 379ppm in 2005. The annual CO_2 growth rate is reported to be larger during the last 10yrs. It is estimated according to their report that about 2/3 of anthropogenic CO_2 emissions have come from fossil burning and about 1/3 from land use. The effects of this increase in CO_2 emission are many, one of which is the uptake of this CO_2 by ocean, seas and rivers resulting in changes in chemical equilibrium. Dissolved CO_2 forms weak acid, so as dissolved CO_2 in 35 creases, pH of the waters decreases. This has drastic effect on aquatic lives and some uses of sea and river water. More threatening is the effect on ozone layer; CO_2 as a greenhouse gas caused depletion of ozone layer leading to global warming. (Solomon, et al 2007). The trend with methane (CH_4) is similar, because the abundance of CH_4 in 1995 of about 1774ppb is more than double its pre-industrial value. N_2O concentration in 2005 was 319ppb, about 18% higher than its pre-industrial value. This increase can be attributed to human activities, particularly agriculture and associated land use. The greatest warming has occurred in the northern hemisphere's (NH) winter and spring. Average arctic temperatures have been increasing as almost twice the rate of the world in the past 100 years. Heat waves have increased in duration beginning in the latter half of the 20th century. The record breaking heat wave over western and central Europe in the summer of 2003 is an example of an exceptional recent extreme. In the tropics and sub-topics, longer droughts have been observed since the 1970s, and get worst with time. The Sahara desert is getting wider and wider. According to the report of the state of the environment in Germany 2005 by the Umwelt Bundes Amt, the concentration of CO_2 has risen by about 30% since 1750 and now exceeds a value of about 370 PPMV due to man-made emission, with industrial emissions as seen in Figure 4, this increase is expected. According to their report the present CO_2 concentration has not been reached in the last 42000 years, or probably in the last 20 million years. The last current annual rate of increase has been given as the highest in the last 2000 years. Nitrous oxide (NO_2) concentration also has risen since 1750 by around 17% and is still rising. The current concentration of NO_2 is the highest in the last 100 years. The trend is similar in SF6 concentration, which has risen by two orders of magnitude since its industrial production began in 1953. This report has a good degree of agreement with the IPCC report quoted above and with many other researchers' results. Environmental pollution has been proved, by all these reports, beyond reasonable doubt to be real and serious. (Solomon, et al 2007).

1.3.3. Removal of Heavy Metals through Bio sorption

Biosorption of heavy metals is defined as the ability/use of the biological materials to remove heavy metals from wastewater through metabolically mediated or physico-chemical uptake of metal (Fourest and Roux, 1992). The most prominent features of biosorption are low cost and highly efficient materials to adsorb heavy metals even when present at very low concentrations (Yu *et al*., 2001).

a) Removal by Low Cost Sorbents and Industrial Wastes

The use of low-cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from solution. Natural materials or waste products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost. (Ahalya *et al*,2003). Modification of the sorbents can also improve adsorption capacity. In this review, an extensive list of sorbent literature has been compiled to provide a summary of available information on a wide range of potentially low-cost sorbents, including bark, chitosan, xanthate, zeolite, clay, peat moss, seaweed, dead biomass, and others. Some of the highest adsorption capacities reported for cadmium, chromium, lead and mercury are: 1587 mg Pb/g lignin, 796 mg Pb/g chitosan, 1123 mg Hg/g chitosan, 1000 mg Hg/g CPEI cotton, 92 mg Cr(III)/g chitosan, 76 mg Cr(III)/g peat, 558 mg Cd/g chitosan, and 215 mg Cd/g seaweed The use of low cost sorbents has been investigated as a replacement for current costly methods of removing heavy metals from solutions (Hawari and Mulligan, 2006).

b) Removal by Plant Biomass

Heavy metal pollution has become one of the most serious problems today, and the use of microbial and plant biomass for the detoxification of industrial effluents for environmental protection and recovery of valuable metals offers a potential alternative to existing treatment technologies.

Sekhar C.K.et al 2003, discovered that the biosorption capacity of a plant biomass as studied for different toxic metals and their removal was found to be higher for Pb, Zn and Cr among the 11 metals studied (As, Se, Zn, Fe, Ni, Co, Pb, Mn, Hg, Cr and Cu). The results of the biosorption revealed higher Pb removal followed by Cr and Zn at lower metal concentrations, less than 250 ppm and with biomass concentrations above 2 g. The results of shake flask experiment revealed enhanced metal removal with 15 min agitation for Pb and 180 min for Zn and Cr removal. Metal removal was higher at lower pH for Cr and Zn and increased pH decreased the percentage metal removal. Lead removal was unaffected by pH changes. The presence of co-ions (As, Se, Hg, etc.) did not affect Pb removal by biomass, but on the other hand, Zn and Cr uptakes decreased. For the reuse of biomass, the used biomass was subjected to desorption studies using HNO_3. The retention capacity of the biomass was almost constant after three cycles of chelation–desorption, suggesting that the lifetime cycle was sufficiently long for continuous industrial application. The suggested process can be used as an alternative to the classical technologies for effluent decontamination and would also be efficient for polishing effluents treated by other methods. The biosorption model developed was applied to a “real life system” successfully. (Sekhar C.K et al 2003).

c) Removal by Microorganisms

The ability of microbial biomass to remove heavy metal ions from polluted aquatic systems has been reported. Microorganisms which have been tested for biosorption of heavy metals include bacteria (Scott and Palmer, 1990).

A study carried out by Rani J. et al in 2010, is considered the first attempt to examine the possible role of the naturally occurring rhizospheric bacteria in heavy metal removal by *Sedum alfredii* Hance, a terrestrial Zn/Cd hyperaccumuluator, from Zn, Cd, Cu and Pb contaminated water using antibiotic ampicillin. Moreover, the toxicity symptom in plants under heavy metal stress expressed as total chlorophyll, chlorophyll *a* and *b* content, growth inhibition, root length, and N, P contents were studied, and the possible relationship among them were also discussed. The researchers further explained that these results indicate that rhizospheric bacteria may play an important role in the uptake of N and P by *S. alfredii*, and consequently result in the increase of Chlorophyll content in the leaves and plant biomass due to improved photosynthesis. At the same time, root length significantly decreased under the treatment with ampicillin, which suggested that rhizospheric bacteria appeared to protect the roots against heavy metal toxicity. The Pb, Zn, Cu and Cd concentrations in the roots, stems and leaves of *S. alfredii* were much higher than those exposed to ampicillin. Accordingly, metal concentrations in the contaminated water without ampicillin treatment were lower than those treated with ampicillin. These results suggest that the rhizospheric bacteria may be useful in plant tolerance to heavy metal toxicity, and also accelerate the metal removal from contaminated water. Yeast has been used for the removal of heavy metals as reported by Volesky *et al*., (1993).

1.4 Composition of Industrial effluents.

In Kaduna, seventeen categories of heavily polluted industries have been identified by KEPA. They are cement, thermal power plant, distilleries, sugar, fertilizer, integrated oil and steel, oil refineries, pulp and paper, petrochemicals, pesticides, tanneries, basic drugs and pharmaceutical, dye and dye intermediates, caustic soda, zinc smelter, copper smelter and aluminium smelter. Generally, these industries discharge their effluents into city sewage system, nearby water bodies or adjoining agricultural lands which cause environmental problem.

1.5 State of the Nigerian Environment

Nigeria like many developing countries with some kind of industrialization faces severe environmental degradation that appears to be threatening the long term development prospects. This is mainly due to the fact that Nigeria relies mainly upon the use of natural resources in its growth and development process. The use of these natural resources is not done in a sustainable way, hence threatening the future generation's ability to meet their own needs. In general there is no proper record of developments that indicate the degrading state of the Nigerian environment like the study by Umwelt bundes amt in Germany; only pockets of isolated cases are reported in the literature, such as pollution by the oil industries in the Niger Delta area. A proper study such as to show certain general trend of indicators are on the increase, showing the degree of environmental degradation, is basically lacking in Nigeria's environmental studies. As such to give the state of the Nigerian environment, only such individual cases will be mentioned here.

Industrial activity in Nigeria is a major contributor to many of the environmental and social problems facing the country. Some industries that are found in Nigeria include gas and oil, chemical, food and beverages, hide and skin, cement, paint industries, iron and steel, paper and pulp, agro-allied, motor assembly etc. These industries all contribute to the environmental pollution in various ways; common amongst them is the drainage of their effluents into open drains and water channels. Some go to the extent of burying their expired and hazardous chemical waste in the ground. The oil industries have some peculiar problems such as breakdown and canalization of oil pipelines causing a lot of water and soil pollution. This has become a threat to the environment, aquatic and human lives (CIA World Fact book-Nigeria 2000).

The oil industries have the bigger effects on the environment compared to the other industries in Nigeria, therefore a review of some specific cases of these pollution will be done here. Most of the oil exploration has thus far been carried out in the Niger Delta area as such most of the reports found in literatures are on the damage done in this area. Greg Campbell quoted the spokesman for the Jesse Town council of elders in the Niger Delta area saying, up to 1000 people were involved in a fuel fire accidents at one time. Pipelines carrying both gas and oil rupture with alarming effects in Nigeria, either at the hand of saboteurs or through human and equipment error. Shell Nigeria reported that up to 50,200 barrels of oil were spilled in 1998 due to human saboteurs. In December 2000, a pipe that had leaked for weeks exploded in Atlas cove, near Lagos, killing about 50 people (CIA World Fact book-Nigeria, 2000).

