AN ASSESSMENT OF HEAVY METALS CONTENT OF WATER, SOIL AND PLANTS IN SOME SELECTED COASTAL COMMUNITIES NEAR THE JUBILEE OIL FIELD IN THE WESTERN REGION OF GHANA.

BY

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DECLARATION

I hereby declare that this thesis does not incorporate, without acknowledgement, any material previously submitted for a degree in any University. To the best of my knowledge and belief, this thesis contains no material published or written by another person except where due reference is made in this thesis.

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ABSTRACT

This study investigated the concentration of seven heavy metals (As, Cd, Cu, Pb, Se and Zn) in water, soil and plant leaves in some selected coastal communities in the Western Region of Ghana near the jubilee oil field using acid digestion and Atomic Absorption Spectrophotometer methods. Some physicochemical properties of water and soils were also determined to evaluate the quality of drinking water and soils. The ranges of metal concentration in water analysed in the wet season were; As (1.23-7.84 µg/L), Cu (4.10- 24.09 µg/L), Pb (4.08-57.98 µg/L), Se (BDL-0.38 µg/L), Zn (2.86-17.75 µg/L) and Hg (0.023-0.068 µg/L) whereas the ranges of metal concentration recorded in the dry season were; As (2.30-5.78 µg/L), Pb (25.47-70.73 µg/L), Se (0.081-0.158 µg/L), Zn (0.79-22.80 µg/L), and Hg (0.004-0.047 µg/L). The results of the analysis carried out showed that the levels of heavy metals were generally higher in the surface soils (0-15 cm) than the subsoil (15-30 cm). The mean concentrations of metals in the surface soil (0-15 cm) were; As (2.06 mg/kg), Cu (6.55 mg/kg), Pb (21.59 mg/kg), Zn (39.49 mg/kg), Se (0.178 mg/kg) and Hg (0.069 mg/kg) whereas the subsoil (15-30 cm) recorded mean concentration of As (1.91 mg/kg), Cu (6.29 mg/kg), Pb (21.54 mg/kg), Zn (38.90 mg/kg), Se (0.169 mg/kg) and Hg (0.003 mg/kg). Similarly, the ranges of metal concentration in plant leaves were; As (1.65-6.31 mg/kg), Cd (16.04-19.06 mg/kg), Cu (0.69-4.03 mg/kg), Pb (85.56-100.91 mg/kg), Se (1.42-1.57 mg/kg), and Zn (9.08-10.89 mg/kg). The results of physicochemical analysis of water samples recorded in the wet season were; pH (6.83 to 7.52), EC (291.15-780.64 µS/cm), TDS (195.07-523.02 mg/L), DO (2.98-4.39 mg/L), BOD (3.33 to 6.84 mg/L), salinity (0.01 to 0.30 ppt), and temperature (27.06-30.94 °C) whereas the dry season were; pH (6.84-6.95), EC (516.83 to 660.67 µS/cm), TDS (307.07-442.65 mg/L), DO (1.71-3.04 mg/L), BOD (4.25-13.38 mg/L), salinity (0.22-0.28 ppt), and temperature (28.46-

30.44°C). The physicochemical analysis of soil samples in the surface soils (0-15 cm) were; pH (6.33-7.66) and EC (137.70-559.20 µS/cm) whereas results obtained in the subsoil (15-30 cm) were; pH (6.17-7.64) and EC (99.50-592.00 µS/cm). The results showed that the concentration of heavy metals in water were below the WHO standard except Pb which exceeded the permissible limit. The concentrations of heavy metals in soil samples were also below the WHO/FAO standards. The concentration of As, Cd and Pb in plant leaves exceeded the WHO/FAO standard except Cu, Se and Zn which were below the limits. The physiochemical analysis of water samples were within the WHO standards except BOD. The enrichment factor of metals ranged from deficient to minimal enrichment except As and Se which ranged from significant and extremely high enrichment respectively. The geoaccumulation indices of all metals examined were practically unpolluted except Se and Pb which recorded moderate pollution. The values for contamination factor of heavy metals recorded low contamination except As, Se and Pb which recorded considerable to moderate contamination.

DEDICATION

I dedicate this thesis to Almighty God, my dear parents, siblings and the entire family for their love, inspiration and unflinching support throughout my education.

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LIST OF ABBREVIATIONS

AAA	Atomic Absorption Spectrophotometer
Al	Aluminium
As	Arsenic
ATSDR	Agency for Toxic Substance and Disease Registry
BOD	Biochemical oxygen demand
CCME	Canadian Council of Ministers of the Environment
Cd	Cadmium
CF	Contamination factor
Cu	Copper
DO	Dissolved oxygen
EC	Electrical conductivity
EF	Enrichment factor
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
Fe	Iron
GNPC	Ghana National Petroleum Corporation
GPS	Global Positioning System
HCL	Hollow Cathode Lamp

IARC	International Agency for Research on Cancer
K	Potassium
PLI	Pollution load index
ppm	parts per million
ppt	parts per thousand
Se	Selenium
Sn	Tin
TDS	Total dissolved solids
UNEP	United Nations Environment Programme
WHO	World Health Organization

CHAPTER ONE

INTRODUCTION

The environment is progressively being altered in recent times through the activities of man and his technological advancement (Essoka *et al.*, 2006). Through urbanization, industrialization and technology, man has developed the capacity to alter the natural interaction to an extent that the environment has been threatened to a devastating point (Greaney, 2005). The role of heavy metals in the environmental matrices is increasingly becoming an issue of global concern to farmers, policy makers and researchers.

Heavy metals have become a widespread problem around the world in recent years (Castro-González and Méndez-Armenta, 2008). However, heavy metals are found ubiquitously in both polluted and unpolluted environments. The level of heavy metals in the environment varies between different regions resulting in spatial variations of its concentration (Morais *et al.*, 2012). Although heavy metals occur naturally in the earth's crust, they tend to be concentrated in agricultural soils because of the application of commercial fertilizers, manures and sewage sludge containing heavy metals (Zeng *et al.*, 2008). According to Essoka *et al.* (2006) oil industries constitute a major source of pollutants to the environment especially through liquid discharges and oil spills as well as gas flaring resulting in atmospheric deposition of metals. Osam *et al.* (2013) added that activities such as burning of fossil fuel, smelting and discharge of industrial, agricultural and domestic waste as well as deliberate application of pesticides are some of the pathways by which heavy metals are released into the environment. Anthropogenic activities such as petroleum prospecting and mining as well as oil spillage are also major sources of heavy metals in the environment (Osuji & Onojake, 2004).

Contamination of the soil ecosystem with heavy metals is thus a critical environmental problem (Babatunde *et al.,* 2014). The presences of heavy metals in the soil subsequently enter the food web through plants which eventually constitutes health risk to plants, humans and animals when they bioaccumulate in the tissues of plants and animals. Boran and Altynok (2010) described heavy metals as one of the most harmful pollutants because of its toxicity.

High concentration of heavy metals impair the quality of the environment which affects human and animal life (Ideriah *et al.*, 2010). The increasing occurrence of heavy metals in soil has increased environmental quality concerns, because these metals can cause changes in the structure and functioning of the soil ecosystem (Kirpichtchikova *et al.*, 2006). Most of the human activities have negative impact on several biological processes and there is no doubt that these activities will affect the functioning of the highly productive coastal ecosystem such as the marine environment of the jubilee oil field in the Western Region of Ghana.

Ghana's oil and gas exploration dates back as far as 1896, but the country discovered crude oil in commercial quantities in the year 2007 (GNPC, 2009). Ghana officially became an oil producing country in the last quarter of 2010 with an initial estimated reserve of 800 million to 1.8 billion barrels and expected peak production of 120,000 barrels per day (Acquah-Sam, 2014; Ayensu, 2013). The Ghana National Petroleum Corporation (GNPC) holds a 13% stake in the oil and the remaining percentage by other major companies as Jubilee partners and is expected to earn about 1 billion USD annually in the short to medium term from the jubilee oil field alone (Rupp, 2013). Edame and Efefiom (2013) emphasised that the discovery of oil in any economy both developed and developing has always been marked with joy signalling the start of economic growth and development as a result of the anticipated flow of revenue. In fact, Darkwah (2010) explained that because of the huge monetary resources that can be accumulated from the industry, the discovery of oil and gas in any location, particularly a developing country like Ghana is always greeted with great optimism.

However, oil and gas exploration and production involve several activities that have detrimental impact, either directly or indirectly on the environment. The impacts can therefore adversely affect the socio-economic, environmental and health of surrounding communities (E&P Foum/UNEP, 1997). According to Baptiste and Nordenstam (2009), oil and gas exploration and production activities are associated with many environmental and socio economic impacts. Achi (2003) also argued that, petroleum exploration and production has resulted in detrimental environmental impacts in the Niger Delta region through the continuous environmental and physical disaster which have occurred over the years due to limited inspection and absence of environmental monitoring.

Prior to exploitation and exploration of crude/petroleum resources at the jubilee oil field, the Ghana Environmental and Protection Agency (GEPA) and Tullow Ghana conducted an off shore environmental impact assessment. However, up to the current time there has been no investigation or onshore environmental impact assessment conducted to predict the impact of off-shore exploitation and exploration on communities at the latter. Hence, large gaps exist in the availability of vital information as far as onshore assessment of heavy metals content is concerned.

1.1 Problem Statement

The rapid growth in industrialization has introduced chemical pollutants such as heavy metals into the environment which leads to the pollution of natural resources such as water, soils, plants as well as the coastal ecosystem. Due to the exploration and production of oil and gas, the environment is being modified and this can affect living organisms and the environment at large (E&P Forum/UNEP, 1997; Asia *et al*., 2007). In exploration and production of oil, various chemical pollutants and materials are released into the environment which includes drill cuttings, drilling mud, produced water, as well as flaring of natural gas into the atmosphere. Atmospheric deposition of metals is one major concern as it causes human health risk because of the large quantities involved, the widespread dispersion and its exposure (Järup, 2003).

Heavy metals such as arsenic, cadmium, copper, lead, mercury, nickel and zinc which are discharged into the environment have been listed by the European Commission as metals of great concern to humans, plants and animals because of their hazardous effect (Förstner & Wittmann, 2012; Fytili & Zabaniotou, 2008; Kloke *et al.*, 1984; Wu *et al.*, 2015). Heavy metals are one of the serious chemical pollutants due to their toxicity, persistence and bioaccumulation (Tam & Wong, 2000). According to Loska and Wiechuła (2003), metals are of high ecological importance because they are not removed by self-purification, but rather end up in reservoirs and eventually enter the food chain. Metals such as aluminium, calcium, cadmium, chromium, copper, iron, lead, magnesium, manganese, zinc etc. may occur in drinking water due to geological reasons or anthropogenic activities such as uncontrolled discharge of waste waters from different industries (Sharma & Tyagi, 2013). Heavy metals disrupt metabolic processes in living organisms which causes various diseases and disorders even at relatively lower concentrations (Pehlivan *et al.*, 2009).

1.2 Justification of the study

Humans rely heavily on the natural environment to provide its ecosystem goods and services. In man's interaction with the environment to better their lives, various chemical pollutants are introduced into it. Heavy metals constitute considerable health threat to humans, animals and plants due to their damaging effects on the various tissues and its associated carcinogenicity. The build-up of heavy metals affects food safety issues and potential health risk.

WHO/IPCS (2000) defined human exposure as the amount of a substance in contact, over time and space, with the outer boundary of the body. The assessment of human exposure to contaminants of hazardous chemicals in the environment can be measured by two major methods, each based on different data profiles. One of the approaches involves environmental monitoring, that is, determining the chemical concentration scenario whiles the second methodology is based on the estimation of exposure through the use of biomarkers (Peterson, 2007). This research seeks to use chemical concentration determination scenario to gather data and information on heavy metals content of water, soils and plants. The quality of the coastal environment is important for the sustenance of both natural and human activities (Karydis & Coccossis, 1990). The essence of the study is to assess the heavy metal content of the selected coastal communities which will add to the information base of the Ghana National Petroleum Corporation (GNPC), Environmental Protection Agency (EPA) and all other major stakeholders in the emerging oil communities. The study therefore seeks to investigate the heavy metals content of water, soils and plants of some selected coastal communities near the Jubilee oil field in the Western Region of Ghana in order to establish baseline data and information for future referencing and comparative studies.

1.3 Objectives of the study

The aim of the study was to undertake an assessment of environmental pollutants in some selected coastal communities near the Jubilee oil field. In other to achieve the aim of the study, the following specific objectives were pursued.

1. To determine the physicochemical parameters of soils and water in selected coastal communities.
2. To determine the level of heavy metals (lead, arsenic, mercury, cadmium, zinc, copper, and selenium) in water, soil and plant samples in selected coastal communities.
3. To assess the extent and sources of heavy metal pollution in soils.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy Metals

There are several meanings that have been assigned to heavy metals. The term “heavy metal” has received several definitions from biologists to toxicologists thereby presenting no rational scientific basis (Duffus, 2002). Duffus (2002) explained that, the term heavy metal is an ill-defined term that means many different things to many different people. Hodson (2004) added that heavy metal is a loose term which is used to show environmentally bad metals.

In Plant Science, Appenroth (2010) defined heavy metals as transition elements except La and Ac, rare earth elements which are subdivided into the series of lanthanides and actinides and heterogeneous group of p-elements, amphoterous oxides and metalloids. Obodai *et al.* (2011) also defined metals as a group of elements with an atomic density greater than 4 g/cm^3 or five times greater than the density of water. Tangahu *et al.* (2011) also added that metals are conventionally defined as elements with metallic characteristics and atomic number greater than 20. Heavy metals are among the most frequently identified persistent pollutants in the environment which can be categorized either essential or non-essential.

2.2 Essential and Non- Essential Trace Elements

Metals are extensively distributed in nature and in biological systems of which they can be categorized as either toxicological or biochemically functional (Duce & Bush, 2010). Heavy metals consist of various groups of elements of which some are essential cofactors for various enzymes whiles others are non-essential (Theron *et al.*, 2011). Essential trace elements are elements which are needed and vital to living organisms for optimal health. The essential heavy metals exert biochemical and physiochemical function in plants and animals. They are important constituents of several key enzymes which play important roles in several oxidation and reduction reactions.

Singh *et al.* (2011) indicated that trace elements such as Cu, Mo and Zn are essential elements required by humans, animals and plants in minute amounts for metabolic processes. They act as catalyst or structural components of large molecules in the body and have specific functions making them indispensable for life and optimum health. Metals such as chromium, copper, iron, manganese, selenium and zinc have been found to be essential by medical researchers and have been proven to prevent and reverse a wide number of diseases and medical conditions. Diseases such as cardiovascular, gastrointestinal, genetic, kidney, etc. have been known to be treated with essential trace elements. Athough essesstial elements are required by humans and other organisms, they can be regarded as potential pollutants when they bioaccumulate and reach toxic levels (Cai *et al.*, 2012). However, Gaur and Adholeya (2004) and Vieira *et al.* (2011) described heavy metals such as As, Cd, Hg, and Pb as elements with no useful effects in humans which can cause toxicity even at very low concentrations and are regarded as non-essential trace elements.

2.3 Properties of Heavy Metals

Soils are the major sink for heavy metals released into the environment and their concentrations in soils persists for a long period of time, even after their introduction (Kirpichtchikova *et al.*, 2006). Some of the properties of heavy metals include the ability to conduct heat, electrical resistance which is directly proportional to temperature, malleable, ductile and luster (Housecroft & Sharpe, 2008). The background concentration of metals varies between regions and its distribution is governed by the properties of the metals themselves as well as the influences posed by environmental factors (Khlifi & Hamza-Chaffai, 2010). Pilon-Smits (2005) explained that heavy metals are highly reactive, toxic even at low concentration and they have the ability to persist in the environment for several years thus posing risk to human and ecosystem health worldwide. Metals cannot be degraded or destroyed, but can be transported by air, which then enter water and human food supply (Kampa & Castanas, 2008). Gall and Rajakaruna (2013) defined bioaccumulation of metals as the process whereby trace metals are transferred from the soil to plant and animal food chain, eventually accumulating in the tissues of plants and animals. The transfer of metal into the food chain is dependent on the mobility of the metal species and its bioavailability in the soil. The bioavailability of metals is influenced by physical factors such as temperature, phase association, adsorption and sequestration. Rajakaruna and Boyd (2008) claimed that bioavailablity of metals depends on soil organic matter and pH beacause they are the most important factors affecting the availablity of metals in soils. Metals such as Cd, Cr, Cu, Ni, Pb and Zn are more bioavailable under acidic soil pH conditions.

2.4 Sources of Heavy Metals in the Environment

Heavy metals occur as natural constituents of the earth crust (Lasat, 2000). The presence of heavy metals in the environment is widespread as a result of both natural and anthropogenic activities and living organism are exposed to them through various pathways (Wilson & Pyatt, 2007). Although heavy metals occur naturally, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operation, industrial, domestic and agricultural use of metals (He *et al.*, 2005).

Metals are released into soils and the hydrologic cycle during erosion of ore bearing rocks, physical and chemical weathering of igneous, sedimentary and metamorphic rocks and volcanic activities. However, the level of heavy metals has been exacerbated in recent times as a result of anthropogenic activities. D'Amore *et al.* (2005) attributed the gradual acceleration and distribution of the naturally low occurring geochemical cycle of metals to human activities and have accumulated above their defined background values. The accelerated source of metals in the environment arising from human activities unlike the natural occurrence tends to be more mobile and bioavailable (Wuana & Okieimen, 2011).

Greaney (2005) claimed that anthropogenic emission of metals into the atmosphere such as Pb, Hg, Zn, Cd and Cu are 1:3 orders of magnitude higher than natural fluxes and are expected to be accumulated in natural reservoirs. Neilson and Rajakaruna (2012) emphasized that heavy metals such as cadmium, copper, chromium, lead, mercury, nickel and zinc and metalloids such as arsenic and selenium do not only pollute the immediate surroundings of the environment within which they were produced but, has the tendency to pollute areas far from the source of pollution through air and water dispersion. Khan *et al.* (2008) revealed that there are a number of anthropogenic activities that release heavy metals into the environment. They occur as a result of rapidly expanding industrial areas, mine tailing, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, vehicular exhaust, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition.