1.6 Statement of the problem

Over the last three decades, there has been increasingly global concern over the public health impacts attributed to water pollution in particular, the global burden of disease. The World Health Organization (WHO,2006) estimated that about a quarter of the disease facing humankind today occur due prolonged exposure to water pollution. Most of these water pollution related disease are however not easily detected and may be acquired during childhood and manifested later in adulthood. The discharge of industrial effluents into water bodies is one of the major causes of environmental pollution which poses risk to health, accessible through the infectious dose and host susceptibility. In developing countries of the world more than 80% polluted water is used for irrigation which continues to pollute the environment with impunity. The effects of the polluted water are recognized immediately, whereas others don't show for months or years.

1.7 Justification of the study

(1)The study may provides the irrigation farmers along Romi River banks with a requisite knowledge concerning some toxic elements (heavy metals) uptake by crops owing to the effluents water used which invariably poses health risks to humankind and that will trigger the need to either abandon the site or devised ways of adequately treating this water before it is used for irrigation.

(2) It may strengthen/awaken enforcement agencies on the need for them to monitor all the units operation in KRPC and make sure the treated effluents meet the permissible standard limits before discharge into the water body.

(3) It may bring about further re-treatment of KRPC effluents before discharge into the river due to the consequences of using such polluted water for irrigation.

(4) similar studies in Nigeria on the impact of chemical fertilizer industrial wastes on the quality of soil in the vicinity of a fertilizer industry located in Port Harcourt was carried out by Godson *et al* (2004) Their results showed very high contents of metals, some heavy metals and other elements in the soil. From all their result, one can confidently say, the threat due to environmental pollution is not limited to our climate, but it is all encompassing. Therefore the state of the environment is not looking good from the studies and these deserve urgent action from individuals, industries, NGOs, scientists, governments, communities, etc.

1.8 Aim of the study

The study aimed at determination of some metal levels in some selected irrigated crops along the banks of Romi River.

Objectives of the study

To evaluate the chemical composition of the KRPC effluent

To evaluate the levels of essential and heavy metals in some selected crops cultivated along the banks of Romi River in dry seasons.

To compare the levels of heavy metals in the upstream crops and the downstream crops

To compare the levels of the assessed parameters with the maximum permissible limit

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

Nigeria has a vast crude oil and gas reserve and attempts to explore it has left the country with unique vulnerabilities (Nduka and Orisakwe, 2009). Industrialization of Kaduna, Warri, and Port Harcourt between 1968 and 1990 created pollution potential that are as high as some sources of pollution. The rivers, estuaries, creeks and air have been contaminated for decades. Refining and petrochemical plants generate solid waste and sludge composed of organic, inorganic compounds including heavy metals. Wastewater released by petrochemical industries are characterized by the presence of polycyclic and aromatic hydrocarbons, phenol etc (Suleiman, 1995). The presences of pollutants in natural waters alter the quality and often pose serious threats to aquatic life. Various studies have shown positive correlation between pollutants from petrochemical and refinery effluents and the health of aquatic organism (Otunkunefor and Obiukwu, 2005).

Vivan et al. (2011), in their study, analyzed the effect of Kaduna refinery effluent discharge on River Romi and concluded that the water in Romi River has been contaminated by effluent discharge from the refinery, it was found that there is difference in the concentration of the pollutants at the upstream, point of entry and downstream, despite the fact that the refinery has a waste water treatment plant.

According to Kirkhan (1983), the use of polluted water in the immediate surroundings of big cities in most countries (Nigeria inclusive) for growing of vegetables is a common practice.

Although this water is considered to be a rich source of organic matter and plant nutrients, it also contains sufficient amounts of soluble salts and heavy metals such as Iron (Fe), Copper (Cu), Zinc (Zn), Lead (Pb) Nickel (Ni), Selenium (Sn), Mercury (Hg), Chromium (Cr), Arsenic (As), and Aluminum (Al) among others. When such water is used for cultivation of crops for a long period, these heavy metals may accumulate in soil, become toxic to the plants and also cause deterioration of soil.

The composition of some of the effluent from different type of industries as reported by Antil *et al*., 2004; Narwal *et al*., 1992 and Zalawadia *et al*.,1997 are variable. Effluents of Zn smelter and paper mill are acidic in nature having pH 3.5 and 4.8, respectively. The effluents of oil refinery, paper mill, distillery and sugar mill are rich in organic carbon C, ranging from 820 to 28350mg/L. when such effluents of high BOD are disposed on soils and water, they may develop anaerobic conditions and the soil or water becomes sick and unproductive due to high amounts of salts accumulations. The organic carbon C, of the soil and water increased with effluent waters at all the locations. However, highest increased in carbon content of soil and water was observed. Narwa l*et al*., 1988 reported that long term application of effluent waters of high organic content resulted into soil sickness due to poor aeration and the concentration of heavy metals increased with effluents water irrigation. Gupta et al., (1986) and Narwal et al.,(1993) found that the application of effluent water on agricultural land for a long period of time increased the total content of Zn, Mn, Pb, Cu, Ni and Cd in soil and crops. The extent of increase in metal content was higher in the sample site which received effluent water irrigation for 15years. The result indicates that amount of Cd increased four (4) times and that of Ni three (3) times in effluent irrigated soil. Mira and Gupta (1997) reported 143 times more accumulation of Cd in sewage effluent irrigated soils over non-effluents irrigated soil, followed by Zn(47 times), Pb(18 times), Cr(5.6 times), Cu(3.6 times), Fe(2.4 times) and Ni(2.3 times). Antil et al., 2007, reported that the long term application of effluents wastewater for irrigation affect the physical and the chemical properties of soil. The bulk density of soils irrigated with effluent water was low (1.2 to 1.39mg/L), the hydraulic conductivity was also higher (1.10 to 1.33cm/h) for different irrigated soils (Kharche *et al*., 2011).

Antil *et al*, 2004 reported after a thorough survey on the composition of industrial effluents and concluded that crops grown on this soil indicated the high accumulation of toxic metals. The health hazard problems due to Ni absorption by crops grown on metal polluted soil or water was more in carrot followed by spinach, fenugreek and wheat. The accumulation of high amount of heavy metal in crops may influence consumer health and the high intake of metals by humans affects the body system and may lead to health deterioration. The application of agro-based industrial effluents water to agricultural lands adversely influences germination and growth of different crops.

Zalawadia *et al*., (1997) surveyed several industrials effluents used for irrigation and found out that there were heavy metals higher in concentration than the permissible level. The released of such effluents on agricultural lands will adversely affect the quality of crops grown on these soils making these crops toxic for animals and humankind consumption.

Gebre and Van Rooijen (2009) reported a situation in Addis Ababa by tracing the origins of pollution and focusing on urban and peri-urban farmers who depend on polluted water sources for agriculture. They concluded that discharge of untreated effluent from industries; solid wastes and wastewater are the main sources of pollution that enters urban surface water bodies. There are over 2,000 registered industries in Addis Ababa (65% of all industries in the country) most of them located along the river banks. According to the Addis Ababa Environmental Pollution Authority (2007) 905 of all industries lack facilities for some degree of treatment and consequently discharge any effluents into the adjacent rivers. According to the Sanitation Beautification and Park's Development Agency; a city total of 2256m^3 or 851 tonnes of solid waste is being generated daily of which 25% is dumped into open spaces, ditches, and water bodies (Gebre and Van Rooijen, 2009), in addition to solid waste, domestic wastewater is a major contributor to crate pollution in Addis Ababa. According to the World Bank report (2007), and estimated one quarter of the household in Addis Ababa lack any form of sanitation facility and as a consequence, they use open spaces, shrubs and river banks to relieve themselves. The presence of trace metals in the tested samples indicate that industries have a significant contribution to surface water pollution which bears two kind of economic costs; firstly, pollution reduces the total amount of adequate water available for household consumption and production and for irrigation agricultural usage. Secondly, there are costs related to the used of polluted water for consumption and production. The cost of using contaminated water for production leads to the decrease in both quality and quantity of products (World Bank, 2007).

Itan 1998, found the concentration of trace metals in vegetables that were grown with wastewater. The high concentrations of cadmium, chromium, copper, mercury, and nickel and zinc give evidence of industrial pollution trace back in agricultural crops; long term exposure to low levels of chemical pollutants can lead to chronic health effects and enhance the risks of adverse pregnancy outcomes. Empirical evidence shows a strong association between water pollution and cancer evidence and mortality. Even though all of these metals have not yet reached the phytotoxic levels, some of the vegetables have surpassed the naturally expected levels. This is particularly true for Cd, Cu, Ni, Hg and Zn in potato and Cr in onion and red-beet that contains high levels of heavy metals, poses risks to human health' Vivan et al., (2011), reported the contamination of River Romi by effluent discharge from KRPC because of the difference in concentration of the pollutants at the upstream, point of entry and downstream, despite the fact that the refinery has a waste water treatment plant, the waste released into the river from the refinery contaminate water because many of the parameters measured were higher than the acceptable limit set by National Standard of Nigeria and World Health Organization. It was discovered that these pollutant present in the river reduce the effect of photosynthesis and slows down natural water purification processes and the long effect of this is environmental degradation and its uptake by crops may cause long term health problems.