2.5 Effects of Heavy Metals on the Environment

Human exposure to heavy metal pollution has risen dramatically as a result of an exponential increase in their use in several industrial, agricultural, domestic and technological applications, which has led to the wide distribution in the environment thus raising concerns over their potential effect on human health (Tchounwou *et al.*, 2012). They added that the toxicity of heavy metals depends on several factors including the dose, route of exposure and chemical species as well as the age, gender, genetics, and the nutritional status of exposed individuals. Metals are known to induce several damages to human organs, even at lower level of exposure thus classified by the US Environmental Protection Agency and the International Agency for Research on Cancer (IARC) as human carcinogen. The availability of heavy metals at higher concentrations in soils has an influence on plant growth and development. It has the capacity to interfere with physiological and biochemical functions of plants which sometimes leads to the death of plants (Gupta & Sandallo, 2011). Miranda *et al.* (2009) found that cattle reared on Ni enriched soils in Spain bioaccumulated toxic levels of Ni in their kidneys and Cu in their livers. Gall and Rajakaruna (2013) argued that there is evidence to explain that toxic amount of toxicological metals can enter the food chain through contaminated sites. Appenroth (2010) indicated that high concentration of heavy metals in food crops and plants may lead to toxicity in humans and animals thereby causing acute and chronic illness which sometimes results in death.

2.6 Selected Trace Metals

2.6.1 Arsenic

Arsenic is a semi metallic element whose chemical symbol is "As". Although it is commonly described as heavy metal, arsenic is a metalloid with a complex chemistry similar to phosphorous (CCME, 2001). Arsenic is a silver-grey brittle crystalline solid with atomic weight 74.9 g/mol, specific gravity 5.73 g/cm^3, melting point 817 °C (at 28 atm), boiling point 613 °C, and vapor pressure 1mm Hg at 372 °C (Mohan & Pittman, 2007). The atomic number of arsenic is 33 and it occurs in group 5 of the periodic table. ATSDR (2007a) reported that arsenic in its elemental form occurs in two forms under ambient conditions, which is, a steel grey coloured brittle metallic solid or a dark grey amorphous solid. The concentration of arsenic in the earth's crust varies widely geologically with an average level of 3–4 ppm (ATSDR, 2007a) and its concentration is associated with rock type and industrial activity.

Arsenic exists in the −3, 0, +3, and +5 valence oxidation states (Mohan & Pittman, 2007). The two most common forms in natural water are arsenite (AsO_3^{3-}) and inorganic arsenate (AsO_4^{3-}) which are referred to as As^{3+} and As^{5+}. As^{3+} is 4 to 10 times more soluble in water than As^{5+}. Ampiah-Bonney *et al.* (2007) reported that the trivalent compounds (arsenites) are more toxic than the pentavalent compounds (arsenates). According to Sawyer *et al.* (2003), arsenic occurs in natural water in the form of arsenous acid (H_3AsO_3) and arsenic acid (H_3AsO_5). Vaclavikova *et al.* (2008) added that the trivalent methylated arsenic species is more toxic than inorganic arsenic because it is efficient in causing DNA breakdown. The toxic effect of arsenic depends particularly on its oxidation state and chemical species. In general, inorganic compounds of arsenic are regarded as more highly toxic than most organic forms

(Chutia *et al.*, 2009). Inorganic arsenic causes lung, kidney, bladder, and skin disorders (ATSDR, 2003). Arsenic in soil results from human activities including pesticide use, mining and ore processing operations, operating coal burning power plants, smelting of copper, zinc and lead and waste disposal (Mirlean *et al.*, 2003).

The toxicity of arsenic in its inorganic form has been known for decades under the following forms: acute toxicity, sub-chronic toxicity, genetic toxicity, developmental and reproductive toxicity (Chakraborti *et al.*, 2004), immunotoxicity (Sakurai, *et al.*, 2004), biochemical and cellular toxicity, and chronic toxicity (Mudhoo *et al.*, 2011). Chen and Ahsan (2004) discovered that arsenic is perhaps a human carcinogen which accounted for the doubling of lifetime mortality risk from liver, bladder, and lung cancer in Bangladesh, as a result of arsenic in drinking water. Arsenic exposure affects virtually all organ systems including the cardiovascular, dermatologic, nervous, hepatobillliary, renal, gastrointestinal, and respiratory systems (Tchounwou *et al.*, 2003).

2.6.2 Cadmium

Cadmium is a chemical element which belongs to group 12, together with zinc and mercury, with atomic number 48 and atomic weight of 112.40. It is a soft white metal in nature. It has a density of 8.64 g/cm^3, melting point of 320.9 °C and a boiling point of 765 °C at 100 kPa (WHO, 2004a). Although, cadmium is a naturally occurring element, it is rarely found as a pure metal in nature. It is not known for any essential biological function, whose concentration in the earth's crust is about 0.1-0.5 ppm (ATSDR, 2012). It is chemically similar to zinc and occurs naturally with zinc and lead in sulphide ore. Cadmium usually has an oxidation number of +2, but it also exists in the +1 state. The ionic form of cadmium (Cd^{2+}) usually combines with ionic forms of oxygen (cadmium oxide), chlorine (cadmium chloride) or sulphur (cadmium sulphide) (Castro-González & Méndez-Armenta, 2008).

Cadmium is a lethal metal originating from industrial and agricultural sources (Järup & Akesson, 2009). The pollution of cadmium in the environment occurs as a result of atmospheric deposition of metal production activities and refining, fossil fuel combustion, waste incineration as the main sources of anthropogenic activities whereas volcanic eruption, forest fire and generation of sea salt (ATSDR, 2012) and the transportation of contaminated soil particles by wind constitutes the major natural activities responsible for introducing Cd into the environment (Adamu, 2010; Joseph, 2009). The anthropogenic sources of cadmium increase the rate of cadmium uptake by crops and vegetables grown for human consumption (Järup & Akesson, 2009). Cadmium emission also occurs from the production of artificial phosphate fertilizers and upon addition the element ends up in the soil (Jennings, 2005).

According to Joseph (2009), substantial quantities of Cd has been introduced into the environment as a result of natural and anthropogenic activities of which anthropogenic activities have contributed to 3 to 10 times more Cd into the environment than natural activities. Peters *et al.* (2010) added that the major known sources of cadmium exposure to the United State are emissions from industrial activities and waste management operations, intake of certain foods and exposure to cigarette smoke. Joseph (2009) added that the occupational and environmental concern associated with cadmium is enormous and has been classified as a human carcinogen by International Agency for Research on Cancer (IARC). The IARC also pointed out that cadmium can be present in the human body for 15 - 20 years because of its extremely long half-life and has the tendency to exert carcinogenic effect long after environmental exposure has stopped.

Cadmium is one of the most toxic heavy metals that can enter the food chain when it bioaccumulates in edible plant tissue (Singh *et al.*, 2011).

Olawoyin *et al. (*2012) explained that cadmium causes damage to the lungs, kidneys and bones. Joseph (2009) demonstrated that cadmium induces cancer by multiple mechanisms and the most important among them are aberrant gene expression, inhibition of DNA damage repair, induction of oxidative stress, and inhibition of apoptosis. Peters *et al.* (2010) also reported that cadmium is a chemical pollutant, which may probably contribute to cardiovascular disease even though existing literature is limited. Filipič and Hei (2004) specified that cadmium has been shown to induce chromosomal deviations, sister chromatid exchanges and DNA strand breaks and DNA-protein crosslinks.

2.6.3 Copper

Copper is a transition metal located in period 4 and group 11 of the periodic table whose chemical symbol is “Cu”. It is a reddish metal with a cubic crystalline structure. Its atomic number is 29, atomic weight 63.546 g/mol, specific density 8.9 g/cm^3, melting point 1083 °C and boiling point 2595 °C. It is found in a variety of rocks and minerals. Copper is one of the essential micronutrient which is necessary for a wide range of metabolic processes for both prokaryotes and eukaryotes (ATSDR, 2004; Georgopoulos *et al.*, 2011). The average concentration of Cu in the earth’s crust is about 50 ppm (ATSDR, 2004). The oxidation states of Cu are copper (0), copper (I), copper (II), and copper (III), although trivalent copper is very rare (Georgopoulos *et al.*, 2011).

Copper occurs in the environment due to the emission and atmospheric deposition of metal dust released from anthropogenic activities (Alaoui-Sossé *et al.*, 2004). Soils may also contain high levels of copper due to the prevalent application of pesticides, indiscriminate land application of sewage sludge as well as mining and smelting activities. It is important in the process of biological transfer of electrons, and is vital for the synthesis of red blood cells and the maintenance of nervous system structure and function but toxic in excess (Medeiros *et al.,* 2012). Chronic Cu toxicity primarily affects the liver, because it is the first site of Cu deposition after it enters the blood and is manifested by the development of liver cirrhosis with incidences of hemolysis and damage to renal tubules, the brain, and other organs (Gaetke & Chow, 2003).

2.6.4 Lead

Lead is a metallic element which belongs to group 4 and period 6 of the periodic table with "Pb" as the chemical symbol (Al-Saleh *et al.*, 2009). It is a bluish or silvery-grey metal with atomic number 82, atomic weight 207.19, specific gravity 11.34 g/cm ^{3}, melting point 327.5°C and boiling point 1725 °C. Lead is widely and evenly distributed in the environment (Harrison, 2001; Tangahu *et al.*, 2011) and its concentration in the earth crust is 12.5 mg/kg (Acta & Ireland, 1964). Lead is used for roofing sheets, screens for X-rays and radioactive emissions. It is also used in the manufacture of pipes, drains and soldering materials and manufacturing of batteries. Lead combines with elements such as sulphur and oxygen to form PbS, $PbSO_4$ and $PbCO_3$ (ATSDR, 2007b; Wuana & Okieimen, 2011).

Oehlenschläger (2002) described lead as a toxicologically relevant element which is introduced into the environment via human activities in extreme amounts despite its low geochemical mobility. Lead pollution in the environment is primarily known to be sourced from industrial production and their emissions, road traffic with leaded petrol, smoke and dust emissions of coal and gas-fired power stations (Véron *et al.,* 1999). Lead is a universal environmental toxin that induces a wide range of physiological, biochemical, and behavioral dysfunctions (Gurer & Ercal, 2000). Lead, like any other heavy metal is not biodegradable and once it enters the soil, it serves as a long term source of exposure to living things. Lead contamination in the environment exists in its insoluble form which pose serious human health problem, namely, brain damage and retardation (Cho-Ruk *et al.*, 2006).

Lead toxicity is a worldwide environmental public health issue and children are particularly susceptible to lead toxicity than adults because of their hand to mouth activity, increased respiratory rates and higher gastrointestinal adsorption per unit body weight (ATSDR, 2007b; Ahamed & Siddiqui, 2007). For instance, children exposed to lead suffer from impaired development, lower IQ, shortened attention span, hyperactivity and mental deterioration. The presence of lead may also affect the gastrointestinal tract, kidney, and the central nervous system. Ogwuebu and Muhanga (2003) reported that lead toxicity has the tendency to reduce haemoglobin synthesis, affects the functioning of the kidney and chronic damage to the central and peripheral nervous system.

2.6.5 Mercury

Mercury is one of the most naturally occurring toxic heavy metal in the environment (Castro-González & Méndez-Armenta, 2008) which occurs in period 6 and group 12 of the periodic table just like Zn and Cd. Elemental mercury is a shiny, silver-white metal which is liquid or vapour at room temperature (Goldman & Shannon, 2001). The atomic number of Hg is 80, atomic weight 200.59 g/mol, density 13.53 g/cm^3, melting point −38.83 °C, and boiling point 356.73 °C. The average concentration of mercury in the earth's crust is about 0.08 ppm (Acta & Ireland, 1964). It combines with other elements, such as chlorine, sulphur, or oxygen, to form inorganic mercury compounds. It is used in thermometers, thermostats, and dental amalgam because of its physical and chemical properties such as low boiling point and easy vaporization. It occurs as metallic element, inorganic mercury and organic compounds. Methylmercury is the predominant form of organic mercury found in the environment (Counter & Buchanan, 2004).

The emission of Hg into the environment through natural and anthropogenic activities have the potential to travel long distances through atmospheric pathways, far from its anthropogenic source (Gustin *et al.*, 2000). According to Murray and Holmes (2004) an investigation made by the US Environmental Protection Agency (EPA) and National Emissions Inventory (NEI) indicated that coal-fired electric utilities accounted for 52.7% of the region's Hg emissions and other activities such as municipal waste combustion, mercury-cell chlor-alkali plants, hazardous-waste incinerators, stationary internal combustion engines , industrial, commercial and institutional (ICI) boiler, lime manufacturing and medical waste incineration accounted for the remaining percentage.

Mercury causes a wide range of adverse health effects in humans (Guzzi & La Porta, 2008). The presence of mercury in fish, dental amalgams, thermometers, vaccine preservatives, and the atmosphere has made this toxic metal the focus of health authorities and interest groups. Humans and wildlife are exposed to mercury, often at levels that raises concern for both health and environmental effects globally (Scheuhammer *et al.,* 2007). The organic form of Hg which is predominantly methylmercury is the most toxic because of its associated health risk, mainly through fish consumption (Zahir *et al.*, 2005). It also accumulates in kidney tissues, directly causing renal toxicity, including proteinuria or nephrotic syndrome (Goldman & Shannon, 2001). Children are mostly vulnerable to Hg intoxication because it may impair developing central nervous system, pulmonary and nephrotic damage (Counter & Buchanan, 2004). Exposure to high levels of metallic, inorganic, or organic mercury can permanently damage the brain, kidneys, and developing fetus (ATSDR, 1999). Exposure to high amount of mercury vapour causes renal toxicity, nausea, vomiting, diarrhoea, high blood pressure, skin rashes, and eye irritation.

2.6.6 Zinc

Zinc is a bluish-white shiny metal in its pure elemental and metallic form (ATSDR, 2005). It is a transitional metal located in period 4 and group 12 with “Zn” as its chemical symbol. Its atomic number is 30, atomic mass 65.4, density 7.14 g/cm^3, melting point 419.5 °C, and boiling point 90 6°C. Zinc occurs naturally in the earth’s crust with an average concentration of about 70 ppm (Acta & Ireland, 1964). It is an essential trace element known for its biological functions in living organism which is responsible for growth and development. The presence of zinc in the environment combines with other elements such as chlorine, oxygen and sulphur to form compounds like zinc chloride, zinc oxide, zinc sulphate, and zinc sulphide (ATSDR, 2005). Zinc compounds are used as ingredients in the drug industry, wood preservation, manufacturing and dyeing fabrics. Zinc oxide for example is used in the manufacture of white paints, ceramic, producing rubber and other related products. Zinc metal is not found freely in nature; rather it occurs in the +2 oxidation state primarily as various minerals such as sphalerite (zinc sulfide), smithsonite (zinc carbonate), and zincite (zinc oxide).

The release of zinc into the environment occurs as a result of mining activities, smelting of zinc, lead, and cadmium ores, steel production, coal burning, and burning of wastes (ATSDR, 2005). Zinc is mobile in soil and factors such as weathering of parent material, atmospheric precipitation, decomposition of organic matter and the use of waste water in soil fertilization increases its availability in soils (Loska *et al.*, 2005). The consequence of zinc deficiency has been recognized for many years, but until recently the attention has been directed to the potential consequence of the excessive exposure to zinc inhalation, ingestion or dermal contact. Zinc is relatively considered to be non-toxic. Stomach cramps, nausea, and vomiting may occur when large doses of zinc are taken by mouth even for a short time. Ingesting high levels of zinc for several months may cause anaemia, damage the pancreas, and decrease lipoprotein (HDL) cholesterol (ATSDR, 2005).

2.6.7 Selenium

Selenium is a naturally occurring metalloid, essential microelement necessary for normal functioning of humans, animal and other living organisms but harmful in excess (Fordyce, 2013). Selenium belongs to the group of chalcogens (periodic table group 16) which displays a chemical behaviour similar to sulphur (Lenz & Lens, 2008). Its atomic number is 34, atomic mass 78.96, density 4.809 g/cm^3, melting point 220.5 °C and boiling point 685 °C. Selenium appears in a number of allotropic forms (ATSDR, 2003). It is extensively used for the manufacture of photoelectric cell because of its photovoltaic and photoconductive property. It is also used in the manufacture of glass (ATSDR, 2003). Selenium is widely distributed in nature originating from most rocks and soils at concentrations between 0.1 and 2.0 ppm (Fishbein, 1983) with an average concentration of 0.05 ppm (Acta & Ireland, 1964).

Selenium exists in four oxidation states as elemental selenium (Se^0), selenide (Se^{2-}), selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) (Barceloux, 1999). Selenium can easily be oxidized from Se^0 to Se^{4+} or Se^{6+}. Selenium VI (as selenate, SeO_4^{2-}) and selenium IV (as selenide, SeO_3^{2}) is the predominant mobile forms whereas selenides (Se^{2-}) and elemental selenium (Se^0) are insoluble. Although Se is contained in some minerals, it occurs most frequently in sulphides of metals (As, Cu, Pb, Hg, Ni etc.) either in the form of selenide or substituting the sulphur ion in the minerals crystal. The reactivity and bioavailability of selenium depends not only on its total content in soil but also on its chemical form. The solubility and availability of Se to plants is predominantly affected by pH and redox potential of the soil.

Elemental selenium is rarely found in nature, but it is sourced predominantly as a by-product of copper refining (Fishbein, 1983). It is associated with natural sulphides like pyrite, chalcopyrite and sphalerite mainly in trace concentrations (Wiberg *et al.*, 2001). The natural pathway of Se may also be sourced from volcanic rocks and metal sulphides from volcanic activity. Geologic materials such as phosphate rocks, organic rich black shale's coals (Lenz & Lens, 2008) and sulphide mineralization contain considerable amount of selenium which can be liberated into environment through natural atmospheric deposition. The presence and absence of selenium in soils may be dependent upon the composition of the parent material, leaching or processes subsequent to soil formation that may have added selenium. Activities such as mining, irrigation of agricultural land, petroleum refining, refining of sulphide ore and coal combustion are some of the anthropogenic sources of selenium (Simmons and Ager, 2005).

Selenium also plays an important anti-carcinogenic role, cellular antioxidant and neutralization of trace element toxicity, cancer and cardiovascular diseases (Medeiros *et al.*, 2012). However, at higher concentration selenium is toxic to humans, animals and plants. The toxicity of Se to living organisms varies with the amount and chemical form of Se ingested. The effects of selenosis in humans are typically dermal or neurological and comprise defective nails and skin, hair loss, unsteady gait and paralysis (Lenz & Lens, 2008).

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Area

The study was conducted in six districts bordering the coastal environment of the Jubilee oil field in the Western Region of Ghana. One community was selected from each district. The study communities were Atuabo in Ellembelle District, Half Assini in Jomoro District, Lower Axim in Nzema East Municipality, Lower Dixcove in Ahanta West District, Shama in Shama District and Takoradi in Sekondi-Takoradi Metropolis. The Western Region of Ghana covers an area of 23,921 km^2, which forms about 10% of Ghana's total land size which is located in the south-western part of the country and lies between 5°23'24.7128" N and 2°8'42.0864". It is bordered on the west by Ivory Coast, to the east by Central Region, on the north by Ashanti and Brong Ahafo Region and on the south by Gulf of Guinea. The total population of the region is 2,376,031 representing 9.6% of Ghana's population (Ghana Statistical Service, 2010). The region has about 75% of its vegetation within the high forest zone of Ghana. The south-western parts of the region are noted for rainforest, interspersed with patches of mangrove forest along the coast and coastal wetlands, whereas high tropical forest and semi-deciduous forest is also found in the northern part of the region. The region lies in the equatorial climatic zone characterized by moderate temperatures from 22 to 34 °C at night and day respectively. The region is the wettest part of Ghana, with a bimodal rainfall pattern averaging 1,600 mm per year. The two rainfall peaks fall between May to July and September to October. The region also experiences intermittent minor rains all year round. The humidity of the region ranges from 70 to 90%.

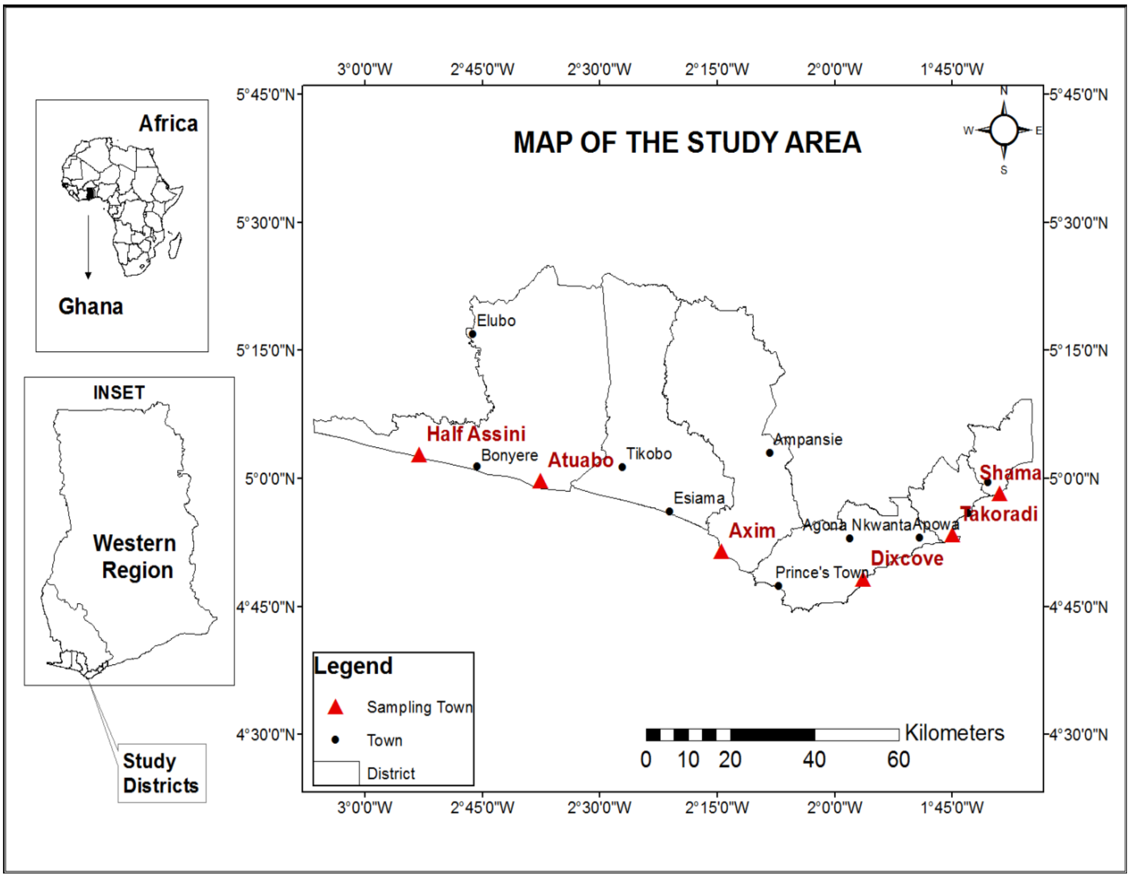


Figure 3.1 Map of the study area showing the coastal communities

3.2 Sampling

3.2.1 Water Sampling

Water samples were collected from twenty different sampling points in four districts in October, 2014 and March, 2015 for the wet and dry season respectively. At each site, five water samples were collected into a 500 mL plastic bottle that was washed and soaked in 10% nitric acid for 24 hours, rinsed thoroughly with double distilled water and oven dried (APHA, 2005). The water samples for heavy metal analysis were acidified with 0.5% nitric acid (HNO_3) to a pH below 2.0. The essence of acidification of collected water samples is to minimize the precipitation and adsorption on the walls of the container (Sharma & Tyagi, 2013) and prevention of microbial activity (Serfor-

Armah *et al.*, 2006). All the samples were well labelled and stored in an ice chest at 4°C and transported to the Ecological Laboratory of the University of Ghana for analysis. Water quality parameters such as temperature, pH, electrical conductivity, total dissolved solids, salinity and dissolved oxygen were measured in-situ. Temperature, pH, electrical conductivity, and salinity were measured using Horiba Digital Water Quality Checker (model U-50). The total dissolved solids (TDS) and dissolved oxygen (DO) were measured using OAKTON® PCD650. To measure each parameter, the probe end of the meter was dipped into the water samples whiles the values were read and recorded. The electrode of the meter was rinsed with distilled water after each sample measurement. Water samples were also collected into a dark air tight glass bottle for biochemical oxygen demand after five days of sampling. Water quality parameters were analysed using standard procedures (APHA, 1995).

3.2.2 Soil sampling

Soil samples were collected from six sampling sites at a depth of 0-15 cm and 15-30 cm using a soil auger. Sixty (60) representative composite soil samples were collected from the study area. Soil samples were stored in well labelled plastic polythene containers and then transported to the laboratory for further soil treatment and analysis. The GERMIN GPS was used to take all the coordinates of the various sampling points in the study sites.

3.2.3 Plant sampling

Ten (10) wild plant species in each of the communities were collected for analysis depending on its dominance in the communities. A total of sixty (60) plant samples were collected from the study area, stored in polythene bags and transported to the Ecological laboratory of University of Ghana for analysis. The names of the wild plants collected from the study area were *Alchonea cordifolia*, *Erythrina senegalesis*, *Ficus umbellata*, *Terminalia catappa*, *Thespesia populnea*, and *Senna siamen.*

3.3 Sample Preparation

After collection, samples were brought to the laboratory for initial treatment and preservation until further analysis. The soil samples were first of all, air dried at a temperature of 21-27 °C for 5 days. The samples were ground using porcelain pestle and mortar, and sieved with a 2 mm sieve to obtain fine sand fraction for various analytical determination. Plant samples were also washed thoroughly with distilled water to remove any particle on the leaves of the plants. Each plant sample was placed in a brown envelope and kept in the oven at 70-80 °C until constant dry weight was attained. The samples were then milled into a powdery form. The milled samples were passed through a 2 mm sieve and then stored in well labelled plastic polythene bags for acid digestion in order to determine the presence of heavy metals in the samples.

3.4 Laboratory Determination

3.4.1 Biochemical Oxygen Demand

Biochemical oxygen demand (BOD) is a measure of organic matter contamination of water. This test was used to measure the amount of oxygen consumed by organisms during a specified period of time usually five days at a specified temperature. The BOD test was done by filling an airtight bottle and incubating it at 20 °C for five days. The dissolved oxygen was measured initially and after incubation, the BOD was found to be the difference between the initial and final DO.

Calculation: $BOD_5 \ (mg/L) = \frac{D_1 - D_2}{P}$

where; $D_{1=}$ DO of diluted sample immediately after preparation, mg/L,

D_{2}= DO of diluted sample after 5 days incubation at 20 ^{0}C, mg/L and

P=Decimal Volumetric fraction of sample used (APHA, 1995).

3.4.2 Determination of soil physicochemical properties (pH and Electrical Conductivity)

In order to determine the pH and electrical conductivity of soils, twenty grammes (20 g) were weighed into a beaker and 20 mL of distilled water added to obtain a soil to water solution ratio of 1:1. The mixture was stirred several times for 30 minutes and left to stand for one hour for the suspended soil particles to settle. The pH meter was first calibrated with standard buffer solution of pH 4 .0 and pH 7.0. The electrode was then immersed into the solution and the pH and the electrical conductivity reading were taken. The electrode was rinsed with distilled water after each sample measurement.

3.5 Digestion and Analysis of Samples

3.5.1 Digestion of soil samples

A 1.0 g of soil sample was measured into a digestion tube and digested with 10 mL of Ternary mixture (20 mL of $HClO_4$; 500 mL of HNO_3; 50 mL of H_2SO_4) which was placed on a hot plate at 95 °C for 30 minutes under a fume hood. After cooling the digested samples was filtered into a 100 mL volumetric flask using Whatman No. 42 filter paper and made up to the mark with distilled water.

3.5.2 Digestion of plant samples

For each plant sample, 0.5 g was weighed into a 100 mL conical flask and 5 mL of concentrated H_2SO_4 was added and left to react overnight. The sample was then placed on a hot sand bath at 95 °C for some time and few drops of hydrogen peroxide (H_2O_2) were added until the samples completely oxidized. After cooling, the digested samples were filtered into 100 mL volumetric flask and made up to the mark with distilled water.

3.6 Determination of Heavy Metals

After digestion, the digested samples were made up to 100 mL with double distilled water and the analytical blank was prepared for each sample. A series of calibration solutions (standards) containing known amounts of analyte elements were also prepared and used to calibrated the PINAAcle 900T Perkin Elmer Atomic Absorption Spectrophotometer. Blanks were atomized followed by the standards and calibration of graphs plotted showing response from the ASS. The concentrations were then calculated based on the absorbance obtained using the Beer Lambert law. Responses of the standard were used to establish accurate performance of the machine and accurate concentration values of elements. Light was generated from a hollow cathode lamp at wavelength characteristic to each analyte. Each analyte was then atomized using an atomizer to create free atoms from the samples. Air acetylene gas was used as the source of energy for the production of free atoms for cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), selenium (Se), and argon-acetylene gas for mercury (Hg) and arsenic (As). The sample was introduced as an aerosol into the flame and the burner aligned in the optical path to allow the light beam to pass through the flame where the light was absorbed. The light was then directed into a monochromator which then isolates the specific analytical wavelength of the light emitted by the hollow cathode lamp from the non-analytical. The sensitive light detected then measures the light and translates the response into the analytical measurements. Calculations of concentration of heavy metals were done using;

$$Final\ Conc.(mg/kg) = \frac{Conc.(analytical\ measurement) \times Volume\ of\ extract}{sample\ weight\ (grams)}$$

3.7 Contamination Assessment Methods

A number of calculation methods have been used for quantifying the degree of metal enrichment or pollution in soils, sediments and dusts (Lim *et al.*, 2006). In this study, geoaccumulation index (I_{geo}), enrichment factor (EF), contamination factor (CF) and pollution load index (PLI) were calculated to assess the heavy metal contamination status in the soil.

3.7.1 Geoaccumulation Index (Igeo)

The index of geoaccumulation (I_{geo}) is widely used in the assessment of contamination by comparing the levels of heavy metal obtained to a background level originally used with bottom sediments (Atiemo, 2011; Muller, 1969). It is calculated using this equation:

$$I_{geo} = log_2\left(\frac{C_n}{1.5B_n}\right) ---------------- [1]$$

where C_n represents the measured concentration of the element in soil being studied and B_n represents the geochemical background value in fossil argillaceous sediment (crusted average or average shale) (Acta & Ireland, 1964). The constant 1.5 is introduced to minimize the effect of possible variation in the background values which may be attributed to lithologic variation in the sediments (Lu *et al.*, 2009). The following classification is given for geoaccumulation index :<0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted and >5 = extremely polluted (Lu *et al.*, 2009).

3.7.2 Enrichment Factor (EF)

Enrichment Factor (EF) of an element in the studied samples is based on the standardization of a measured element against a reference element. A reference element is often the one characterized by low occurrence variability, such as Al, Fe, Ti, Si, Sr, K, Sn, etc. (Turner & Simmonds, 2006). Al was used as the reference element in this study. Enrichment factor is used to differentiate heavy metals originating from human activities and those of natural sources. This is determined by the relation:

$$EF_x = \frac{[C_x/C_{ref}]sample}{[B_x/B_{ref}]Background} \text{----------------------------------} [2]$$

where EF is the enrichment factor for the element, C_x is the concentration of element of interest in sample, C_{ref} is the concentration of the reference element used for normalization in the sample, B_x is the concentration of the element in the crust and B_{ref} is the concentration of the reference element used for normalization in the crust (Acta & Ireland, 1964). Five contamination categories are recognized on the basis of the enrichment factor: EF< 2 states deficiency to minimal enrichment, EF = 2-5 moderate enrichment, EF = 5 - 20 significant enrichment, EF = 20 - 40 very high enrichment and EF > 40 extremely high enrichment (Yongming *et al.*, 2006).

3.7.3 Contamination Factor and Pollution Index (PI)

The level of contamination of soil by metal is expressed in terms of a contamination factor (CF) calculated as;

$$\text{CF} = \frac{C_{sample}}{C_{backround}} - [3]$$

where the contamination factor CF < 1 refers to low contamination; 1 ≤ CF < 3 means moderate contamination; 3 ≤ CF < 6 indicates considerable contamination and CF > 6 indicates very high contamination. Pollution index is also commonly used to assess environmental quality. The PI is defined as the ratio of element concentration in the study to the background content of the abundance of chemical elements in the continental crust. The PI of each element is classified as either low (PI ≤ 1), middle (1 < PI ≤ 3) or high (PI > 3) (Chen *et al.*, 2005). The pollution load index calculation provides valuable information and advice for policy and decision makers to evaluate the pollution status of an area.

3.8 Quality Assurance and Quality Control

Quality assurance procedure and precautions were taken to ensure the reliability of results. The samples were carefully handled to avoid any external influences that could interfere with the integrity of the result. Blank and replicate samples were analysed and compared to actual values obtained. Before the analysis, equipment was calibrated using appropriate standards. Triplicate determination of the samples was made and data presented as mean. All glassware and plastic bottles were soaked overnight in 10% (v/v) nitric acid, followed by washing with 10% (v/v) hydrochloric acid, and rinsed with double distilled water and dried before use (Boadi *et al.*, 2011). Distilled water was used in the preparation of samples and deionized water was used in the preparation of reagents.

3.9 Statistical Analysis

Different analytical tools were employed for various segments of the statistical analysis. Statistical Package for Social Sciences (SPSS 20.0) version was used to determine descriptive statistics of water and soil samples and Pearson's correlation. Pearson's correlation test (2-tailed) was used to determine the relationship between physicochemical parameters and heavy metals of soil and water samples. The t – test and F – test (analysis of variance, ANOVA) were used to determine statistical inference of parameters using GenStat Statistical Software 12th edition.

CHAPTER FOUR

RESULTS

4.1 Physicochemical properties

The summary of the results for the physicochemical properties of soil samples are presented in Table 4.1.

Table 4.1 Physicochemical properties of soil samples of the study area in the Western Region.

Communities	Descriptive statistics	pH 0-15 cm	pH 15-30 cm	EC (µS/cm) 0-15 cm	EC (µS/cm) 15-30 cm
EA	Min	5.06	5.15	104.00	75.00
	Max	7.94	7.73	308.00	299.00
	Mean	6.66	6.68	212.00	173.00
	SD	1.17	1.01	57.73	71.03
JH	Min	5.57	5.36	42.00	43.00
	Max	7.15	7.25	255.00	222.20
	Mean	6.14	6.17	134.70	99.50
	SD	0.54	0.58	66.13	47.71
NL	Min	7.34	7.12	332.00	338.00
	Max	7.98	7.84	802.00	809.00
	Mean	7.66	7.64	559.20	592.00
	SD	0.16	0.18	169.26	168.67
AD	Min	4.86	5.02	127.00	54.00
	Max	7.54	7.60	793.00	724.00
	Mean	6.33	6.39	334.00	289.60
	SD	0.89	0.70	190.88	188.17
SA	Min	5.85	6.66	123.00	107.00
	Max	8.45	8.26	880.00	924.00
	Mean	7.33	7.39	406.10	352.60
	SD	0.79	0.49	255.03	238.60
SN	Min	5.66	5.02	74.00	101.00
	Max	7.30	7.33	809.00	844.00
	Mean	6.74	6.69	387.20	342.50
	SD	0.55	0.66	252.44	238.68

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

4.1.1 pH of soil

The pH of soils at 0–15 cm was higher than 15–30 cm. However, statistical analysis revealed that, at 0–15 cm the mean values of pH were not different (p>0.05) among the communities but significant differences (p<0.05) were observed among the communities at 15–30 cm. The pH of soil at 0–15 cm ranged from 6.14 to 7.66 whereas 15–30 cm ranged from 6.17 to 7.64 (Table 4.1). The mean values of pH at 0-15 cm and 15-30 cm were 6.86±0.48 and 6.82±0.53 respectively. The lowest value at 0–15 cm and 15-30 cm were recorded at JH and NL respectively.