The Ministry for Environment in Germany always carries out a study every two years to see how people's sensitivity to environmental issues is doing. The last study carried out in 2006 by Kuckariz U; Rädiker S and Rheingans H, (2006) showed that one third of Germans rate the quality of the German environment as very bad, and 91% rate the global environment as very bad. This is almost double the number in the same study carried out in 2004. People are now taking environmental pollution very serious as such this reflects on their opinion on the environment. In the same study many people believed that environmental pollution is responsible for world's health problems, especially particulate matter in the atmosphere, but also chemicals in our day to day products as well as harmful substances in food which is posing a great risk to human health. This study shows that environmental protection is becoming more and more important in the minds of people. It is a general believe that the world is heading for an environmental catastrophe if human beings continue in the present pattern of destruction to the environment. On the weekend of 14-16 September 2007 about 35 million people across the planet took part in community-based action on climate change. This confirms the awareness that is being created in our society and hence a good percentage of our communities are well informed about the state of the environment. Clean up the World at: (http://www.cleanuptheworld.org/en/NewsandMedia/cuw---unep-global release. html). This action is in agreement with the findings of the German studies given above; people worldwide are now very conscious of the environmental problems around them and are making every effort to see how they can contribute. Figure 2.4 below is an example of these community involvements, people at the grass root willing to contribute their part in keeping our environment safe and healthy. Apart from physical cleanup, many communities focus on limiting the impacts of environmental pollution through activities such as waste reduction and recycling, water and energy conservation and planting of trees. A good lesson that should be learned from such community involvement is that each human being on the face of the earth should be ready to clean up, fix up and conserve his/her environment, and the industries should do even more especially in making sure they have reliable analytical instruments for pollution control.

From the foregoing, it has been demonstrated that the use of industrial effluents and wastewaters for growing of vegetables have serious impacts in contamination of soils by heavy metals and subsequent accumulation of metals by vegetables. A number of research have been carried out on the concentration of heavy metals of romi river and Makera Drain (Ali et al., 2005; Dadi et al., 2011; Etonihu and Lawal, 2011), but none have considered a leafy vegetable, maize, tomatoe, okra or garden egg around river romi.

In Nigeria, the environmental pollution has been mainly due to the oil exploration, spillage of oils, refineries activities for oil production, other industrial activities such as fertilizer industries, mining industries, and cement production. Several studies have been conducted on the impact of industrial wastes and chemical contaminants on soil.Many different soil contaminants can leach

from landfills or other garbage disposal sites, including petroleum products, solvents, pesticides, lead and other heavy metals. The chemicals that may be present in soils near locations used for waste disposal (currently or in the past) will depend on the specific conditions of a particular site, and on what types of materials were disposed of at that site.
(http://cwmi.css.cornell.edu/sourcesandimpacts.pdf) . Ogoke (1980) reported that crude oil pollution significantly reduced weed weight and increased organic matter content, nitrogen and pH of the soil. Odu (1977) reported on the impact of oil spillage on soil microbial population. Tripathi (1990) reported that effluents discharged from a chemical fertilizer factory in India affected the physio-chemical properties of soil, its mineral composition and germination of wheat. The study showed that the concentration of Na was 40 times higher in the effluent than in the nearby well water. The effluent Na showed a positive significant correlation and significantly negative correlation with K and Ca. The soil cation exchange capacity (CEC), porosity and water holding capacity were reduced in effluent-polluted soils. In a related study, Manoylovic (1989) reported that fertilizers were considered as possible pollutants of soil, water and plants, Kudeyarava (1989) also reported that excessive phosphorus fertilization as used in Moscow, Leningrad and other areas of the Russian Republic led to soil degradation and water pollution by the leached soil constituents. Studies on the effects of industrial pollution on soil trace elements indicated that the solubility of salts increased from 0.5 to 2.2% in subtropical semi-desert solon chalk and gray-brown soils and enriched Pb 2.9, Cr 2.9. Cu 1.8, B and V1.7, CO 1.6 and Zn 1.3 fold, whereas Sr decreased 0.7 fold while Ba, Mn, Na as well as Ni were not altered.

Sayo (2005) made an impact assessment of the industrial effluent on water quality of a receiving river Alaro in Ibadan, Nigeria. He assessed the water quality of the river upstream and downstream after the point of effluent discharged. The results of his study revealed that the water qualities of Alaro River was adversely affected and impaired by the discharge of industrial effluent. According to him, the water of the river became gray-black, stagnant with offensive odor after the point of discharge. The studied parameters like BOD had poor values after the point of discharge. Another means of pollution in Nigeria is domestic solid waste management; it is one of the critical environmental problems in urban cities of Nigeria. This could be attributed to the increase in urbanization (population increase), haphazard urban planning, poverty and weak enforcement of environmental laws (Ajao et al, 1981). The results of such pollution is wide spread cases of different disease. Adelegan J.A (2004) reported that there are estimated 4 million cases of guinea worm in West Africa with a large contribution from Nigeria. According to him hospital records have confirmed high incidence of typhoid, cholera, dysentery, infectious hepatitis and guinea worm in urban settlements of Nigeria, and these are highly associated with environmental pollution. A serious threat posed by oil related pollution is the impact on underground waters. When oil spills or when there is an effluent discharge or acid rain, it seeps into the ground and becomes mixed in the underground water system. It has been found that polluted underground water take many years before it can be remedied. Yet this underground water moves into streams and wells which are the only sources of local water supply in the community which results in the rise of water borne diseases. In a recent research report released by a group of scientists from the Faculty of Pharmacy, University of Lagos, it was found that water samples collected from the sea, river, bore holes, lagoons, beach and so on from the Niger Delta region – especially in Delta and River States, indicates that more than 70% of the water in the Niger Delta contains a chemical called Benzo () pyrene, with a high concentration between 0.54 µg/l to 4µg/l, far above the World Health Organization (WHO 2006) recommendation of 0.7ug/1 for drinking water. The report further asserted that if the level of the harmful chemicals could be this high in ordinary water, the sediments which fish and other aquatic creatures feed on are definitely higher in Benzo () pyrene concentration, and the people dependent on these marine creatures for food, automatically take in much more higher level of the cancerous chemical. This report is consistent with the experience that we have had amongst our people in the past thirty years who had lived to see an increase in the occurrence of cancer and other respiratory problems traceable to oil pollution in the area. The diseases include respiratory problems, skin ailments such as rash and dermatitis, eye problems, gastro-intestinal disorders, water borne diseases and nutritional problems associated with poor diet.

CHAPTER THREE

Materials and Methods

3.0 Sample Collection

Maize, tomato, egg-plant, spinach, okra and their controls were collected at the downstream (effluent water), upstream (non-effluent water) of Romi river and the control samples from neighboring irrigated farmlands. Samples of each crop collected were wrapped in sample bags and properly labeled. All the samples from upstream, downstream and control were stored in dried polythene bags and transported for further analysis. The samples were labeled according to their location, washed with deionized distilled water, cut into pieces and dried under a shed for a week to avoid contamination.

The effluent samples were also collected in much cleaned, well labeled sterilized plastic bottles at the point of discharge and taken to the laboratory for analysis.

3.1The physico-chemical Analysis of KRPC Effluents

The physic-chemical parameters were determined according to procedures outlined in the Standard Method for the Examination of Effluents (HACH, DR 2010, and ASTM). The parameters analyzed were electrical conductivity, temperature, total solids, total dissolved solids, turbidity, potassium (K), lead (Pb), zinc (Zn), copper (Cu), iron (Fe) and cadmium (Cd).

3.2 Digestion of the effluent samples (USEPA, 2000).

50mL aliquot of waste water was digested in a beaker covered with a watch glass by adding 1mL of concentrated HNO_3 and 2.5mL on concentrated HCl and heated on a hot plate at 90^oC until the volume was reduced to about 15mL. Then the beaker was removed and cooled. The solution was filtered and finally diluted to 100mL with distilled water. The level of heavy metals in the filtrate was determined by AAS (Model 2380 Perkins Elmer InC. Norwalk, CT, USA).

3.3 Digestion of the plant samples

The dried plant samples were ground and 5g of each sample was taken and poured in a crucible and then placed in a pre-heated muffle furnace at 250^{o}C for 30min and then ashed for 4hrs at 480^{o}C. The samples were removed from the furnace and cooled then 2mL of 5M HNO_3 were added and the solution evaporated to dryness on a sand bath. The samples were then placed in a muffle furnace and heated to 400^{o}C for 15min it was removed from the furnace, cooled in a desiccator.

3.4 Analytical Procedure for Heavy Metal Analysis

Each of the digested crop samples was filtered using Whatman no 42 filter paper and the filtrate was made up to 50mL with deionized water. Determinations of heavy metals in the filtrate were done by atomic absorption spectrophotometer (Model 2380 Perkine Elmer InC. Norwalk, CT, USA). The instrument has an internal calibration mechanism standard solution of respective heavy metals with their corresponding lamps for identification and quantification.

3.5Null Hypothesis

In inferential statistics, the term "null hypothesis" usually refers to a general statement or default position that there is no relationship between two measured phenomena, or no difference among groups. Rejecting or disproving the null hypothesis—and thus concluding that there are grounds for believing that there *is* a relationship between two phenomena (e.g. that a potential treatment has a measurable effect) is a central task in the modern practice of science, and gives a precise criterion for rejecting a hypothesis.

The null hypothesis is generally assumed to be true until evidence indicates otherwise. In statistics, it is often denoted H_0 .