4.1.2 Electrical Conductivity of soil

The electrical conductivity of soils at 0-15 cm was higher than 15-30 cm nevertheless the results showed that electrical conductivity significantly differed (p<0.05) among the communities at both depths. The EC of soils at 0–15cm varied from 137.70 to 559.20 µS/cm with a mean value of 338.97±137.36 whereas 15–30 cm varied from 99.50 to 592.00 µS/cm with a mean value of 308.20±155.90 (Table 4.1). The highest value of EC at 0-15 cm and 15-30 cm was recorded at NL while the lowest value was recorded at JH for 0-15 cm and 15-30 cm (Table 4.1).

The results of the physicochemical parameters of water samples analysed in the wet and dry seasons are presented in Table 4.2 and 4.3 respectively.

Table 4.2 Summary of statistical analysis for the physicochemical parameters of water samples analysed in the wet season

Communities	Statistics	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	BOD (mg/L)	Salinity (ppt)	Temp. (°C)
EA	Min	6.14	82.04	55.06	2.99	1.64	0.00	27.70
	Max	7.17	610.37	408.95	4.90	4.14	0.20	36.20
	Mean	6.83	291.15	195.07	4.39	3.33	0.10	30.94
	SD	0.39	196.85	131.87	0.92	0.88	0.06	3.38
JH	Min.	7.06	46.45	31.12	1.34	1.43	0.00	26.50
	Max	7.24	935.80	630.00	5.35	20.10	0.30	32.85
	Mean	7.13	334.91	225.01	4.31	5.25	0.12	28.99
	SD	0.07	310.35	209.10	1.51	7.42	0.10	2.170
NL	Min	7.11	162.30	108.74	2.08	2.47	0.10	27.75
	Max	7.32	1557.00	1043.19	3.69	15.3	0.60	29.80
	Mean	7.23	780.60	523.02	2.98	6.84	0.30	28.61
	SD	0.08	508.65	340.80	0.65	4.85	0.19	0.70
AD	Min	7.35	194.60	130.35	2.05	1.56	0.10	25.80
	Max	7.56	870.38	583.10	5.07	11.90	0.30	28.50
	Mean	7.50	560.65	375.61	3.20	6.21	0.18	27.66
	SD	0.08	267.75	176.72	1.12	3.52	0.07	0.96

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove

Table 4.3 Summary of statistical analysis for the physicochemical parameters of water samples analysed in the dry season

Communities	Statistics	pH	EC (µS/cm)	TDS (mg/L)	DO (mg/L)	BOD (mg/L)	Salinity (ppt)	Temp. (°C)
EA	Min	6.92	306.43	205.31	2.51	3.42	0.13	29.30
	Max	6.98	784.87	525.86	2.93	5.20	0.33	30.03
	Mean	6.95	516.83	346.45	2.66	4.25	0.22	29.73
	SD	0.05	199.53	133.64	0.19	0.75	0.08	0.31
JH	Min.	6.71	63.40	42.48	1.09	1.65	0.07	26.50
	Max	6.92	2100.33	1046.78	4.19	11.25	1.08	30.20
	Mean	6.84	564.11	307.07	3.04	6.69	0.28	28.46
	SD	0.06	772.62	374.26	1.08	3.37	0.40	1.17
NL	Min	6.76	166.93	111.84	1.81	5.80	0.09	29.65
	Max	6.93	1010.67	677.15	3.25	20.25	0.38	31.20
	Mean	6.85	660.67	442.65	2.58	10.46	0.27	30.44
	SD	0.04	360.60	241.60	0.63	5.31	0.13	0.64
AD	Min	6.78	105.20	70.48	1.26	10.30	0.12	26.20
	Max	6.89	854.67	572.67	2.37	16.50	0.41	30.05
	Mean	6.86	531.53	356.12	1.71	13.34	0.28	28.56
	SD	0.05	289.00	193.63	0.40	2.27	0.10	1.55

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove

4.1.3 pH of water

The mean pH of water recorded in the dry season was not statistically different (p>0.05) from the wet season. The results showed that significant differences (p<0.05) were observed among the communities in the wet season but no significant difference (p>0.05) were observed among the communities in the dry season. The pH values in the wet season ranged from 6.83 to 7.50 (Table 4.2) with a mean value of 7.17±0.24 whereas the dry season ranged from 6.84 to 6.95 (Table 4.3) with a mean of 6.88±0.04. The lowest pH value was recorded at EA while the highest was recorded at AD in the wet season. JH and EA recorded the lowest and highest values of pH in the dry season respectively.

4.1.4 Electrical conductivity (EC)

The electrical conductivity of water in the dry season was generally higher than the wet season, however statistical analysis showed that the means were not different (p>0.05) from each other. The mean EC values among the communities in the wet and dry season revealed that there were no significant differences (p>0.05). The EC values in the wet season ranged from 291.15 to 780.64 µS/cm (Table 4.2) with a mean of 491.84±402.80 µS/cm whereas the dry season ranged from 516.83 to 660.67µS/cm (Table 4. 3) with a mean of 574.29±498.70 µS/cm. The lowest value of EC was recorded at EA in the wet and dry season whereas the highest was recorded at NL in the wet and dry seasons.

4.1.5 Total dissolved solids (TDS)

Generally, the values of total dissolved solids in the dry season were higher than the wet season. However, the results of the wet season were not significantly different (p>0.05) from the dry season. The mean values of TDS observed among the communities in wet and dry seasons were not significantly different (p>0.05) from each other. The TDS of water in the wet season ranged from 195.07 to 523.02 mg/L (Table

4.2) with a mean value of 329.68±270 mg/L whereas the dry season ranged from 307.07 to 442.65 mg/L (Table 4.3) with a mean value of 364.90±274.6 mg/L. The lowest value of TDS in the wet season was recorded at EA and the highest at NL while the dry season recorded the lowest value at JH and the highest at NL.

4.1.6 Dissolved oxygen

The results of dissolved oxygen in the wet season were higher than the dry season. The DO of water showed no significant difference (p>0.05) between the wet and dry seasons. The mean values of DO among the communities in both seasons were not different (p>0.05) from each other. The wet season recorded DO values ranging from 2.98 to 4.39 mg/L (Table 4.2) whereas the dry season ranged from 1.71 to 3.04 mg/L (Table 4.3). The mean values of DO in the wet and dry seasons were 3.72±1.29 and 2.48±0.89 mg/L respectively. The lowest value in the wet season was observed at NL and the highest at EA. Additionally, AD and JH recorded the lowest and highest values of DO in the dry season respectively.

4.1.7 Biochemical Oxygen Demand

The biochemical oxygen demand of water was generally higher in the dry season than the wet season. The results of BOD in the wet season, significantly differed (p<0.05) from the dry season. However, statistical analysis revealed that the means of BOD among the communities in the wet and dry seasons were not different (p>0.05) from each other. The BOD in the wet season ranged from 3.33 to 6.84 mg/L (Table 4.2) and 4.25 to 13.38 mg/L (Table 4.3) in the dry season. The mean values of BOD in the wet and dry seasons were 5.41±5.10 and 9.18±4.99 mg/L respectively. EA and NL recorded the lowest and highest values of BOD whiles EA and AD recorded the lowest and highest respectively.

4.1.8 Salinity

The results of water salinity recorded in the dry season were generally higher than the wet season. However, there were no significant difference ($p>0.05$) between the dry and the wet seasons. The results of water salinity among the communities in the wet and dry seasons showed no statistical difference ($p>0.05$). The values of salinity in the wet season ranged from 0.01 to 0.30 ppt (Table 4.2) with a mean value of 0.18±0.14 ppt and 0.22 to 0.28 ppt (Table 4.3) in the dry season with a mean of 0.27±0.24 ppt. EA and NL recorded the lowest and highest values in the wet season respectively while JH and AD recorded the lowest and highest in the dry season respectively.

4.1.9 Temperature of water

Results of water temperature in the dry season were higher than the wet season. However, there were no significant differences ($p>0.05$) between the wet and dry seasons. No statistical difference ($p>0.05$) were observed among the communities in the wet and dry seasons. Water temperature ranged from 27.66 to 30.94 °C (Table 4.2) with a mean value of 29.05±2.47 °C in the wet season whereas the dry season ranged from 28.46 to 30.44 °C (Table 4.3) with a mean value of 29.23±1.44 °C. The lowest and highest values of temperature in the wet season were recorded at AD and EA respectively. On the other hand, the lowest and highest values in the dry season were recorded at JH and NL respectively.

4.2 Metal Results

4.2.1 Heavy metals in water samples

Table 4.4 Summary of statistical analysis of heavy metal in water samples analysed in the wet season

Communities	Statistics	As	Cu	Pb (µg/L)	Se	Zn	Hg
EA	Min	0.46	1.30	39.07	0.33	3.98	0.05
	Max	20.72	18.62	46.26	0.44	56.79	0.63
	Mean	7.84	9.41	42.42	0.39	22.19	0.023
	SD	7.71	6.16	3.13	0.04	20.39	0.27
JH	Min	0.94	6.37	34.58	0.07	ND	0.07
	Max	1.57	53.08	82.14	0.32	14.87	1.39
	Mean	1.23	24.09	49.39	0.23	9.78	0.068
	SD	0.27	17.56	18.06	0.10	5.10	0.50
NL	Min	0.95	5.78	48.26	ND	ND	0.03
	Max	4.13	9.27	70.39	0.44	8.45	1.58
	Mean	2.46	8.40	57.98	0.24	7.12	0.047
	SD	1.19	1.32	8.31	0.16	1.34	0.57
AD	Min	0.65	2.29	31.88	ND	ND	0.005
	Max	5.33	7.32	50.85	ND	30.70	0.97
	Mean	3.12	4.10	40.88	ND	22.68	0.033
	SD	1.85	2.01	7.75	ND	8.02	0.36

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, ND = Not detected

Table 4.5 Summary of statistical analysis of heavy metal in water sample in dry season (µg/L)

Communities	Statistics	As	Pb	Se (µg/L)	Zn	Hg
EA	Min	0.65	ND	ND	ND	ND
	Max	9.24	97.30	1.49	59.13	0.06
	Mean	5.78	53.85	0.08	17.37	0.004
	SD	3.70	44.17	0.07	23.48	0.002
JH	Min	1.73	20.64	0.97	ND	ND
	Max	3.42	102.80	1.57	65.35	1.02
	Mean	2.36	70.73	0.12	22.80	0.047
	SD	0.67	34.88	0.02	24.20	0.037
NL	Min	0.18	38.82	0.94	ND	0.05
	Max	6.17	85.59	1.80	2.94	0.92
	Mean	2.30	62.17	0.12	0.79	0.03
	SD	2.18	16.85	0.04	1.49	0.029
AD	Min	0.48	4.63	1.33	ND	0.004
	Max	7.48	38.38	1.86	182.70	0.91
	Mean	3.26	25.47	0.16	19.36	0.039
	SD	3.00	13.95	0.02	13.71	0.033

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, ND = Not detected

The summary of metal results for the wet and dry seasons are presented in Table 4.4 and 4.5 respectively. Cadmium was not detected in water samples analysed in both seasons.

The wet season recorded the highest concentration of arsenic in water than the dry season. However, the mean concentration of arsenic showed no significant difference (p>0.05) between the wet and dry seasons. Statistical difference (p>0.05) were not observed among the communities during the wet and dry seasons. Arsenic in water ranged from 1.23 to 7.84 µg/L (Table 4.4) in the wet season and 2.30 to 5.78 µg/L (Table 4.5) in the dry season. The mean concentration of arsenic in the wet and dry seasons were 3.66±2.50 and 3.21±2.56 µg/L respectively. The wet season recorded the lowest and highest concentrations of arsenic at JH and EA whereas the dry season recorded the lowest and highest at NL and EA respectively.

Copper was not detected in all the water samples analysed in the dry season. Statistical analysis revealed that there were significant differences (p<0.05) among the communities in the wet season. Copper ranged from 4.10 to 24.09 µg/L with a mean value of 11.50±7.54. The lowest concentration was recorded at AD whereas JH recorded the highest concentration of copper.

The results of water samples analysed in the dry season showed a higher concentration of lead than the wet season. All samples analysed in the wet and dry seasons showed no significant difference (p>0.05) in the concentration of lead. The mean values of lead among the communities in the wet season showed no significant difference (p>0.05) but statistical difference (p<0.05) were observed among the communities in the dry season. Lead in water ranged from 40.88 to 57.98 µg/L (Table 4.4) in the wet season and 25.47 to 70.73 µg/L (Table 4.5) in the dry season. The mean concentration of lead in the wet and dry seasons were 47.67±6.76 and 53.06±17.01 µg/L respectively. The lowest concentration of lead was recorded at AD and the highest at NL in the wet season whereas the lowest and highest were observed at AD and JH respectively in the dry season.

Selenium in water was higher in the wet season than the dry season. Selenium showed significant difference (p<0.05) between the wet and dry seasons. However, the wet season showed significant difference (p<0.05) among the communities, but no statistical difference (p>0.05) were observed among the communities in the dry season. Selenium in water ranged from below detection limit to 0.38 µg/L (Table 4.4) in the wet season and 0.081 to 0.158 µg/L (Table 4.5) in the dry season. The mean concentration of selenium inr the wet and dry seasons were 0.22±0.14 and 0.12±0.03 µg/L respectively. AD and EA recorded the lowest and highest concentration in the wet season whereas EA and AD recorded the lowest and highest concentration in the dry season respectively.

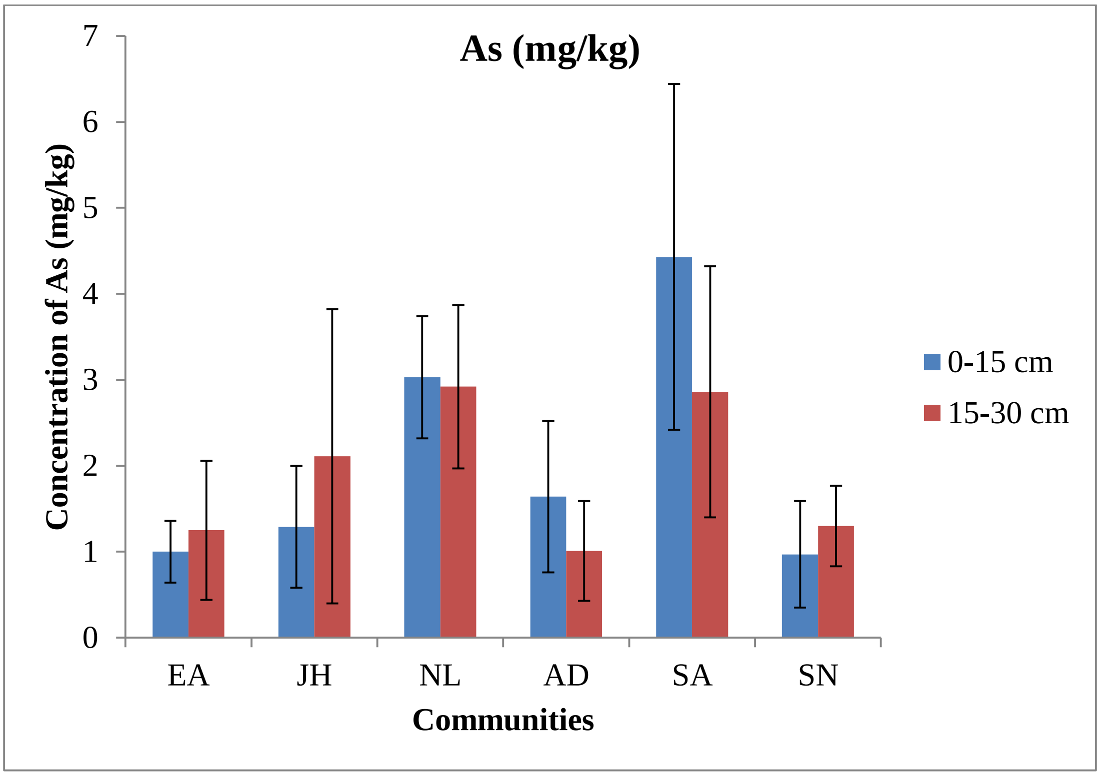
The concentration of zinc in water was higher in the wet season than the dry season. The mean concentration of zinc inr the wet and dry seasons were not different (p>0.05) from each other. All the water samples analysed in the wet and dry seasons showed no statistical difference (p>0.05) among the communities. Zinc in water ranged from 7.12 to 22.60 µg/L (Table 4.4) with a mean value of 15.44±5.89 µg/L. in the wet season and 0.79 to 22.80 µg/L (Table 4.5) with a mean value of 15.08±8.48 µg/L in the dry season. The lowest and highest values of lead in the wet season were recorded at NL and EA whereas NL and JH registered the lowest and highest concentration of zinc in the dry season respectively.

The wet season recorded the highest concentration of mercury in water samples than the dry season. The results of mercury in water samples analysed in the wet and dry seasons were not significantly different ($p>0.05$) from each other. The mean concentration of mercury among the communities showed no significant differences ($p>0.05$) in the wet and dry seasons. Mercury ranged from 0.023 to 0.068 µg/L (Table 4.4) in the wet season and 0.004 to 0.047 µg/L (Table 4.5) in the dry season. EA and JH recorded the lowest and highest concentration of mercury in the wet and dry seasons respectively.

4.2.2 Heavy metals in soil

4.2.2.1 Concentration of arsenic in soil

The mean concentration of arsenic at 0-15 cm was relatively higher than 15-30 cm. The concentration of arsenic at 0-15 cm showed significant difference at $p<0.05$, but no statistical difference ($p>0.05$) were observed among the communities at 15-30 cm. The concentration of arsenic in the surface soils (0-15 cm) ranged from 0.39 to 7.97 mg/kg whereas the subsoil (15-30 cm) ranged from 0.44 to 6.18mg/kg. The mean concentration of arsenic at 0-15 cm and 15-30 cm were 2.06±1.87 mg/kg and 1.91±1.56 mg/kg. The highest and lowest concentrations of arsenic in the surface soils (0-15 cm) were recorded at SA and SN respectively. On the other hand, the lowest and highest concentrations of arsenic in the subsoils (15-30 cm) were recorded at AD and NL respectively.

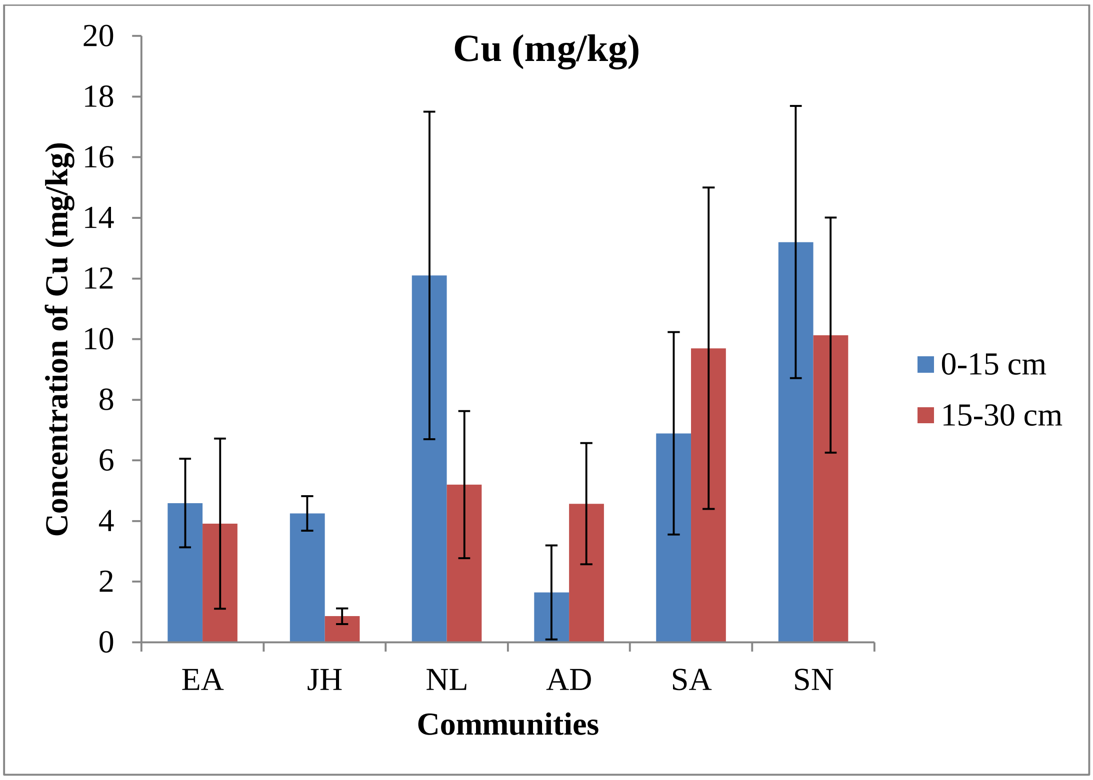


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.1 Concentration of arsenic (As) in soil

4.2.2.2 Concentration of copper in soil

The mean concentration of copper in the surface soils (0-15 cm) were higher than subsoils (15-30 cm). The concentration of copper in the surface and subsoils showed no statistical difference (*p*>0.05) among the communities. The concentration of copper at 0-15 cm ranged from 0.048 to 46.51 mg/kg whereas 15-30 cm ranged from 0.06 to 42.50 mg/kg. The mean concentration of copper in the surface soil (0-15 cm) and the subsoil (15-30 cm) were 6.55±8.98 as 6.29±15.38 mg/kg respectively. At 0-15 cm, the lowest and highest concentrations of copper were recorded at JH and SN whereas EA and SN recorded the lowest and highest concentrations at 15-30 cm respectively (Figure 4.2).

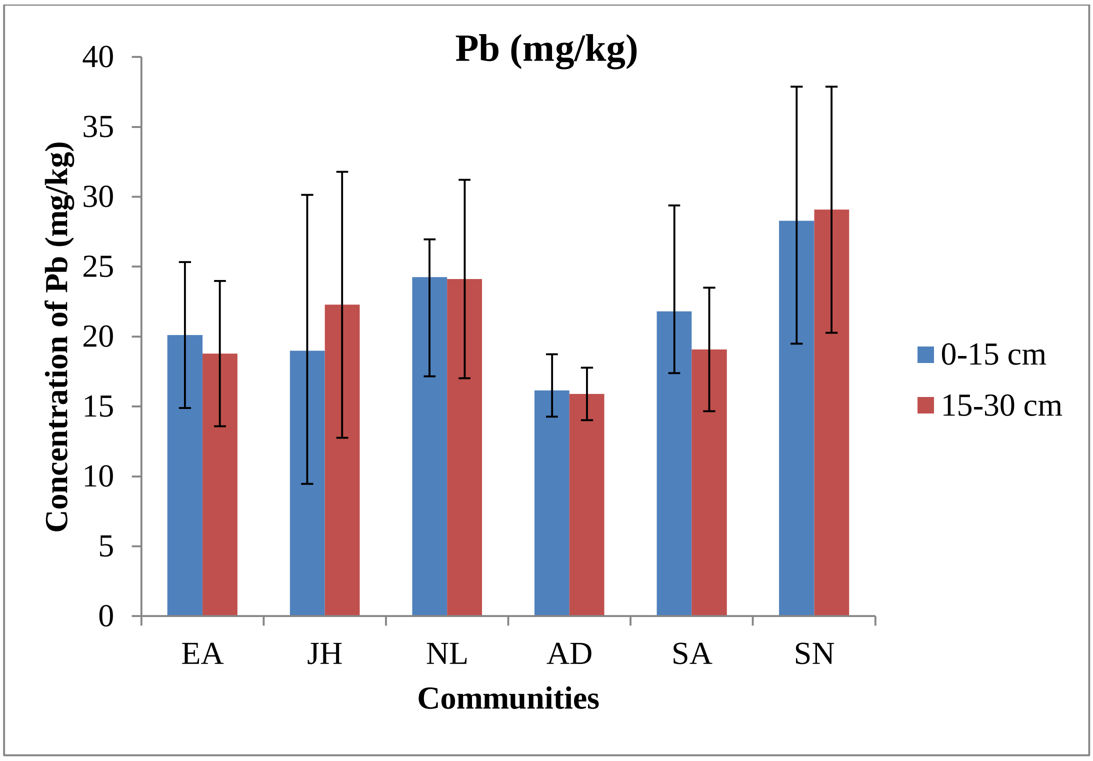


EA= Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.2 Concentration of copper (Cu) in soil

4.2.2.3 Concentration of lead in soil

The mean concentration of lead at 0-15 cm was higher than 15-30 cm. Statistical analysis revealed that there were no significant differences (p>0.05) among the communities in the surface and subsoils. At 0-15 cm, copper in the soil ranged from 16.14 to 28.28 mg/kg whereas 15-30 cm ranged from 15.90 to 29.08 mg/kg. The mean concentration of lead at 0-15 cm and 15-30 cm were 21.59±3.89 mg/kg and 21.54±4.27 mg/kg respectively. At 0-15 cm, the lowest concentration of lead was recorded at AD and the highest at SN whereas AD and SN recorded the lowest and highest concentrations at 15-30 cm respectively (Figure 4.3).

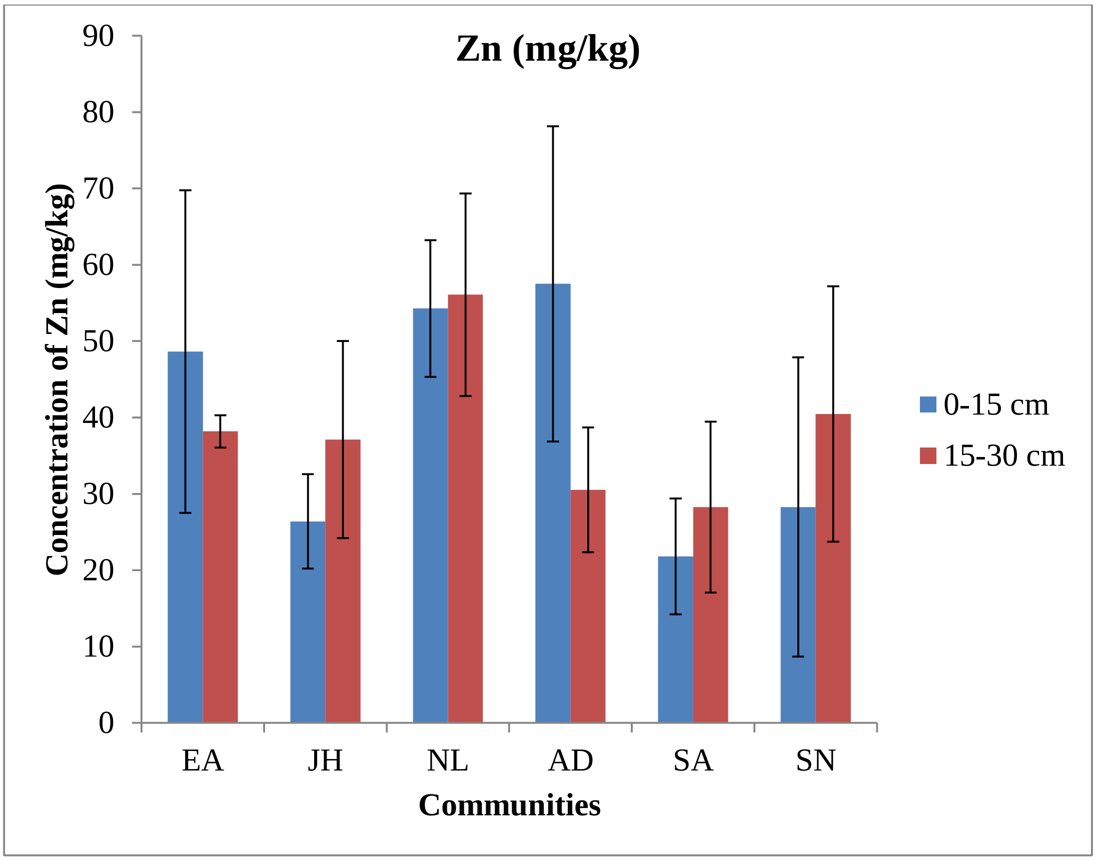


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.3 Concentration of lead (Pb) in soil

4.2.2.4 Concentration of zinc in soil

The mean concentration of zinc at 0-15 cm was comparatively higher than 15-30 cm. The concentration of zinc among the communities did not differ (p>0.05) from each other. Zinc in soil at 0-15 cm ranged from 21.80 to 57.51 mg/kg with an average concentration of 39.49±14.36 mg/kg whereas 15-30 cm ranged from 28.26 to 56.10 mg/kg with a mean value of 38.44 mg/kg. At 0-15 cm the minimum and maximum concentrations of zinc were recorded at SA and AD respectively. Additionally, SA and NL recorded the lowest and highest concentrations of zinc at 15-30 cm (Figure 4.4).

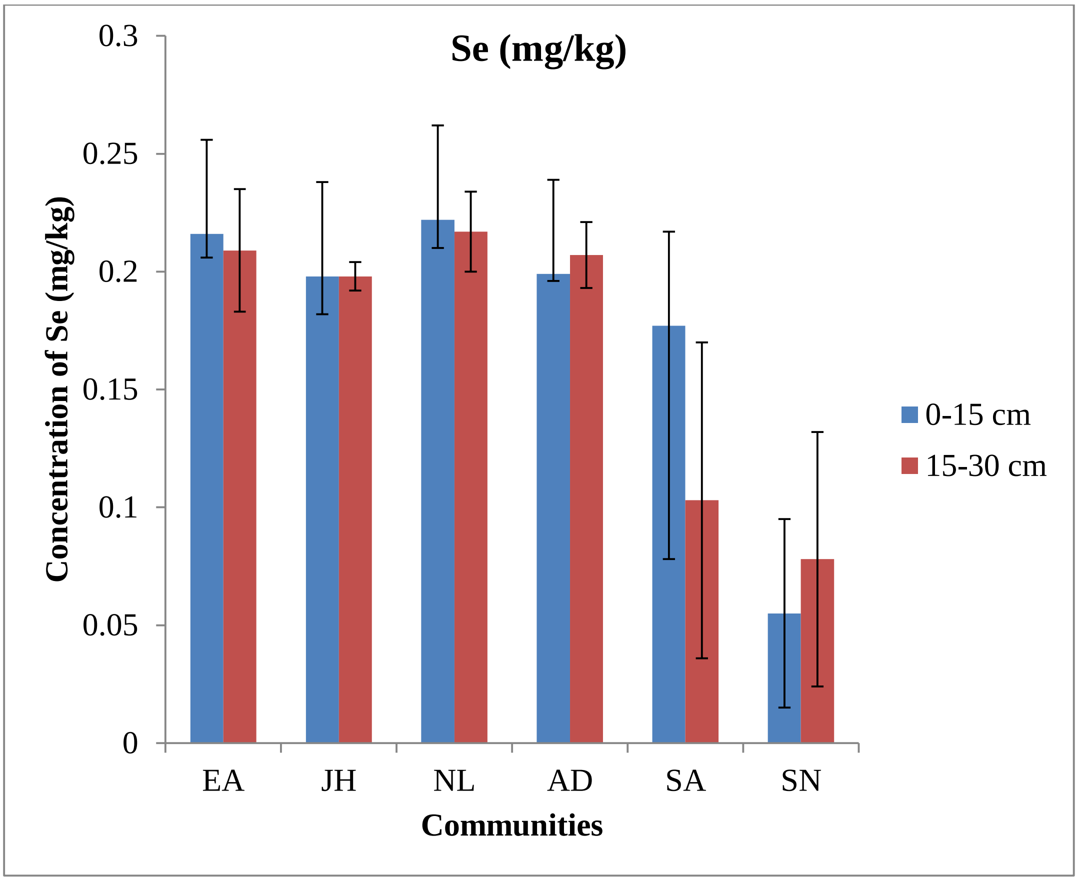


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.4 Concentration of zinc (Zn) in soil

4.2.2.5 Concentration of selenium in soil

The mean concentration of selenium in the surface soil (0-15 cm) was higher than the subsoil (15-30 cm). The concentration of selenium in the surface and subsoil, statistically differed (p<0.05) among the communities. The mean concentration of selenium at 0-15 cm and 15-30 cm were 0.178±0.057 and 0.169±0.056 mg/kg respectively. Selenium in soil ranged from 0.055 to 0.222 mg/kg at 0-15 cm and 0.078 to 0.217 mg/kg at 15-30 cm. The lowest and highest concentrations of selenium at 0-15 cm were recorded at SN and NL respectively. At 15-30 cm, the lowest concentration was recorded at SN whereas the highest was recorded at NL (Figure 4.5).

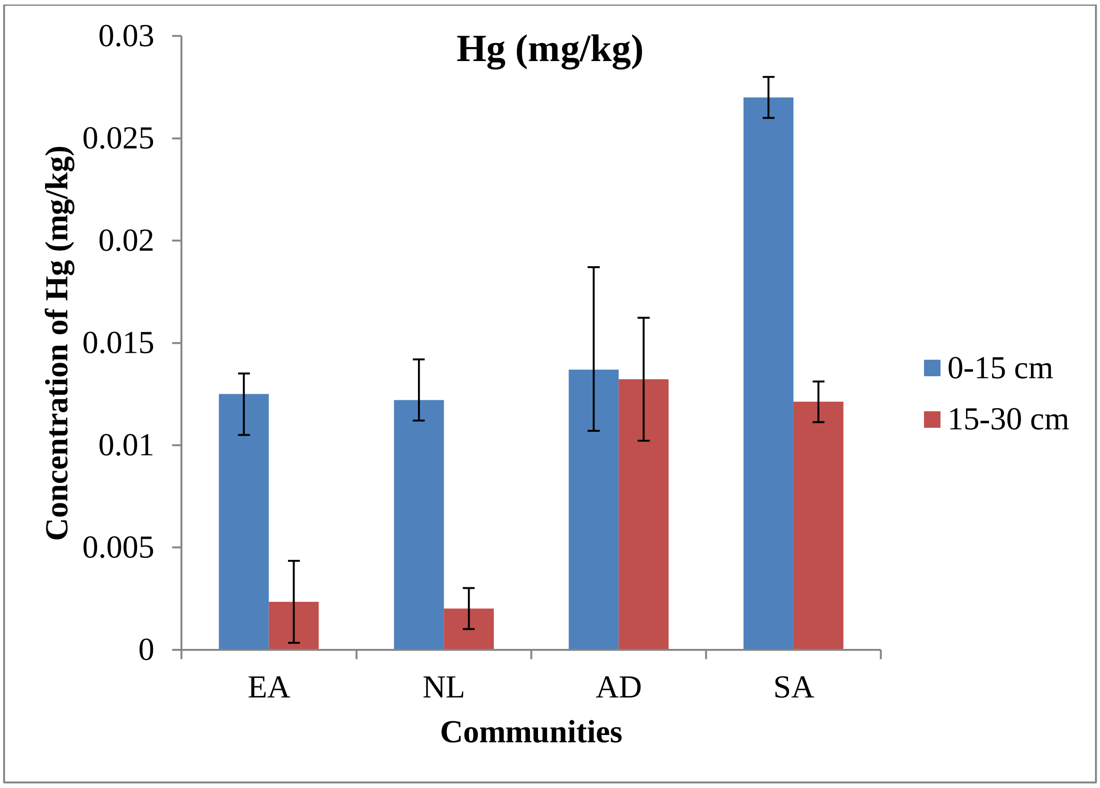


EA= Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.5 Concentration of selenium (Se) in soil

4. 2.2.6 Concentration of mercury in soil

The mean concentration of mercury at 0-15 cm was higher than 15-30 cm. The mean concentrations of mercury at 0-15 cm showed no significant difference ($p>0.05$) among the communities but statistical difference ($p<0.05$) were observed among the communities at 15-30 cm. The concentration of mercury at 0-15 cm ranged from below detection limit to 0.137 mg/kg with a mean value of 0.069±0.06 mg/kg whereas 15-30 cm ranged from below detection limit to 0.0132 mg/kg with a mean value of 0.003±0.05 mg/kg. Mercury was not detected in soil samples at JH and SN. The highest and lowest values of mercury in both surface and subsoils were recorded at AD and SA respectively. (Figure 4.6)