Basic definitions

The *null hypothesis* and the *alternate hypothesis* are terms used in statistical tests, which are formal methods of reaching conclusions or making decisions on the basis of data. The hypotheses are conjectures about a statistical model of the population, which are based on a sample of the population. "The statement being tested in a test of [statistical] significance is called the null hypothesis. The test of significance is designed to assess the strength of the evidence against the null hypothesis. Usually the null hypothesis is a statement of 'no effect' or 'no difference'. It is often symbolized as H_0.

The statement that is hoped or expected to be true instead of the null hypothesis is the alternative hypothesis. Symbols include H_1 and H_a.

Null Hypothesis statement of the problem

H_o Effluent from KRPC has effects on some selected irrigated crops cultivated along Romi River

H_1 Effluent from KRPC has no effects on some selected irrigated crops cultivated along Romi River.

3.6 Statistical Analysis

Results were presented as the mean standard deviation (SD). A one-way analysis of variance was performed using SPSS-20 software. Turkey's test was used for comparing between the crops and the heavy metals at the downstream and upstream. The values were considered significantly different when the p value was lower than 0.05.

CHAPTER FOUR

4.0 Results and Discussion

Table 4.1 shows the composition of the KRPC effluent before being discharged into the water body (Romi River). The results clearly shows high levels of the heavy metals (Pb=0.65 mg/l, Cd=0.52 mg/l instead of 0.03 mg/l and 0.002mg/l) respectively, which gives an insight to a corresponding high content of the heavy metals in water used in irrigation.

The result of the Physico-chemical analysis indicates that the mean value of pH and temperature (i.e 7.54 and 28.20 ^{o}C) were below the FAO/ WHO (2006) standards which between 6.5 – 8.0 for pH and 30 ^{o}C for the temperature. Turbidity, Total solids, Total Dissolve solids and Conductivity values were above the required standards and hence point out the potential danger when discharged into the water body.

Potassium and copper were also below the FAO/WHO, (2006) standard requirement and do not pose any health hazard.

Continuous application of irrigation water from downstream of river Romi could contribute to heavy metal accumulation in soil and crops.

Related studies on wastewater irrigation in two cities in India have similar trends. In Varanasi, Singh *et al.,*(2010) reported equally low levels of Cd (0.002mg/L), Pb (0.009mg/L), Zn(0.13mg/L), Ni(0.06mg/L) and Cr(0.05mg/L) in vegetables. However, when irrigation water is from urban streams, downstream of industrial activities, elevated levels have been reported. For example, studies from a number of streams flowing through Addis Ababa and its neighborhoods have reported elevated values of Cd, Co, Cu, with levels as high as Cd (0.33mg/L), Co(0.219mg/L) and Cu(0.37mg/L) (Weldegebriel *et al*.,2012). Continuous application of irrigation water from downstream of river Romi could contribute to heavy metal accumulation in soil and, hence, crops.

In spite of the low level, care must be taken especially when using more polluted urban stream receiving water from different sources with higher concentration of heavy metals such as waste dumping sites, car washing bays, fuel stations, and from the increasing light industries such as textile, paint, (dyes) and plastics.

Table 4.2 shows the heavy metals (Pb, Cd, Zn, Cu and Fe) analyzed in crops cultivated along Romi River (both the upstream and downstream) and also the percentage pollution of each heavy metal on the crops..

That only Cd, Pb and Zn concentrations in the five (5) selected vegetables/crops (okro, spinach, maize, garden egg and tomato) were elevated in the downstream above the maximum permissible limit provided by FAO/WHO (2006) in table 4.2. The concentrations of Pb,Cd and Zn were very high in the downstream than the maximum permissible levels whereas the concentrations of Cu and Fe were below the maximum permissible limits,

4.1 Downstream heavy metal concentrations in the crops

The trend of concentrations of the metal in downstream (DW) crops is as follows:

Copper (Cu) = maize> spinach>tomato> garden egg> okra.

Cadmium (Cd) =okra> spinach> tomato >maize >garden egg

Lead (Pb) =spinach>garden egg>tomato>maize>okra.

Iron (Fe) =spinach> okra>maize> tomato> garden egg.

Zinc (Zn) = garden egg>tomato >spinach >okra >maize

The percentage pollution of heavy metals in the crops shows that

Copper (Cu) = tomato>garden egg>okra>spinach>maize.

Cadmium (Cd) = spinach>okra>tomato>maize>garden egg.

Lead (Pb)= Maize>tomato>spinach>okra>garden egg.

Iron (Fe) = garden egg>spinach>okra>maize>tomato.

Zinc (Zn) = garden egg>okra>tomato>spinach>maize

Higher concentrations in cadmium and lead in the downstream irrigated crops as compared to crops irrigated in the surrounding of the Romi River (control) and the FAO/WHO (2006) standards may be due to the accumulations of metals from the irrigation water.

Among the crops with the highest concentration of copper and lead in the downstream is spinach, okro is highest in cadmium concentration in the downstream having 3.5 (μg/g) against 0.1(μg/g) accepted value for FAO/WHO (2006). Garden egg and maize has higher values in iron and zinc in the downstream.

Garden egg has the lowest concentrations in copper, cadmium and zinc in the downstream and may be preferred for consumption as compared to the other four crops with higher concentrations of heavy metals.

4.2 Upstream heavy metal concentrations in crops

The trend of concentrations of the metal in upstream (Up) crops is as follows:

Copper (Cu) = maize> tomato>spinach> okra>garden egg

Cadmium (Cd) =maize>garden egg>tomato >okra>spinach

Lead (Pb) = garden egg>spinach> okra>tomato >maize

Iron (Fe) =spinach>maize>okra >tomato> garden egg

Zinc (Zn) =maize > spinach>tomato> garden egg>okra

The low levels of heavy metals in the upstream may be due to the absence of localized industrial activities in the region of the water source.

Table 4.3 shows the results of the concentration of essential metals in the crops.

The concentrations of the essential elements (K, P, Na, Mg and Ca) in the irrigated crops were not significantly different as shown in table 4.3. Their levels were within the acceptable limits except calcium which was far above the limits. These essential metals plays various roles in the body metabolism hence their presence in large quantities in the body cannot be overemphasized. The plants too need these essential metals as part of their nutritional requirement and much need to be done to ensure their presence in large and appreciable quantities.

4.3 The levels of the essential metals in the crops at downstream and upstream are of the trends:

Downstream crops

Na: okra> garden egg> tomato >spinach>maize

Ca: garden egg >okra >tomato> spinach >maize

Mg: garden egg >okra>spinach>maize>tomato

K: spinach >maize> garden egg > okra>tomato

P: maize>okra> tomato>garden egg> spinach

Upstream crops

Na: tomato> okra>spinach> garden egg > maize

Ca: okra> garden egg> spinach> tomato>maize

Mg: garden egg>okra> maize>tomato> spinach

K: tomato> okra> spinach>maize> garden egg

P: garden egg>okra>tomato> spinach>maize

The higher concentrations of Na,Ca,P and K in spinach (downstream and upstream) shows that it can be recommended for consumption as the body needs most of these essential metals for metabolism. Downstream okra has the highest concentration of magnesium while garden egg upstream has higher concentration of magnesium.

Based on the concentrations of these essential elements in these crops, their consumptions in appreciable amount and recommended ratio will help in building and maintaining a good body posture and body tissues for metabolism and proper functioning of the body.

In table 4.4, the results obtained from some surrounding irrigation farmlands around the Romi River shows the various concentrations of heavy metals in the selected crops. The concentrations of Zn in okra (13.0(μg/g) and maize(11.0μg/g) is higher than the maximum permissible limit of 9.4(μg/g) according to FAO/WHO,(2006) while spinach, garden egg and tomato 8.2 μg/g,7.0 μg/g and 6.0 μg/g respectively are below the maximum permissible levels thus the result serves as a control in addition to the upstream crops and the FAO/WHO,(2006). The low concentrations of these heavy metals in the surrounding crops may be due to the absence of industrial activities and other potential sources of environmental pollution through water.

Iron (Fe) concentration in the same crops is only elevated in Okra 19.0 μg/g as against 15.0 μg/g FAO/WHO, 2006 standard. The other crops i.e spinach 13.8 μg/g, garden egg9.3 μg/g, maize 14.2 μg/g and tomato 12.5 μg/g are below the standard.

Lead(Pb), Copper (Cu) and Cadmium (Cd) concentrations in all the crops cultivated at some irrigated farmlands surrounding Romi river have lower or equal levels with the FAO/ WHO,(2006).this attributes may be due to the absence of industrial activities and other potential sources of environmental pollution through water. The major source of the water for the surrounding farmlands is from good natural source with no localized industrial activities.

4.4 Null hypothesis

H_o Effluent from KRPC has effects on some selected irrigated crops cultivated along Romi River

H_1 Effluent from KRPC has no effects on some selected irrigated crops cultivated along Romi River

Null hypothesis of the result shows that the heavy metal content that is Pb and Cd is high in the irrigated crops as compared to the allowable limits and the control, hence the test on the hypothesis is

H_o = is accepted

H_1= is rejected

The alternative hypothesis is accepted in terms of essential metals composition in both the upstream and downstream of the crops irrigated with the effluent water.

H_o = is rejected

H_1= is accepted

4.5 Discussion on the bar chart illustration of heavy and essential metals in the crops.

Figures 4.1 to 4.5 below, shows bar charts of heavy metal concentrations in the five selected crops while figure 4.6 to 5.0 shows the bar charts of the essential metals in the same five selected crops i.e garden egg, spinach, okra, maize and tomato

Fig. 4.1shows the bar chart of heavy metals in okra with the higher concentrations of cadmium and lead as compared to the upstream and maximum permissible limits concentrations,

Fig. 4.2shows the bar chart of the heavy metals in tomato where the cadmium and lead concentrations shows higher bars as compared to the upstream and maximum permissible limits bars,

Fig 4.3 shows the bar chart of the heavy metals in garden egg; also cadmium and lead are higher in concentrations than the maximum permissible limits and the upstream.

Fig 4.4 shows the bar chart of the heavy metals in maize; cadmium and lead are higher in concentrations than the maximum permissible limits and the upstream.

Fig 4.5 shows mean concentration in spinach where cadmium and lead again is higher than the control (upstream) and maximum permissible limits.

Fig 4.6 to 5.0 shows the different bar charts of the essential metal concentrations which are higher than the maximum permissible limits and it means these crops can be used as sources of this essential element, and the rates of consumption should be regulated as higher intake although essential to the body may have side effects.

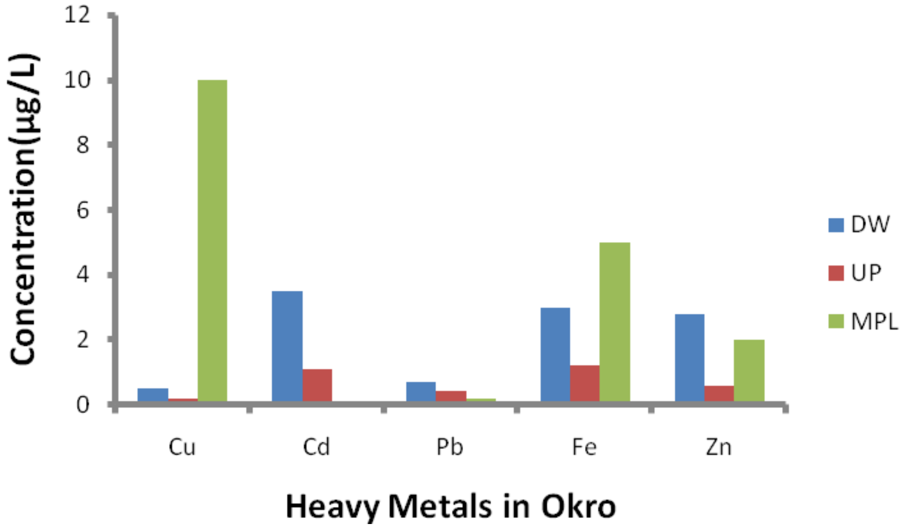

Figure 4.1: Mean concentration of Heavy metals in Okra

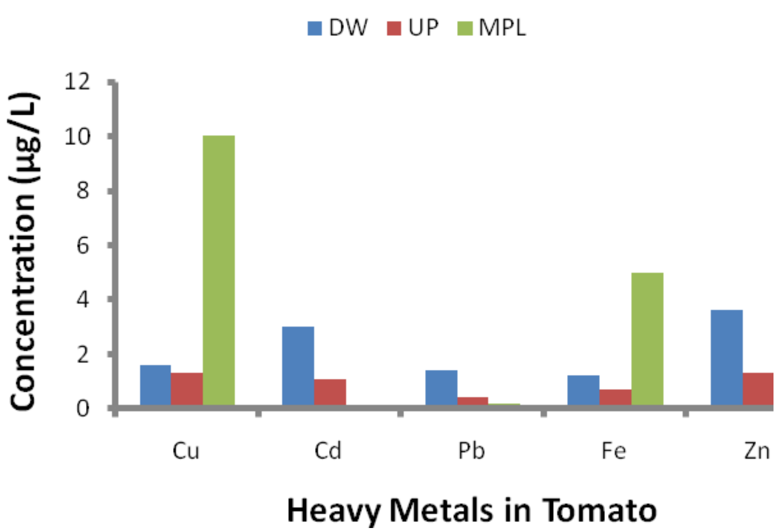

Figure 4.2: Mean concentration of Heavy metals in Tomato

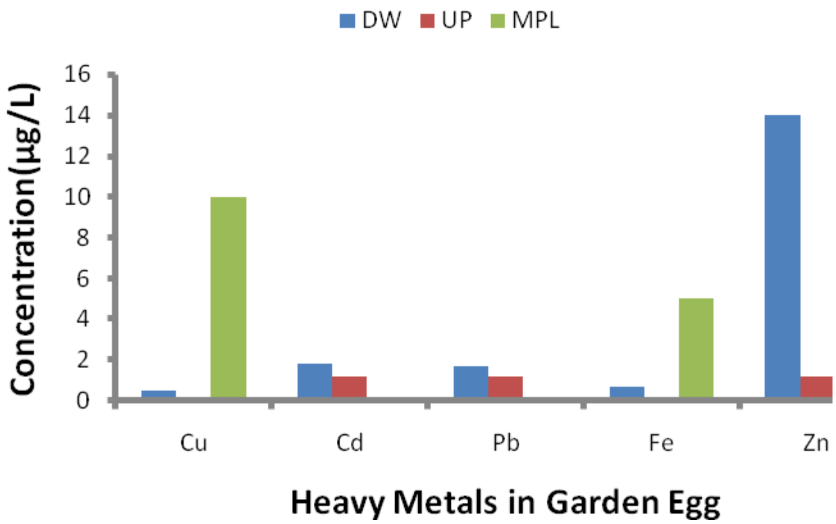

Figure 4.3: Mean concentration of Heavy metals in Garden egg

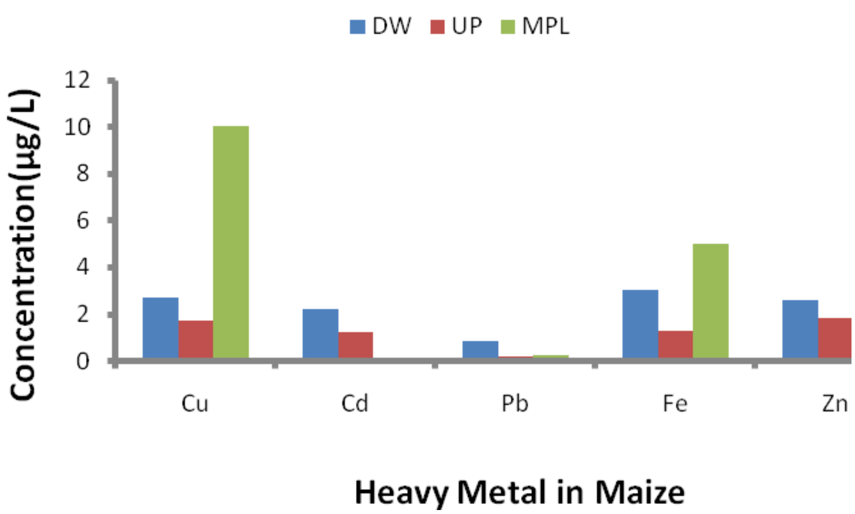

Figure 4.4: Mean concentration of Heavy metals in Maize

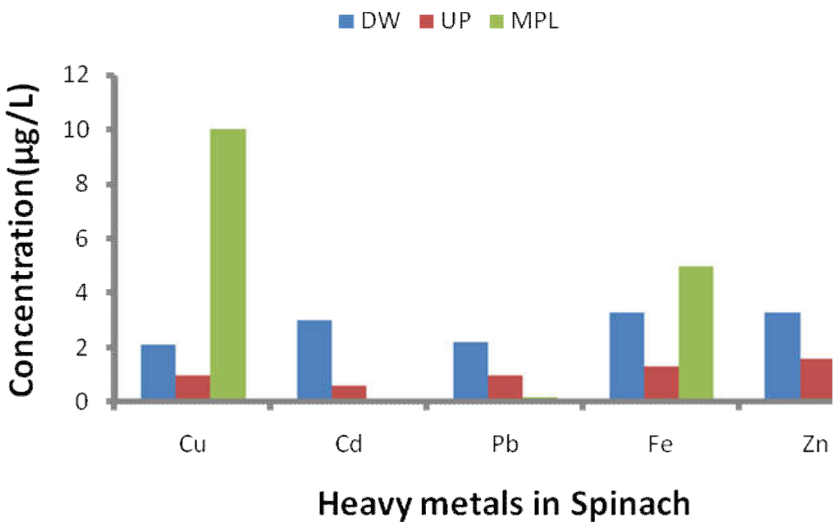

Figure 4.5: Mean concentration of Heavy metals in spinach

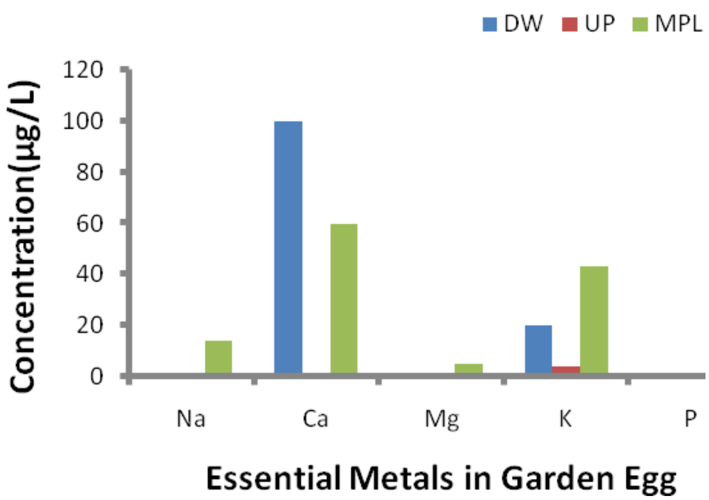

Figure 4.6: Mean concentration of essential metals in Garden egg

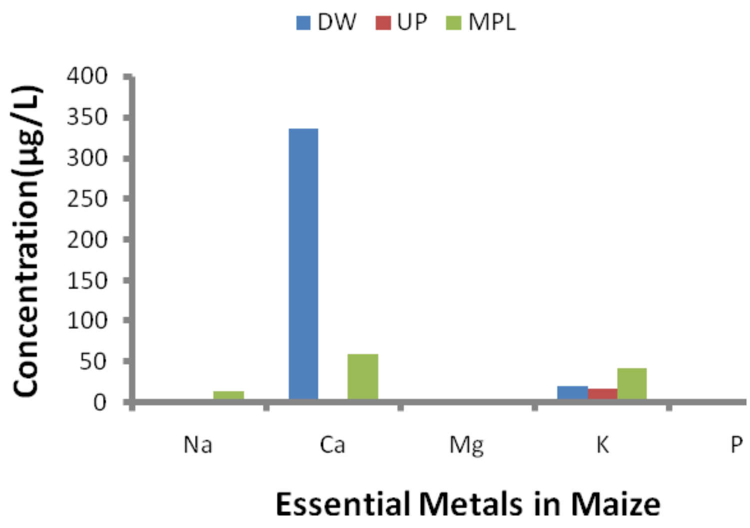

Figure 4.7: Mean concentration of Essential metals in Maize

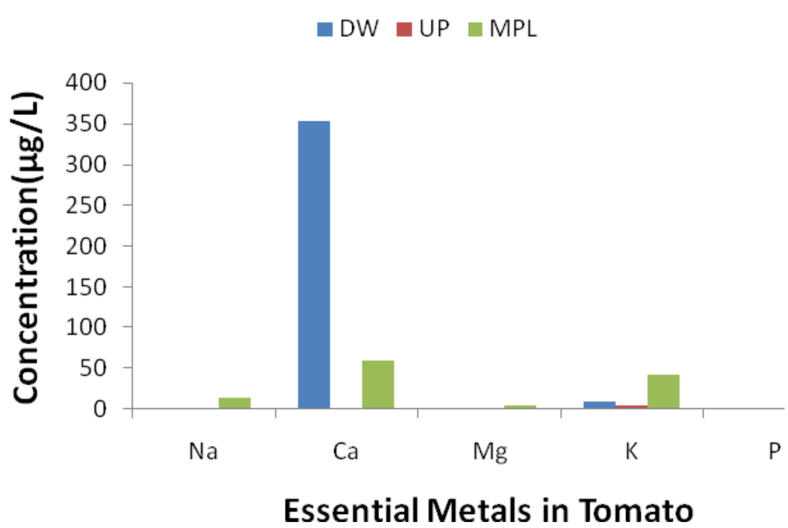

Figure 4.8: Mean concentration of Essential metals in Tomato

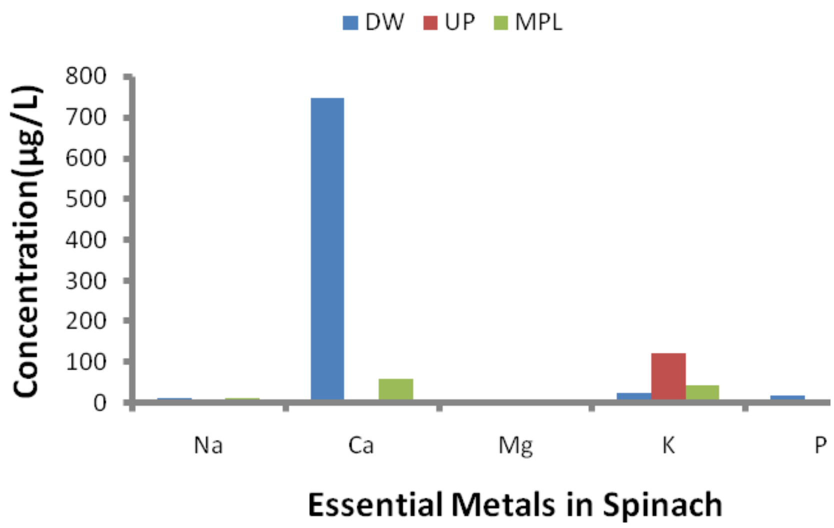

Figure 4.9 Mean concentration of essential metals in Spinach

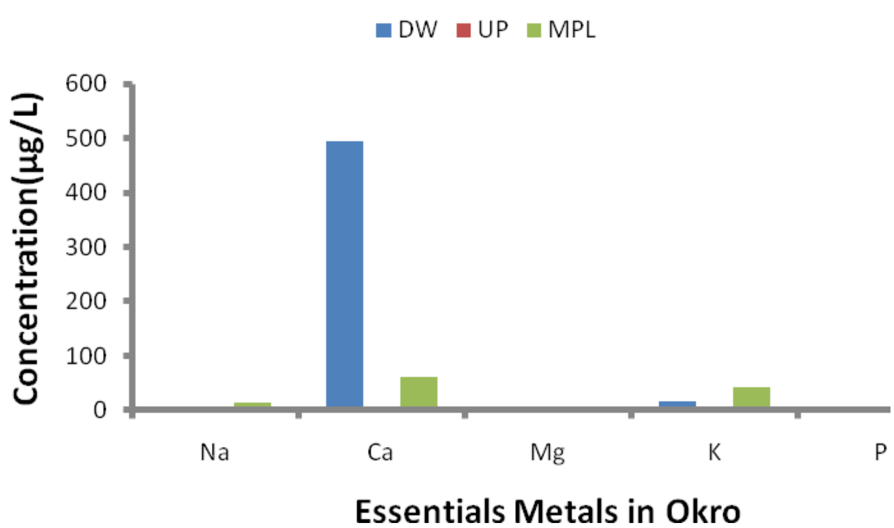

Figure 5.0: Mean concentration of essential metals in Okra

CHAPTER FIVE

5.0 Conclusion

Irrigation farming with effluent can lead to the accumulation of heavy metals in the soil and, consequently, in the crops and vegetables, which when consumed in excessive quantities can pose health risks. This study shows that crops irrigated with diluted effluent (downstream) water had slightly higher but not significantly different levels of heavy metals, compared to control site (upstream) where KRPC effluent water was not used. Heavy metal concentrations in effluent and crops were above the permissible levels. Health risk assessments done shows that normal consumption of crops assessed poses a higher risk from heavy metal toxicities since daily intake rates and the hazard indices obtained were all above the minimal risk levels.

Garden egg, Okra, maize, tomato and spinach showed highest hazard indices but remained well under the respective thresholds.

The possible risk from Pb and Cd should alert policy makers to take a drastic measure in checkmating the inappropriate treatment and strict adherence to regulation guiding effluent treatment before discharge into the environment. Compared with previous studies which focused on microbial hazards from using the same water sources (Amoah *et al.,* 2011), the current study showed that the risk from heavy metals is of higher significance than that from pathogens.

5.1 Recommendation.

It is recommended here that SON, NASREA should do the same standardization of its laws and regulation to include the analytical instruments and methods for various parameters so as to ensure zero discharge in respect to some dangerous pollutants.