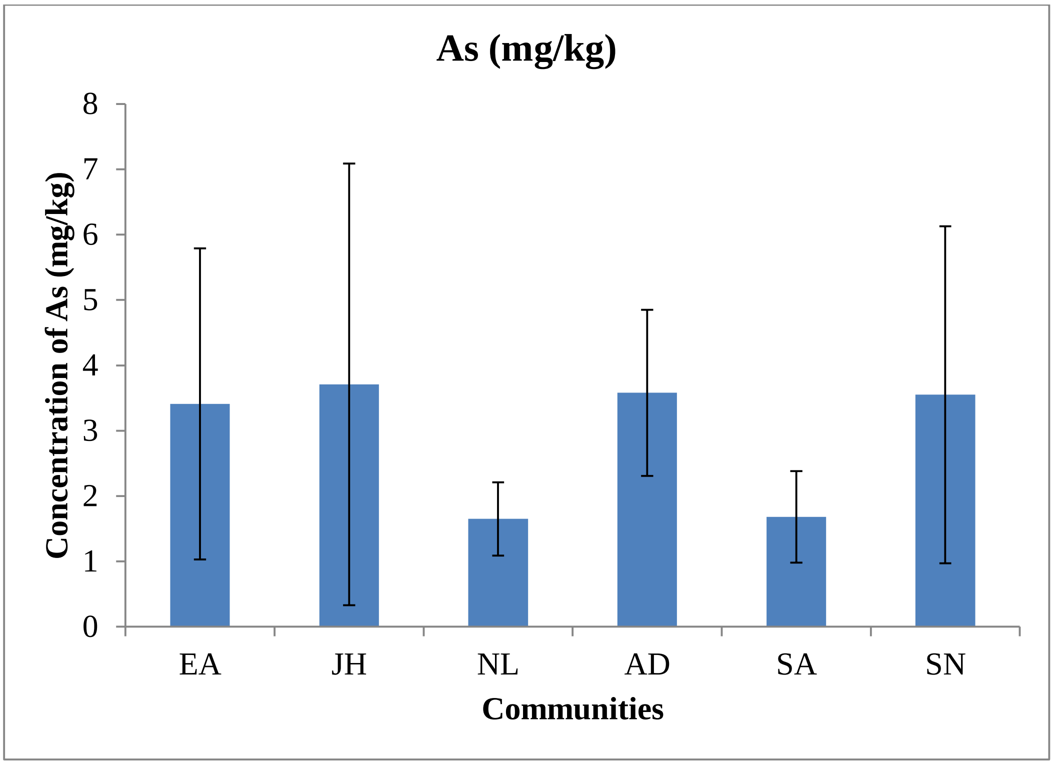
EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.6 Concentration of mercury (Hg) in soil

4.2.3 Heavy metals in plants

4.2.3.1 Concentration of arsenic in plant

Statistical analysis revealed that the concentrations of arsenic among the communities were not significantly different ($p>0.05$) from each other. The mean concentrations of arsenic among the communities ranged from 1.65 to 3.71 mg/kg. Figure 4.7 shows the highest mean concentration of arsenic at JH and the lowest at NL.

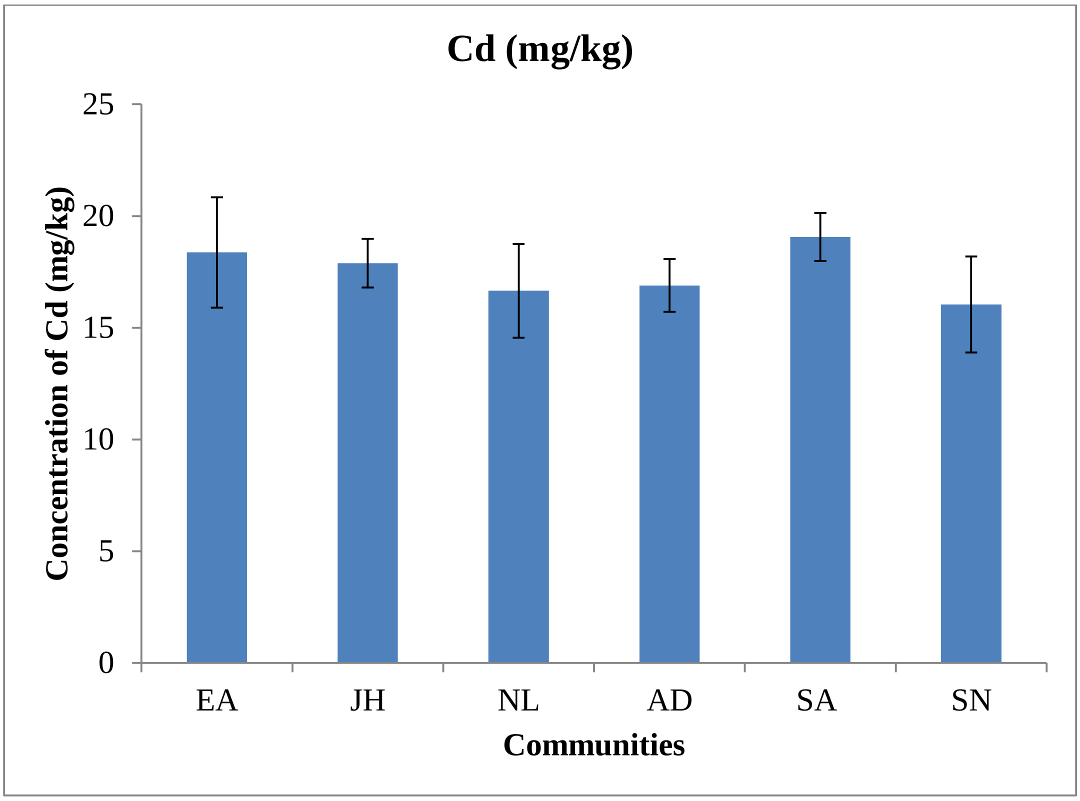


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.7 Concentration of arsenic (As) in plant

4.2.3.2 Concentration of cadmium in plant

Analysis of variance (ANOVA) revealed that, the concentrations of cadmium among the communities showed significant difference ($p<0.05$). The mean concentrations of cadmium in plant samples ranged from 16.04 to 19.06 mg/kg (Figure 4.8). The lowest mean concentration of cadmium was recorded at SN whereas the highest was recorded at SA.

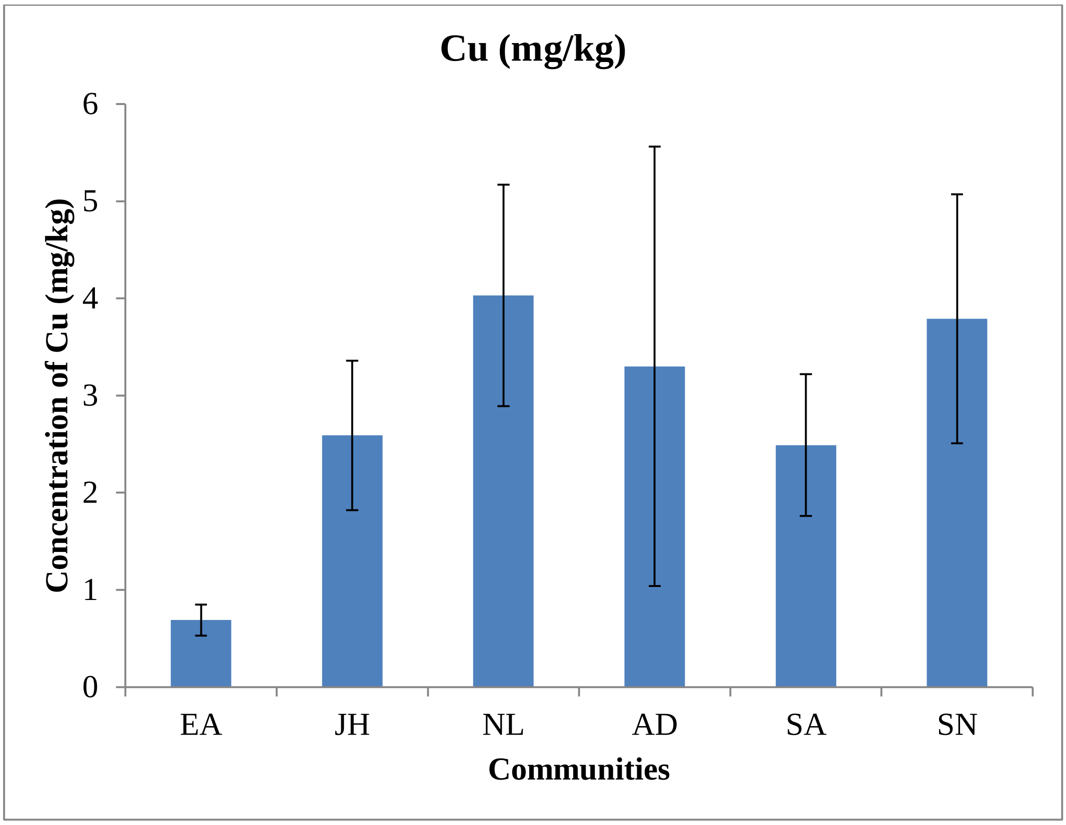


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.8 Concentration of cadmium (Cd) in plant

4.2.3.3 Concentration of copper in plant

Analysis of variance showed that the concentrations of copper among the communities were not different (p>0.05) form each other. The mean concentrations of copper in plant leaves among the communities ranged from 0.69 to 4.03 mg/kg. Figure 4.9 shows the graphical concentration of copper among the communities. The lowest concentration of copper was recorded at EA whereas the highest concentration was recorded at NL.

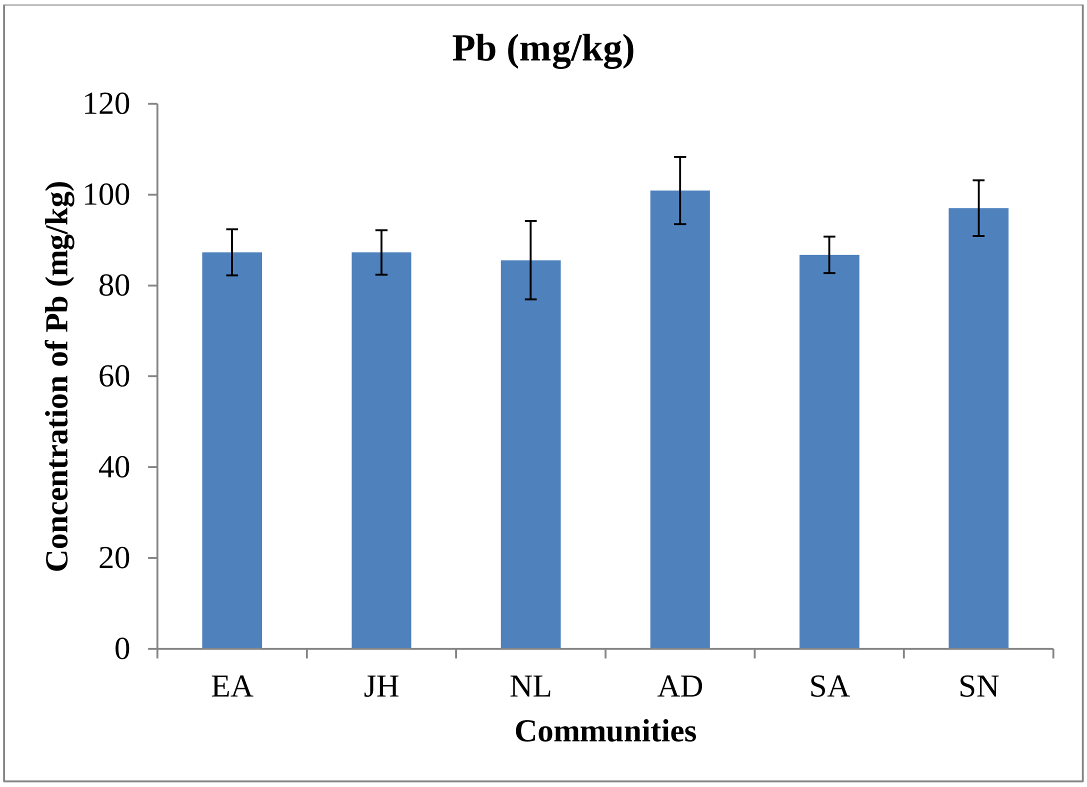


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.9 Concentration of copper (Cu) in plant

4.2.3.4 Concentration of lead in plant

A statistically significant difference (p<0.05) were observed among the communities. The mean concentrations of lead ranged from 85.56 to 100.91 mg/kg. Figure 4.10 illustrates the graphical concentration of lead in plant leaves. The lowest and highest concentrations of lead were recorded at NL and AS respectively.

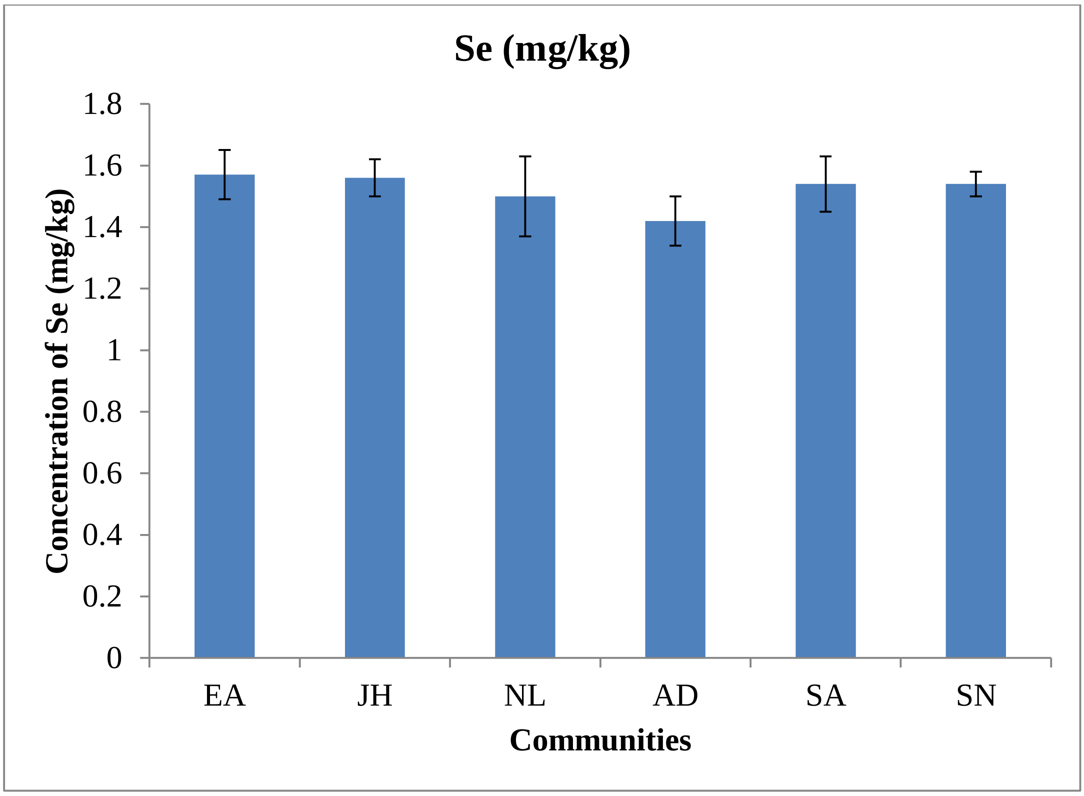


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.10 Concentration of lead (Pb) in plant

4.2.3.5 Concentration of selenium in plant

There were significant differences ($p<0.05$) in the concentrations of lead among the communities. The mean concentrations of selenium in plant leaves ranged from 1.42 to 1.57 mg/kg. The lowest concentration of selenium was recorded at AD whereas the highest was recorded at EA (Figure 4.11).

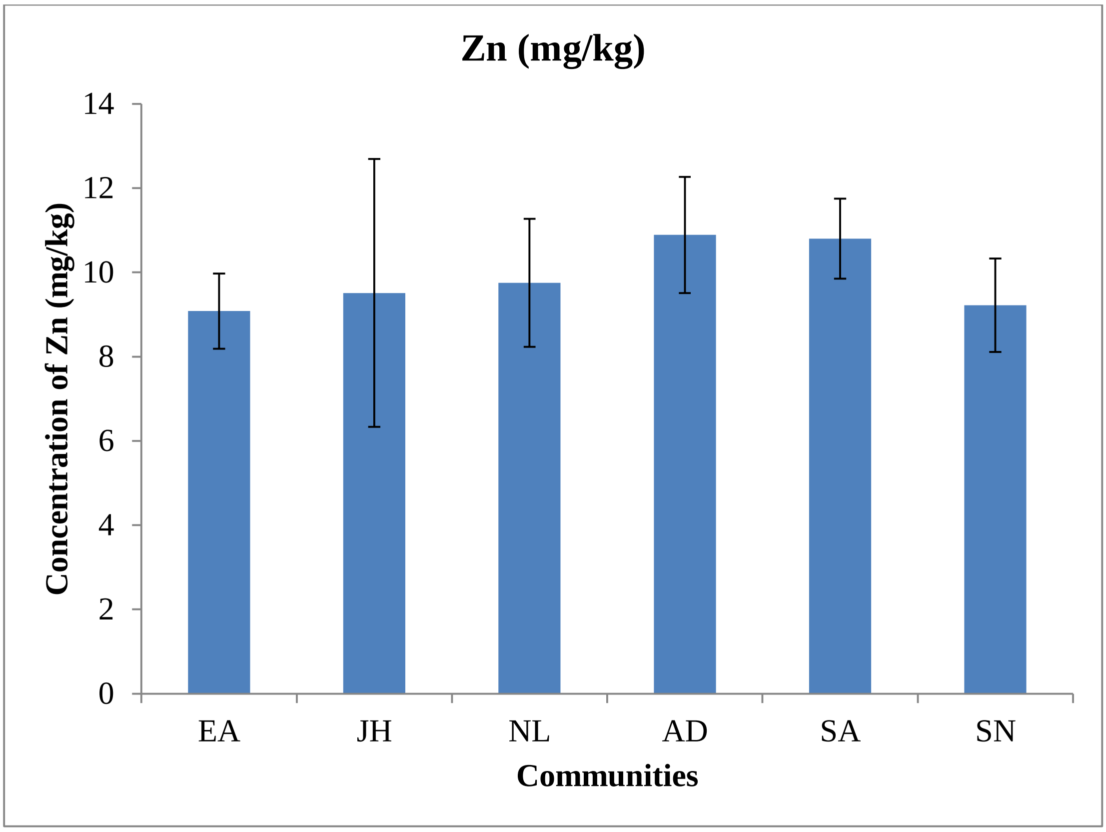


EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.11 Concentration of selenium (Se) in plant

4.2.3.6 Concentration of zinc in plant

The concentrations of zinc in the plant leaves among the communities showed significant difference (p<0.05). The mean concentrations of zinc ranged from 9.08 to 10.89 mg/kg. Figure 4.12 shows the mean concentrations of zinc in the plant leaves analysed. The lowest concentration was recorded at EA whereas the highest was recorded at AD.



EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Figure 4.12 Concentration of zinc (Zn) in plant

4.3 Contamination Assessment

4.3.1 Enrichment Factor

The mean values of enrichment factor of soils at 0-15 cm and 15-30 cm are presented in Table 4.6 and 4.7 respectively.

Table 4.6 Enrichment Factor of soil at 0-15 cm

Communities	As	Cu	Hg	Pb	Se	Zn
EA	2.548	0.0124	1.606	1.059	49.2024	0.0817
JH	3.267	0.0023	ND	0.999	45.053	0.0443
NL	7.686	0.0329	1.574	1.277	50.570	0.0912
AD	4.158	0.0045	1.759	0.850	45.463	0.0965
SA	11.240	0.0187	0.3415	1.148	40.356	0.0458
SN	2.465	0.0359	ND	1.489	12.449	0.0599
Min	2.465	0.0023	ND	0.850	12.449	0.0443
Max	11.240	0.0359	1.758	1.489	50.570	0.0965
Mean	**5.227**	**0.0178**	**0.880**	**1.137**	**40.516**	**0.0699**
SD	3.214	0.0129	0.777	0.205	12.971	0.0209

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

The values of enrichment factor (EF) for As, Cu, Hg, Pb, Se, and Zn in the surface soils (0-15 cm) of the study area ranged from 2.47 to 11.24, 0.002 to 0.036, 0.00 to 1.76, 0.85 to 1.49, 12.45 to 50.57, and 0.04 to 0.09 with mean values of 5.23, 0.018, 0.88, 1.14, 40.52, and 0.07 respectively (Table 4.6). The mean values of enrichment factor in the surface soils (0-15 cm) increased in the order of Cu<Zn<Hg<Pb<As<Se.

Table 4.7 Enrichment Factor of soil at 15-30 cm

Communities	As	Cu	Hg	Pb	Se	Zn
EA	3.167	0.0106	3.012	0.989	47.789	2.011
JH	5.362	0.0531	ND	1.173	45.189	1.955
NL	7.408	0.0141	0.258	1.270	49.430	2.954
AD	2.571	0.0124	1.701	0.837	47.242	1.608
SA	7.263	0.0263	0.156	1.005	23.529	1.488
SN	3.310	0.0414	ND	1.532	17.784	2.131
Min	2.571	0.0106	ND	0.837	17.784	1.488
Max	7.409	0.0531	3.012	1.532	49.430	2.954
Mean	**4.847**	**0.0264**	**0.854**	**1.135**	**38.494**	**2.025**
SD	1.959	0.0159	1.131	0.225	12.781	0.473

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

Similarly, the EF value of As, Cu, Pb, Se, and Zn in the subsoil (15–30 cm) ranged from 2.57 to 7.41, 0.011 to 0.053, 0.00 to 3.01, 0.84 to 1.53, 17.78 to 49.43, and 1.49 to 2.95 with mean values of 4.83, 0.026, 0.85, 1.13, 38.49, and 2.02 respectively (Table 4.7). The mean values of EF in the subsoil (15–30 cm) increased in the order of Cu<Hg<Pb<Zn<As<Se.

4.3.2 Geaoaccumulation Index (I_{geo})

The mean values of geoaccumulation index (I_{geo}) in the surface soil (0-15 cm) and subsoil (15-30 cm) are presented in Table 4.8 and 4.9 respectively.

Table 4.8 Geoaccumulation index (I_{geo}) of soil at 0–15 cm

Communities	As	Cu	Hg	Pb	Se	Zn
EA	-1.549	-4.539	-2.219	-2.445	1.523	-1.313
JH	-1.290	-6.884	-	-2.658	1.393	-2.025
NL	0.125	-4.903	-5.344	-2.124	1.562	-0.971
AD	-0.969	-7.089	-4.952	-2.720	1.410	-1.011
SA	0.215	-4.154	-6.0914	-2.354	0.943	-2.136
SN	-1.756	-2.718	-	-2.184	-0.308	-1.882
Min	-1.756	-7.089	-6.091	-2.720	-0.308	-2.136
Max	0.215	-2.718	0	-2.123	1.562	-0.971
Mean	**-0.871**	**-5.048**	**-3.101**	**-2.414**	**1.087**	**-1.556**
SD	0.7746	1.530	2.497	0.2216	0.656	0.476

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

The geoaccumulation indices (I_{geo}) of soils at 0–15 cm are presented in Table 4.8. The I_{geo} values of arsenic ranged from -1.756 to 0.215 with a mean value of -0.871. Copper ranged from -7.089 to -2.719 with a mean value of -5.048. Mercury ranged from -6.091 to 0.000 with a mean value of -3.101. Lead ranged from -2.720 to -2.124 with a mean value of – 2.414. Selenium ranged from -0.309 to 1.5he 62 with a mean value of 1.087. Zinc ranged from -2.136 to -0.971 with a mean value of -1.556. The mean values of (I_{geo}) in increased in the order of Cu<Hg<Pb<Z n<As<Se.

Table 4.9 Geoaccumulation Index (I_{geo}) of soils at 15-30 cm

Communities	As	Cu	Hg	Pb	Se	Zn
EA	-1.375	-4.994	-3.002	-0.072	1.472	-1.731
JH	-0.735	-4.577	-	0.119	1.401	-1.589
NL	0.027	-6.266	-3.289	0.297	1.526	-0.946
AD	-1.615	-4.844	-5.116	-0.247	1.462	-1.836
SA	-0.556	-3.454	-5.623	-0.010	0.136	-1.993
SN	-1.150	-2.484	-	0.3426	0.140	-1.525
Min	-1.615	-6.267	-5.623	-0.247	0.136	-1.993
Max	0.028	-2.484	-	0.3426	1.526	-0.946
Mean	**-0.901**	**-4.437**	**-2.838**	**0.071**	**1.023**	**-1.603**
SD	0.549	1.199	2.209	0.206	0.626	0.332

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi

The geoaccumulation indices (I_{geo}) of soil at 15–30 cm are presented in Table 4.9. The I_{geo} values of arsenic ranged from -1.615 to 0.028 with a mean value of -0.901. Copper ranged from – 6.267 to -2.484 with a mean value of -4.437. Mercury ranged from -5.623 to 0.000 with a mean value of -2.839. Lead ranged from -0.248 to 0.347 with a mean value of 0.071. Selenium ranged from 0.136 to 1.527 with a mean value of 1.023. Zinc ranged from -1.994 to -0.946 with a mean value of -1.604.The mean values of (I_{geo}) increased in the order of Cu<Hg< Zn<As<Pb<Se.

4.3.3 Contamination Factor and Pollution Load Index

The mean values of the contamination factor and pollution index of soils at 0-15 cm and 15-30 cm are presented in Table 4.10 and 4.11 respectively.

Table 4.10 Contamination Factor and Pollution Load Index at 0–15 cm

Communities	As	Cu	Hg	Pb	Se	Zn	PLI
EA	0.557	0.083	0.016	1.608	4.316	0.695	0.0006
JH	0.714	0.016	-	1.518	3.952	0.377	0.0050
NL	1.681	0.220	0.015	1.939	4.436	0.776	0.0060
AD	0.909	0.029	0.017	1.291	3.988	0.822	0.0003
SA	2.458	0.125	0.003	1.744	3.540	0.389	0.0004
SN	0.539	0.239	-	2.262	1.092	0.510	0.0380
Min	0.539	0.016	-	1.291	1.092	0.377	0.0003
Max	2.458	0.239	0.017	2.262	4.436	0.822	0.0380
Mean	**1.143**	**0.119**	**0.009**	**1.727**	**3.554**	**0.595**	**0.0084**
SD	0.703	0.086	0.008	0.310	1.138	0.178	0.0134

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi,

PLI = Pollution Load Index

The values for contamination factor (CF) of soils at 0–15 cm are presented in Table 4.10. The CF values of arsenic ranged from 0.539 to 2.458 with a mean value of 1.14. The CF values of copper ranged from 0.016 to 0.239 with a mean value of 0.119. Mercury also ranged from 0.000 to 0.017 with a mean value of 0.009. The CF value of lead ranged from 1.292 to 2.260 with a mean value of 1.727. Selenium ranged from 1.092 to 4.436 with a mean value of 3.554. The CF value of zinc ranged from 0.377 to 0.822 with a mean value of 0.595. The mean values of CF at 0-15 cm increased in the order of Hg<Cu<Zn<As<Pb<Se. All the sampling sites recorded PLI values less than 1.0.

Table 4.11 Contamination Factor and Pollution Load Index at soil 15-30 cm

Communities	As	Cu	Hg	Pb	Se	Zn	PLI
EA	0.693	0.071	0.029	1.503	4.192	0.545	0.0008
JH	1.172	0.355	-	1.783	3.964	0.530	0.3120
NL	1.620	0.095	0.003	1.929	4.336	0.801	0.0005
AD	0.562	0.083	0.017	1.271	4.144	0.436	0.0003
SA	1.588	0.176	0.002	1.527	2.064	0.404	0.0001
SN	0.724	0.277	-	2.327	1.56	0.578	0.0840
Min	0.562	0.071	-	1.272	1.56	0.404	0.0001
Max	1.620	0.355	0.029	2.327	4.336	0.801	0.3120
Mean	**1.060**	**0.176**	**0.008**	**1.723**	**3.376**	**0.549**	**0.0663**
SD	0.428	0.107	0.011	0.342	1.122	0.128	0.1140

EA = Atuabo, JH = Half Assini, NL = Lower Axim, AD = Dixcove, SA = Shama, SN = Takoradi,

PLI= Pollution Load Index

The values for contamination factors (CF) of soils at 15–30 cm are presented in Table 4.11. The CF values of arsenic ranged from 0.562 to 1.620 with a mean value of 1.06. The CF value of copper ranged from 0.071 to 0.355 with a mean value of 0.176. Mercury also ranged from 0.000 to 0.029 with a mean value of 0.008. The CF value of lead ranged from 1.272 to 2.327 with a mean value of 1.723. Selenium ranged from 1.560 to 4.336 with a mean value of 3.377. The CF value of zinc ranged from 0.404 to 0.801 with a mean value of 0.549. The mean values of CF at 15-30 cm increased in the order of Hg<Cu<Zn<As<Pb<Se. All the sampling sites recorded PLI values less than 1.0.

4.4 Correlation of heavy metals concentration and physicochemical properties

Pearson's product of correlation coefficient was used to determine the relationship between the physicochemical properties and heavy metal concentration of water and soil samples. For correlation significance, the criteria value of probabilities (p<0.05 and

$p<0.01$) was used. At 0–15 cm, strong positive correlation was established between EC/pH, As/pH, Cu/EC, Hg/As, Pb/Cu. Similarly, strong negative correlation was established between Se/Hg, and Zn/Hg. Moderate correlation was established between As/EC, Cu/pH, Pb/pH, Pb/EC, Se/Cu, Se/Pb, and Zn/Se (Table 4.12). Correspondingly, at 15–30 cm, strong positive correlation was established between EC/pH and As/pH. Strong negative correlation was also established between Pb/Hg, Se/Cu, and Zn/Hg. Likewise, moderate correlation was also established between As/EC, Hg/Cu, Zn/EC, Zn/Pb and Se/Hg (Table 4.13).

The water samples analysed in the wet season recorded strong correlation between TDS/pH, BOD/pH, BOD/EC, BOD/TDS, salinity/BOD, temperature/DO, As/temperature, Hg/Cu, Pb/salinity, Se/As, Se/As, Zn/As, and Zn/Se. Also, strong negative correlation was noticed between DO/pH, DO/EC, DO/TDS, BOD/DO, temperature/pH, temperature/BOD, As/BOD, Hg/As, Se/pH, Se/BOD, Se/Hg, Se/Pb, Zn/BOD, Zn/Hg, Zn/Pb. Positive moderate correlation was established between EC/pH, Cu/DO, Pb/EC, Pb/TDS, Pb/BOD, Pb/Hg, and Zn/temperature whereas negative moderate correlation was noted between temperature/EC, temperature/TDS, temperature/salinity, As/pH, Cu/EC, Cu/TDS, Pb/As, Se/EC, Se/TDS, Se/salinity. Se/Cu, Zn/pH, Zn/EC, Zn/TDS, and Zn/salinity (Table 4.14). Moreover, water samples in the dry season recorded strong positive correlation between TDS/EC, temperature/TDS, salinity/BOD, As/pH, Hg/BOD, Pb/DO, Se/BOD, Se/salinity, and Se/Hg. Furthermore, strong negative correlation was also observed between salinity/pH, As/salinity, Hg/DO, Se/pH, Zn/EC, Zn/TDS and Zn/temperature. Moderate correlation was also established between temperature/EC, Hg/TDS, Hg/salinity, EC/pH, BOD/pH, BOD/DO, As/EC, As/BOD, Pb/BOD, Se/DO, Se/As, and Se/Pb (Table 4.15).

Table 4.12 Pearson's correlation coefficient between physicochemical parameter and heavy metals content at soil depth 0–15 cm.

	pH	EC	As	Cu	Hg	Pb	Se	Zn
pH	1.000							
EC	0.809	1.000						
As	0.763	0.588	1.000					
Cu	0.659	0.753	0.187	1.000				
Hg	0.297	0.097	0.809	0.012	1.000			
Pb	0.519	0.527	0.059	0.946**	0.149	1.000		
Se	0.131	-0.112	0.255	-0.559	-0.921	-0.698	1.000	
Zn	-0.014	0.248	-0.206	-0.085	-0.957*	-0.343	0.515	1.000

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

Table 4.13 Pearson's correlation coefficient between physicochemical parameter and heavy metals content at soil depth 15–30 cm.

	pH	EC	As	Cu	Hg	Pb	Se	Zn
pH	1.000							
EC	0.851*	1.000						
As	0.741	0.515	1.000					
Cu	0.362	0.310	0.211	1.000				
Hg	-0.330	-0.232	-0.151	0.504	1.000			
Pb	0.154	0.302	0.138	0.489	-0.709	1.000		
Se	-0.157	-0.091	-0.056	-0.972**	-0.561	-0.492	1.000	
Zn	0.451	0.606	0.335	-0.209	-0.817	0.566	0.324	1.000

*Correlation is significant at the 0.05 level (2-tailed)

**Correlation is significant at the 0.01 level (2-tailed)

Table 4.14 Pearson's correlation coefficient between physicochemical parameter and heavy metals of water in the wet season

	pH	EC	TDS	DO	BOD	Salinity	Temp	As	Cu	Hg	Pb	Se	Zn
pH	1.000												
EC	0.611	1.000											
TDS	0.611	0.999**	1.000										
DO	-0.767	-0.959*	-0.958*	1.000									
BOD	0.836	0.877	0.878	-0.879	1.000								
Salinity	0.493	0.986*	0.986*	-0.898	0.840	1.000							
Temp	-0.983*	-0.634	-0.635	0.751	-0.894	-0.538	1.000						
As	-0.656	-0.429	-0.431	0.398	-0.786	-0.426	0.779	1.000					
Cu	-0.335	-0.502	-0.501	0.635	-0.201	-0.409	0.193	-0.419	1.000				
Hg	0.169	0.042	0.044	0.084	0.394	0.109	-0.337	-0.849	0.821	1.000			
Pb	0.015	0.623	0.624	-0.384	0.556	0.737	-0.159	-0.514	0.250	0.563	1.000		
Se	-0.950	-0.504	-0.506	0.478	-0.855	-0.513	0.974	0.995	-0.516	-0.918	-0.790	1.000	
Zn	-0.551	-0.592	-0.593	0.492	-0.836	-0.623	0.691	0.954*	-0.360	-0.825	-0.744	0.990	1.000

*Correlation is significant at the 0.05 level (2-tailed) **Correlation is significant at the 0.01 level (2-tailed)

Table 4.15 Pearson's correlation coefficient between physicochemical parameter and heavy metals content of water in the dry season

	pH	EC	TDS	DO	BOD	Salinity	Temp.	As	Hg	Pb	Se	Zn
pH	1.000											
EC	-0.557	1.000										
TDS	-0.135	0.784	1.000									
DO	0.035	0.238	-0.218	1.000								
BOD	-0.616	0.291	0.425	-0.787	1.000							
Salinity	-0.974*	0.388	0.041	-0.218	0.716	1.000						
Temp.	0.306	0.616	0.818	0.207	-0.167	-0.459	1.000					
As	0.987*	-0.678	-0.243	-0.057	-0.562	-0.926	0.159	1.000				
Hg	-0.444	0.322	0.586	-0.835	0.968*	0.535	0.041	-0.411	1.000			
Pb	-0.125	0.457	-0.026	0.972*	-0.640	-0.082	0.314	-0.236	-0.683	1.000		
Se	-0.751	0.160	0.130	-0.676	0.940	0.866	-0.464	-0.666	0.825	-0.562	1.000	
Zn	0.131	-0.857	-0.976*	0.001	-0.260	0.007	-0.884	0.262	-0.414	-0.191	0.017	1.000

*Correlation is significant at the 0.05 level (2-tailed)

CHAPTER FIVE

DISCUSSION

5.1 Physicochemical properties of samples

5.1.1 pH of water

The pH of water ranged from slightly acidic to slightly alkaline which fell within the WHO (2004b) permissible limit of 6.5-8.5 for drinking water. The pH value of water below 6.5 is regarded as acidic for human consumption because it can cause health issues such as acidosis and damage to the digestive and lymphatic system (Nkansah *et al.*, 2010). At lower pH, the solubility of toxic metals in water increases and makes it harmful for consumption. According to Kim *et al.* (2002) the pH of this range may be attributed to the effects of bicarbonates, geology of the area and the buffering capacity of the water system. This result is in line with those reported by Koffi *et al.* (2014) and Mohamed & Zahir (2013) in Ivory Coast and India respectively.