Nigeria Water Aid has seen that the ability of local governments and water boards to test for water quality for irrigation has been limited by the availability of suitable equipment and the absence of sector wide standards that all testing bodies must adhere to. In the past, Nigeria and the World Health Organization water quality guidelines have loosely formed the basis for testing water quality parameters due to insufficient water quality testing equipment.

This findings by Water Aid Nigeria has been established in this work that analytical instruments in environmental monitoring is a problem in Nigeria and the standards, laws and regulations are not adequate for proper monitoring. Therefore the following recommendations are made for the consideration of the Nigerian environmental stake holders, that

1. The regulatory bodies in Nigeria need to have a method for developing a comprehensive, universally acceptable guidelines and standards on heavy metal contamination to make sound inter-study comparisons and risk estimations.

2. Safe disposal of industrial effluents should be practiced by operators and relevant legislations for protection of our water bodies should be enforced.

3. There is the need for regular monitoring of the River as it is designated for use for irrigation purposes.

4. The effluent from KRPC should be treated properly to ensure conformity with the stipulated permissible limits as required by the regulatory bodies.

REFERENCE

Allchin, D. 1999. "The Tragedy and Triumph of Minamata." American Biology Teacher **61**(June): 413-19

Ali, N; Oniye, S.J; Balarabe, M.L. and Auta, J. (2004). Concentration of Fe, Cu, Cr, Zn and Pb in Makera Drain, Kaduna, Nigeria. Chemclass J. **2**: 69

Ahalya, N; Ramachanda,T.V; and Kanamadi, R.D.(2003).”Biosorption of heavy metals,” Res,J. Chem. Environ **7**,71-78

Akyuz, M. and Roberts, D.J. (1993). Determination of Linear Alkylbenzene Sulphonates and their Biodegradation Intermediates by Isocratic RP-HPLC

Amoah, P; Keraita, B; Akple, M; Drechsel, P; Abaidoo, R.C. and Konradsen, F. (2011). Low cost options for health risk reduction where crops are irrigated with polluted water inWest Africa. IWMI Research Report Series **141**. Colombo

Adelegan, J.A. (1960-2004).The history of environmental policy and pollution of water sources in Nigeria: The way forward

Anderson, J.M. and Ingram, J.S.J. (1989).Tropical Soil Biology and Fertility. A handbook of methods. CAN International UK. 1-100

Antil, R.S.; Dinesh & Dahiya, S.S. (2007). Utilization of sewer water and its significance in INM. Proceedings of ICAR sponsored Winter School on Integrated Nutrient Management,pp 79-83

Antil, R.S.; Kumar, V., Kethpal, T.S., Narwal, R.P., Sharma, S.K., Mittal, S.B., Singh, J. & Kuhad, M.S. (2004). Extent of land degradation in different agro-climatic zones of Haryana. *Fertilizer News,* **49**: 47-59

Antil, S. and Narwaz, M.F. (2008). Uptake and Distribution of Minerals and heavy metals in commonly grown leafy vegetables species irrigated with sewage water.

Antil R.S. (2012), Impact of sewage and industrial effluents on soil-plant health. INTECH open Access Publisher. ISBN: 978-953-51-0253-3

Arora, B.R; Azad, A.S; Singh, B. and Sekhon, G.S. (1985). Pollution potential of municipal waste waters of Ludhiana, Punjab. *Indian Journal of Ecology,* 12: 1-7

APHA (American Public Health Association) (1988), Standard Methods for the examination of water and waste water (20th Ed.) Washington: APHA

Arora, M; Weuve, J; Schwartz, J. and Wright, R.O. (2009). Association of Environmental Cadmium esposure with periodontal disease in United State, Environmental Health Perspective **117**:738-744

Bay, S., Jones, B.H., Schiff, K and Washburn, L. (2003). Marine Environmental Research, **56**, 205-223

Beeby, A. (1993). Measuring the effect of pollution In: Applying Ecology.Chapman and Hall, London, New York

Begum, A; Ramaiah, M; Khan, H.I. and Veena, K. (2009). Heavy Metal Pollution and Chemical Profile of Couvery River Water. E- Journal of Chemistry, 6(**1**):47-52

Bishop P.L. (2002) and Volesky B. (1990), Pollution prevention: fundamentals and practice; and Biosorption and biosorbents

Bubb, J.M. and Lester, J.N. (1991). The impact of heavy metals on lowland rivers and the implications for man and the environment. Science of the total environment vol.**100:**207-233

Christopher, R. (2005).Historical emission of Black and organic carbon aerosol from energy-related combustion. 1850-2000

Connell, W.D. (2005). Basic concepts of Environmental Chemistry. CRC press, USA

Dadi-Mamud, NJ; Oniye, S; Balarabe, M.L; Auta, J. and Gudugi, I.A.S. (2011). Toxicological Implications of Polluted Water from Makera Drain, Kaduna on Some Cereals and Horticultural Crops, Mediterranean J. Social Sci. Vol. 3(**16**).

EPA http://www.epa.gov/safewater/contaminants/index.html. Accessed 07.08.2008.

Etonihu, A.C. and Lawal, K, (2012). Continental J. Water, Air and Soil Pollution 4 (**1**): 1-7

FAO/WHO (2006) codex Alimentarius commission food additive and contaminants. Joint FAO/WHO food standards programme, Alinorm

Ferner, D.J. (2001). Toxicity, Heavy Metals, eMed.J., 2(**5**):1

Fourest, E. and Roux, J.C. (1999). Heavy metal biosorption by fungal mycelia byproduct-springer

Gebre, G. and Van Rooijen, D. (2009). Urban water pollution and irrigated vegetable farming in Addis Ababa,Ethiopia. In: Shaw, R. [Ed.] Water, sanitation and hygiene. Sustainable development and multisectoral approaches. Proceedings of the 34th WEDC International Conference, United Nations Conference Centre, Addis Ababa, Ethiopia

WHO (1993).Guidelines for drinking water quality; **2nd** Edition; WHO; Geneva

Hawari, H. A. And Mulligan, N. C. (2006), Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass, Biores. Tech **97**, p. 692-700

https://en.wikipedia.org/wiki/HELCOM

Htt://www.epa.gov (Accessed 17. 11.2007)

http://www.atmos.Uiuc.edu/course/atms Accessed 10. 04. 2007

http://www.ifc.org/ehs guidelines. 2007

http://www.kochmembrane.com: Application bulletin on Ultra filtration in heavy metals treatment

Jarup, L. (2003) Hazards of heavy metal contamination, Br. Med. Bull; **68**:167-82

Kharche, V.K; Desai, V.N. & Pharande, A.L. (2011). Effect of sewage irrigation on soil properties, essential nutrients and pollutant element status of soils and plants in a vegetable growing area around Ahmednagar city in Maharashtra. Journal of Indian Society of Soil Science, **59**: 177-184

Kirkhan, M.B. (1983). Study on Accumulation of Heavy metals in Soil receiving Sewage and Effluent Water, Agric. Ecosystem. Environ, **9**: 251

Kudeyarava, A. Y. (1989).Possible Changes in Environment connected with application of Phosphorus containing fertilizers.Inst. Soil Sc. and Photosynthesis, Puschinoi, USSR) Izu. Akad, Nauk, ISSR. Ser. Bol (**4**): 589 – 604

Lenntech (2011). Heavy Metals.http://www.Lenntech.com/processes/heavy/heavy-metals.html.

Lide, D.R. (1992). Warnings about heavy metal toxicity and natural solutions

http://www.naturalhealth365.com/heavy-metal.html/

Manoylovic, S. (1989).Soil pollution by fertilizers and regulation of the soil fertility and fertilizer use or protection of the agroecosystem. Environment and the biosphere. Faculty of Agric Univ. Novisad, Nov. sad. Yuogoslavia (Vodoprireda)(**21**)3 – 4, 351 – 36

Mathias A.D. (2004). Environmental monitoring and characterization; Edited by J.F. Artiolo; I.L pepper and M. Brusseav Elsevier Amsterdam pp 163-187

Mehta, S.K. and Gaur, J.K. (2001). Removal of Heavy metals by biosorption using freshwater algae

Mehta, S.K. and Gaur, J.P. (2008). Critical reviews in Biotechnology 25 (**3**): 113-52.

Mildvan, A.S, (1970). Metals in Enzymes Catalysis, in D, D,. Boyer (ed) The Enzymes Academic Press, London.pp 445-536

Mohammadi, T; Sadrzadeh, M; Ivakpour, J. and Kasiri, N. (2008). Chemical Engineering Journal Vol.**144**, Issue 3, pp 431-441

Mustapha, I.A. and Adeboye, B.O. (2014). African Journal of Environment Science and Technology Vol. 8 (8), pp 460-463

Narwal, R.P; Singh, M. & Gupta, A.P. (1988).Effect of different sources of irrigation on the physico-chemical properties of soil.Indian Journal of Environment and Agriculture, **3**:27-34

Narwal, R.P; Antil, R.S. & Gupta, A.P. (1992). Soil pollution through industrial effluent and its management. Journal of Soil Contamination, **1**: 265-272

Narwal, R.P; Gupta, A.P; Singh, A. & Karwasra, S.P.S. (1992).Composition of some city waste waters and their effect on soil characteristics. Annuals of Biology, **9**:239-245

Nduka, J.K. and Orisakwe, O.E. (2009). Effect of effluents from warri refinery petrochemical company WRPC on water and soil qualities of contiguous host and impacted on communities of Delta State, Nigeria. Open Environ. Pollut. Toxicol. J., **1**: 11-17

Obodo, G.A. (2001), Toxic metals in River Niger and its tributaries, J.IAEM, **28**,147-151

Odu,C .T I. (1977). Oil Pollution and the Environment. Bull. Sci. Assoc.Nigeria.Vol No.Nigerian National Committee of Scope: Environmental PoblemsinNigeria.Pg286

Ogoke, N. J. (1980). Rehabilitating Crude Oil Polluted Land. The Petroleum Industry and Environmental Impact in Nigeria. Federal Environmental Protection Agency Monograph 5

Ozaki H. and Li H. (2002). Rejection of Organic compounds by ultra low pressure reverse osmosis membrane. Water Research Vol. **36**, Issue 1 pp. 123-130

Otis, R.J. (1984). In onsite treatment. 4th National Symposium on Individual and small community sewage systems, New Orleans, Lousiana, December 10-11

Otokunefor, T; & Obiukwu, C. (2005), Impact of refinery effluent on water body. - 61 - .Applied Ecology

Raikwar, M.K; Kumar P; Singh, M. and Singh, A. (2008). Toxic Effect of Heavy Metals in Livestock Health. Veterinary World, I (**1**): 28-30

Rani, J.M; Hemambika, B; Hemapriya, J. and Rajeshkannan, V. (2010). Comparative assessment of heavy metal removal by immobilized and dead bacteria cells; a biosorption approach. Global Journal Environment Research 4 (**1**) 23-30

Scott, J.A. and palmer, S.J, (1990). Sites of Cadmium uptake in bacteria used for biosorption. Vol. **33**, issue 2, pp 221-225

Seckher, C.K. (2003). High exposure to arsenic from drinking water at several locations in eastern Crotia. Science of the total environment Vol.339, issue 1-3 pp 277-282

Sharma, K; Kumar, R; Agarwal, M. and Marshall, F.M. (2004). Effects of Waste Water Irrigation on Heavy Metal Accumulation in Soil and Plants.Paper Presentation at a National Seminar, Bangalore University, Bangalore Abst. No.**7**, p.8

Singh, A; Sharma, K.R; Angrawa, M. and Marshall F.M. (2010). Risk assessment of heavy metal toxicity through contaminated vegetables from wastewater irrigated areas in Varanasi, India. Trop. Eco. Iss 51. 2:375-387

Solomon, S; Peltier, W.R. and Penner J.E. (2007) Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

Suleiman, R.A. (1995). MedicsinaTrudai PromyShlennaial Ekologiia, 12:31-36

The Helsinki Convention. (http://www.helcom.F/convention/en-GB/convention/ Accessed 21. 12.2007

Tripathi, B. D; Durvedi, R. K. & Tripathi, A. (1990). Influence of Industrial Wastes on Physiochemical Properties of Soil and Germination and Mineral Composition of Wheat. India Water, Air, Soil Pollution. **49** (1-2)

Turk, J. (2002), Chem.**26** :669-679

Vivan, E.L; Adamu, I.C; Ayuba; K.N. (2011). Effects of effluent discharge of Kaduna Refinery on the Water Quality of River Romi. J. Res. Environ. Sci. Toxicol. 1(**3**): 41-46

Volesky, B. (1993), Cadmium biosorption by Saccharomyces cerevisiae. Biotechnol Bioeng 41, 826–829

Weldegebriel, Y. Chandravanshi, B.S. and Wondimu, T. (2012). Concentration levels of metals in vegetables grown in soils irrigated with river water in Addis Ababa, Ethiopia, Ecotex

WHO (1993). Guidelines for Drinking-Water Quality - Second Edition - Volume 1 – Recommendations

WHO (1998). Environmental health criteria 202,.selected non-heterocyclic polycyclic aromatic hydrocarbon

World Bank (2007). World Development Report 2008: Agriculture for Development. Washington,DC. WorldBank

WHO (2004).www.who.int/water-sanitation health, publications, facts 2004, en, index.html.

WHO (2006), Guideline for Drinking Water Quality Vol.**2**. Recommendations World

Health Organisation, Geneva, pp: 130

CIA (2000).World Facts Books on Nigeria- Central Intelligence Agency

Yakasai et al ( ), Journal of Applied Sciences Volume 7 No 22, pp 3572-3575. Asian Network for Scientific information

Yu, H; Kaufman; Y.J; Feingold, and Remer, L.A. (2001). A review of measurement- based assessments of the aerosol direct effect pg 613-666

Zalawadia, A. and Shah, S. (1997). Influence of diluted spent wash of sugar industries on yield and nutrient uptake by sugarcane and changes in soil properties. Journal of Indian society of Soil Science, **45**: 767-769

Table 4.1: Physicochemical parameters obtained from KRPC effluents as compared with WHO/FAO standards

Parameters	Mean ± S.D	WHO/FAO
pH	7.54±0.60	6.5-8.0
Turbidity(NTU)	18.83±1.30*	5/5
Temperature (^{o}C)	28.20±1.40*	30/30
Total Solids (mg/L)	351.00±52.00*	150/150
Total Dissolve Solids (mg/L)	210.00±5.00*	200/200
Conductivity(µs/cm)	278.00±9.00*	240/250
Potassium(mg/L)	27.37±1.10*	45/45
Cadmium(mg/L)	0.52±0.01*	0.002
Lead(mg/L)	0.65±0.2 0*	0.03/0.03
Copper(mg/L)	0.05±0.02*	10/10
Iron (mg/L)	0.49±0.05*	2.0/2.0
Zinc (mg/L)	1.00±0.05*	2.0/2.0

Values are Mean ± S.D. values with asterix are significantly different from the standards at $p \leq 0.05$

Table 4.1b: Physico-Chemical parameters of KRPC Effluents

Parameter					Mean±S.D	WHO/FAO
pH	7.51	8.40	7.36	6.86	7.54±0.6	6.5-8.0
Turbidity(NTU)	12.60	3.40	15.60	37.00	18.83±1.3	5/5
Temperature (^{o}C)	27.00	29.90	28.40	26.30	28.20±1.4	30/30
Total Solids (mg/L)	194.00	300.00	424.00	329.00	351±52	150/150
Total Dissolve Solids (mg/L)	137.00	240.00	252.00	140.00	210±5.0	200/200
Conductivity(µs/cm)	102.00	163.00	289.00	283.00	278±9.0	240/250
Potassium(mg/L)	25.61	27.01	26.20	28.91	27.37±1.1	45/45
Cadmium(mg/L)	0.52	0.46	0.47	0.50	0.52±0.01	0.002
Lead(mg/L)	0.61	0.64	0.63	0.57	0.65±0.2	0.03/0.03
Copper(mg/L)	0.04	0.02	0.05	0.07	0.046±0.02	10/10
Iron (mg/L)	0.42	0.60	0.51	O,45	0.49±0.05	2.0/2.0
Zinc (mg/L)	0.92	1.10	0.85	1.02	1.00±0.05	2.0/2.0

Key: NA – Not applicable.

Table 4.2a: Concentration (μ/g) of heavy metals in Crops cultivated along Romi River

Crops	Cu			Cd			Pb		
	DW	UP	%P	DW	UP	%P	DW	UP	%P
G/Egg	0.5±0.10	0.19±0.05	62	1.8±0.3	1.2±06	33	1.7±0.4	1.21±0.4	28
Okra	0.5±0.10	0.23±0.02	54	3.5±0.4	1.1±0.4	69	0.7±0.1	0.44±0.3	37
Maize	2.7±0.20	1.7±0.10	39	2.2±0.4	1.2±0.3	45	0.8±0.3	0.15±0.4	81
Tomato	1.6±0.15	1.3±0.50	79	3.0±0.3	1.1±0.1	63	1.4±0.4	0.42±0.3	70
Spinach	2.1±0.20	1.0±0.4	52	3.0±0.5	0.6±0.1	80	2.2±0.3	1.01±0.2	54
MPL	10.0			0.1			0.2		

Values are given as Mean ± S.D. values are significantly different from the standards at $p \leq 0.05$

DW= Downstream, UP= Upstream, %P =Percentage pollution and MPL=Maximum Permissible Limit by WHO/FAO.2006

Table 4.2b: Concentration (μ/g) of heavy metals in Crops cultivated along Romi River

	Fe			Zn		
Crops	DW	UP	%P	DW	UP	%P
G/egg	0.7±0.1	0.19±0.03	72	14.0±0.30	1.2±0.60	91
Okra	3.0±0.05	1.23±0.02	59	2.8±0.20	0.6±0.40	79
Maize	3.0±0.20	1.27±0.30	57	2.6±0.20	1.8±0.10	31
Tomato	1.2±0.15	0.7±0.03	42	3.6±0.30	1.3±0.20	63
Spinach	3.3±0.2	1.31±0.40	60	3.30±0.50	1.6±0.50	52
MPL	5.00			2.0		

Values are given as Mean ± S.D. values are significantly different from the standards at $p \leq 0.05$

DW= Downstream, UP= Upstream, %P =Percentage pollution and MPL=Maximum Permissible Limit by WHO/FAO.2006

Table 4.3: Essential Metals of crops cultivated along Romi River downstream and upstream

Crops	Essential Metal concentration (µg/g)									
	Na		Ca		Mg		K		P	
	DW	UP	DW	UP	DW	UP	DW	UP	DW	UP
Garden egg	0.5±0.2	0.002±0.5	100±0.7	0.12±0.4	1±0.5	0.55±0.2	20±0.9	4±0.5	1.38±0.4	0.51±0.1
Okra	1.6±0.1	0.233±0.1	495±0.3	0.59±0.3	3±0.4	0.35±0.2	15±0.8	3±0.4	1.3±0.5	0.48±0.2
Maize	1.5±0.4	1.242±0.3	335±0.2	0.41±0.2	2±0.3	0.32±0.1	20±0.7	18±0.6	1.24±0.6	0.46±0.3
Tomato	0.4±0.2	0.263±0.2	353±0.1	0.42±0.2	1±0.2	0.32±0.1	10±0.6	5±0.4	1.22±0.5	0.47±0.1
Spinach	10.3±0.3	2.283±0.4	747±0.4	0.89±0.1	2±0.1	0.21±0.1	25±0.5	123±0.5	17.5±0.7	0.85±0.2
MPL	14.00		60.00		5.00		43.00		25.00	

Values are given as Mean ± S.D. values are significantly different from the standards at p≤0.05

DW= Downstream, UP= Upstream and M PL=Maximum Permissible Limit.

Table 4.4: Heavy Metals in Crops cultivated at some irrigated farmland surroundings to Romi River (control)

CROP	Zn(µg/g)	Fe(µg/g)	Pb(µg/g)	Cu(µg/g)	Cd(µg/g)
SPINACH	0.0132 ±0.3	4.384±0.3	0.2295±0.2	0.0045±0.3	0.0005 ±0.1
OKRA	0.0313±0.2	1.9095±0.4	0.0399 ±0.3	0.0008±0.2	-0.005 ±0.2
EGG. PLANT	0.0001±0.1	3.0937±0.2	-0.0094±0.1	0.0039±0.2	0.0002±0.1
MAIZE	0.0011±0.3	1.4294±0.3	-0.0172 ±0.1	0.0006±0.1	0.000 ±0.0
TOMATO	0.02±0.2	3.2025±0.2	0.0136±0.1	0.0083±0.1	0.0004±0.1
WHO/FAO	9.4	15	0.3	73.3	0.2

Values are given as Mean ± S.D. values are significantly different from the standards at $p \leq 0.05$