5.1.2 Electrical Conductivity and Total Dissolved Solids

The conductivity of water is a function of the concentration of dissolved ions and inorganic materials (APHA, 1995). The results of electrical conductivity were below the WHO (2004) limit of 1000 μS/cm. Although conductivity is not a human or aquatic health concern, it serves as an indication of other water quality problems (Dan *et al.*, 2014). The high values of electrical conductivity recorded could be attributed to sea water intrusion because of proximity of the water sources to the ocean. The values of electrical conductivity recorded in this study is similar to those found by Gyamfi *et al.* (2012) in some selected suburbs of Accra, Ghana.

Total dissolved solids (TDS) of water measures the amount of inorganic and organic substances dissolved in water. The values of TDS measured at all sampling sites were below the WHO (2004) permissible limit of 1000 mg/L. The TDS value of water close to 600 mg/L is acceptable whereas those greater than 1000 mg/L is unpalatable for human consumption (Apau *et al.*, 2014). According to WHO (1996) the concentration of TDS in water from natural sources varies from 30 mg/L to 600 mg/L depending on the solubility of minerals in different geological regions. The results of TDS in this study is similar to those reported by Amfo-Otu *et al.* (2012) in the Ga East Municipality of Ghana. The high positive correlation between EC and TDS implies that, an increase in EC causes an increase in TDS which shows a direct relationship between the variables.

5.1.3 Dissolved Oxygen and Biochemical Oxygen Demand

Dissolved oxygen (DO) is the amount of gaseous oxygen dissolved in water. The DO in water is a very important parameter in water quality because it serves as an indicator of the physical, chemical and biological activities of the water body (Manikannan *et al.*, 2011). The DO values measured were below the WHO standard of 7.5 mg/L. The presence of high concentration of organic matter, dissolved gases and domestic effluents leaching into the water system decreases the oxygen content of water. High salinity and temperature is known to affect the dissolution of oxygen in water bodies (Manikannan *et al.*, 2011). The DO values recorded in this study was lower than those reported by Garg *et al.* (2008) at Bharatpur area, India.

Biochemical oxygen demand is used to measure the amount of biochemically degradable organic matter present in water. According to Oluyemi *et al.* (2010), BOD values less than 6 mg/L suggests that the water is least polluted with organic matter.

The high negative correlation between DO and BOD implies that a decrease in the value of DO causes an increase in the values of BOD and vice versa, which indicates some source of water pollution.

5.1.4 Salinity and Temperature

Salinity is defined as the amount of dissolved salt in a body of water. The mean values of salinity recorded in the wet season were closer to the WHO limit of 200 mg/L of dissolved salts. On the contrary, the dry season was higher than the permissible limit. The high levels of salinity in the dry season may be attributed to high surface evaporation, low rate of water flow, decrease in water level and sea water intrusion (Dan *et al.*, 2014). This results is contrary to those reported by Manikannan *et al.* (2011).

Temperature may also be influenced by the depth of water, season, groundwater influx and air circulation as well as the time of sampling (Peirce *et al.*, 1998). These results agree with those found by Koffi *et al.* (2014) in Ivory Coast.

5.2. Heavy metals

5.2.1 Heavy metals in water

The concentration of arsenic in groundwater at all the sampling sites was below the WHO (2004b) permissible limit of 10 µg/L. This result is contrary to those reported by Mukherjee *et al.* (2006) who found arsenic to be in the range of 1 to 64 µg/L at Obuasi and Bolgatanga in Ghana. They attributed the high concentration of arsenic in water to the presence of arsenopyrites and pyrites in the rock basement of the area. According to Bhattacharya *et al.* (2007), arsenic in groundwater has been detected in some countries which exceeded the WHO guideline value of 10 µg/L.

Copper enters the water system through mineral dissolution, industrial effluents or use of pesticides (Gyamfi *et al.*, 2012). The amount of copper detected in water at all sampling points was below the WHO permissible limit of 2000 µg/L. Gyamfi *et al.* (2012) reported higher values of Cu ranging from 3 to 308 µg/L than those obtained in this study which were also below the guideline values. However, some amount of copper are required for metabolism and the synthesis of haemoglobin, myoglobin, cytochromes and several enzymes (Maughan, 1999) whereas high consumption of copper may lead to neurological complications, hypertension, liver and kidney problems (Krishna & Govil, 2004).

Lead naturally occurs in lead sulphide and other minerals. The concentration of lead in water at all sites exceeded the WHO (2004b) permissible limits of 10 µg/L. Hence, the consumption of water can pose a significant risk to the consumers. The findings of lead in water which ranged from 90 to 200 µg/L by Apau *et al.* (2014) were higher than those reported in this study. Lead is known to induce a broad range of physiological, biochemical, and behavioural dysfunction in human and animals which affects the central and peripheral nervous system, haemopoietic system, cardiovascular system, kidney, and liver (Hsu & Leon, 2002).

Zinc is an essential element required by human for optimum growth and development. The WHO permissible limit of zinc in drinking water is 3000 µg/L. The concentration of zinc fell below this limit thus suitable for human consumption. Gyamfi *et al.* (2012) recorded mean values of Zn ranging from 108 to 1876 µg/L which was higher than those reported in this study but below the recommended limit. The presence of high amount of zinc in water may cause a bitter taste and opalescence in water.

Mercury is a naturally occurring metal which occurs in trace amount in water, soil and rocks. It is volatile in nature which is released into the atmosphere through natural degassing of the earth crust. The most important anthropogenic sources of mercury pollution in the environment are urban discharge, agricultural materials, mining, combustion and industrial discharge (Zhang & Wong, 2007). Mercury content in water samples analysed were below the WHO (2004b) permissible limit of 1 µg/L hence suitable for consumption. Similar observations have been reported by Adjei-Kyereme *et al.* (2015) who found the concentration of Hg in water to be less than 1.0 µg/L.

The amount of selenium in water at all sampling sites were below the WHO (2004b) permissible limits of 10 µg/L although significant difference were observed between the wet and dry season.

The level of heavy metals concentration in water samples analysed in the study area increased in the order of $Hg<Se<As<Zn<Cu<Pb$.

5.2.2 Heavy metals in soil

Arsenic occurs naturally in the earth's crust and is detected at low concentrations in virtually all environmental matrices (ATSDR, 2000).The concentration of arsenic in all soil samples were below the WHO/FAO (2001) permissible limit of 20.00 mg/kg. Antwi-Agyei *et al.* (2009) recorded high values of arsenic in soil ranging from 84.53 to 1711 mg/kg. They attributed the high values of As to the presence of pyrites in the bedrock of the area.

Similarly, the concentration of Cu recorded in soils at the study area was below the WHO/FAO (2001) permissible limit of 100 mg/kg. These values recorded are within the normal range required by plants in the natural soil concentration. The concentration of copper recorded in this study was lower than 47.0 mg/kg reported by Fisseha *et al.*

(2008) and 22.14 mg/kg by Babatunde *et al.* (2014) around an oil depot at Jos in Nigeria.

Lead is an environmental and industrial pollutant that has been detected in almost all phases of environmental and biological systems (Hsu & Leon, 2002). The concentration of lead in soil samples of the study area was below the WHO/FAO (2001) permissible limit of 50 mg/kg. However, substantial amount of lead concentration was recorded at the study area indicating some anthropogenic source of lead pollution in the environment. The values recorded in this study were higher than 14.13 mg/ kg and 13.53 mg/kg recorded by Babatunde *et al*. (2014).

The zinc content of soils analysed were below the WHO/FAO (2001) permissible limit of 300 mg/kg. However, the values of zinc recorded in this study are within the normal range of zinc required by plants. The concentration of zinc observed in this study was lower than 237.96 mg/kg reported by Okunola *et al.* (2007). A similar study conducted by Srinivas *et al.* (2009) showed that zinc concentration in the industrial area was 49.7 mg/kg and 32.20 mg/kg in the rural area.

The concentration of mercury recorded at the study area fell below the WHO/FAO (2001) permissible limit of 2.00 mg/kg. The mean value of mercury (0.141 mg/kg) recorded in soils by Kpan *et al.* (2014) was higher than those detected in this study. Mercury is an environmental pollutant which induces severe alteration in the body tissue and causes a wide range of adverse health effects.

The mean values of heavy metal concentration recorded at 0-15 cm (topsoil) and 15-30 cm (subsoil) increased in the order of Hg<Se<As<Cu<Pb<Zn.

5.2.3 Heavy metals in plants

The WHO/FAO (2007) guideline value of arsenic in plant is 0.15 mg/kg. The mean concentration of arsenic in the wild plant analysed was above the permissible limit recommended by WHO/FAO. High concentration of arsenic in plants can cause nausea, vomiting, diarrhoea, cough, headache, cardiovascular disease etc. to animals especially livestock.

The mean concentration of cadmium recorded in this study was above the WHO/FAO (2007) permissible limit of 0.20 mg/kg. The concentration of Cd reported in this study was higher than those reported by Nazir *et al.* (2015). The high concentration of Cd could be as a result of domestic effluents or atmospheric deposition resulting from industrial activities from the surrounding areas. High levels of cadmium causes both acute and chronic poisoning, adverse effect on kidney, liver, vascular and immune system (Jabeen *et al.*, 2010) and gastrointestinal and reproductive effects (Maobe *et al.*, 2012).

According to Taber (2009) normal Cu content in plants should range from 2 - 20 mg/kg and WHO/FAO (2007) recommended a guideline value of 40 mg/kg. The concentration of copper recorded in this study fell within the normal range of Cu required by plants for growth and development. However, the concentration of Cu recorded in this study was below the permissible limit set by WHO/FAO. Odai *et al.* (2008) reported the concentration of copper ranging from 16.17 to 90.33 mg/kg in vegetables in a dump soil in Kumasi.

The mean concentration of lead in the wild plant analysed, exceeded the WHO/FAO (2007) guideline value of 5 mg/kg. The concentration of lead in the leaves of the wild plants analysed was higher than those of *Xanthium strumarium, Dodonae viscosa,* and

Tamarix aphyda recorded by Nazir *et al.* (2015) and was below the permissible limit. The high concentration of lead found in the leaves of the wild plants may be attributed to the release of domestic effluent containing lead, automobile exhaust, industrial emissions, smoke and dust emissions from gas and petrol fired stations. The high level of lead in plants can cause anaemia, headache, brain damage, and nervous system disorder to humans and animals (Rehman *et al.*, 2013).

The mean concentrations of zinc in plants were below the permissible limits of 60 mg/kg recommended by WHO/FAO (2007). A similar study conducted by Shah *et al.* (2013) reported higher values of Zn as compared to those reported in this study. Zinc is one of the essential trace element which plays a vital role in physiological and metabolic processes of many living organism but can be harmful when it reaches higher concentration (Nazir *et al.*, 2015).

5.3 Contamination Assessment

5.3.1 Enrichment Factor

In order to evaluate the natural and anthropogenic sources of heavy metals, enrichment factor (EF) was calculated to determine the extent of pollution. The enrichment factor computation at 0–15 cm for Cu, Hg, Pb, and Zn was less than 2 according to the contamination categories of EF indicating minimal to deficient enrichment. However, As and Se exhibited some degree of contamination. The EF values of As at EA, SN, JH and SA showed significant enrichment of As. However, the mean EF value of As revealed that the soils were enriched with As. The mean EF value of selenium among the communities was extremely high except SN which showed significant enrichment. Similarly, the mean EF values of Cu, Hg, and Pb at 15–30 cm indicated deficient to minimal enrichment. However, EA showed moderate enrichment of mercury. The mean EF value of As and Zn at 15-30 cm showed moderate enrichment. At 15-30 cm, all the samples showed extremely high enrichment of Se except SN and SA which showed significant enrichment and very high enrichment respectively. Basically, as the EF values of heavy metals increases the contribution of anthropogenic origin also increases (Sutherland *et al.*, 2000). According to Zhang and Lui (2002), the EF value of 0.5 – 1.5 indicates that the presence of metals are as a result of crusted materials or natural processes whereas EF values greater than 1.5 suggest the source is more likely to be anthropogenic.

5.3.2 Geoaccumulation Index (I_{geo})

The mean I_{geo} values of As, Cu, Hg, Pb, and Zn at 0–15 cm were practically unpolluted among the communities. However, the mean I_{geo} of Se showed moderate pollution. On the other hand, at 15–30 cm the level of As, Cu, Hg, and Zn in soils were practically uncontaminated. The mean I_{geo} values of Pb showed unpolluted to moderate pollution. The mean I_{geo} of Se was registered within class 3 indicating moderate pollution. The geoaccumulation index (I_{geo}) of heavy metals of the study area revealed that 75% of the elements belonged to class 1 (practically unpolluted), 15% belonged to class 2 (unpolluted to moderately polluted) and, 10% belonged to moderate pollution.

5.3.3 Contamination Factor and Pollution Load Assessment

The mean contamination factor (CF) values of Cu, Hg, and Zn at 0-15 cm exhibited low contamination. The CF values of As among the communities were less than 1 indicating low contamination except NL and SA which showed moderate and considerable contamination respectively. However, the mean CF value of As indicated considerable contamination. Similarly, the mean CF value of Zn also showed moderate contamination. Additionally, the mean CF value of Se showed considerable contamination. On the other hand, at 15–30 cm, the mean CF values of Cu, Hg, and Zn showed low contamination. The mean CF value of As and Pb at the study area showed moderate contamination. The mean CF of Se also indicated considerable contamination.

The pollution load index (PLI) is used to effectively compare whether the study area has suffered contamination or not. The PLI was used to measure the degree of contamination. However, PLI of the study area was less than 1 indicating low level of pollution. The low value of PLI is an indication of the low or minimal level of pollution at the study area.

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Conclusions

The physiochemical parameters of water and soil samples were examined to evaluate the quality of drinking water. The results of the physicochemical parameters of water samples revealed that most of the water quality parameters were within the World Health Organization limits with the exception of biochemical oxygen demand in the dry season which was relatively higher indicating some source of pollution.

The concentration of the heavy metals in water was below the WHO standards except lead which exceeded the permissible limit. The concentration of heavy metals in water increased in the order of Hg<Se<As<Zn<Cu<Pb. Similarly, the concentration of the studied metals in the soil revealed that they were below the WHO/FAO standards which indicate the fact that all the metals analysed were within their background values. The concentration of heavy metals at 0-15 cm and 15-30 cm of the study area increased in the order of Hg<Se<As<Cu<Pb<Zn. Additionally, the concentration of As, Cd and Pb in plant samples analysed exceeded the permissible limits of WHO/FAO except Cu, Se and Zn which were below the standards. The high concentration of As, Cd and Pb in the wild plants can be attributed to the fact the plants bioaccumulate these metals into their tissues from the soil over a period of time.

The heavy metals concentration of soils was used to calculate the enrichment factor, geoaccumulation index, contamination factor and pollution load index of soils. The contamination assessment methods used in this study showed that heavy metal contamination in soil at the study area was generally low.

6.2 Recommendations

Considering the findings of this study, the following recommendations are made:

1. Although the metal loading of the study area is presently low, further investigations should be conducted periodically to assess the level of heavy metals in the marine environment of the Western Region in order to assess health risk of the communities.
2. Research should be conducted to assess the socioeconomic effect of oil drilling on the coastal communities.
3. The government and regulatory agencies should ensure that the operations or activities of the oil mining companies are periodically checked to ensure that standards are adhered, to protect and safeguard the marine environment.
4. There should be effective collaboration between policy makers and regulatory bodies to ensure proper planning and monitoring activities of the oil and gas industries.

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APPENDICE

Appendix 1 Sampling sites showing their GPS coordinates

Sampling sites	GPS coordinates
EA1	(4º 59' 7.296"N, 2º 33' 10.332"W)
EA2	(4º 59' 0.636"N, 2º 33' 22.608"W)
EA3	(4º 58' 54.228"N, 2º 33' 26.352"W)
EA4	(4º 58' 47.136"N, 2º 33' 27.288"W)
EA5	(4º 58' 49.152"N, 2º 33' 10.872"W)
JHI	5º 2' 54.456"N, 2º 53' 20.76"W)
JH2	(5º 2' 56.724"N, 2º 53' 12.084"W)
JH3	(5º 2' 58.002"N, 2º 48' 46.62"W)
JH4	(5º 4' 19.668"N, 2º 52' 34.932"W)
JH5	(5º 3' 31.896"N, 2º 52' 51.276"W)
NL1	(4º 51' 53.28"N, 2º 14' 34.116"W)
NL2	(4º 51' 57.312"N, 2º 14' 30.408"W)
NL3	(4º 51' 44.388"N, 2º 14' 23.856"W)
NL4	(4º 51' 50.364"N, 2º 14' 17.52"W)
NL5	(4º 51' 44.496"N, 2º 14' 10.932"W)
AD1	(4º 28' 30.252"N, 1º 34' 12.108"W)
AD2	(4º 28' 42.276"N, 1º 34' 18.588"W)
AD3	(4º 29' 39.408"N, 1º 34' 31.224"W)
AD4	(4º 47' 51.792"N, 1º 56' 38.472"W)
AD5	(4º 47' 51.792"N, 1º 56' 52.98"W)
SA1	(4º 51' 57.952"N, 2º 14' 30.505"W)
SA2	(4º 51' 44.836"N, 2º 14' 23.292"W)
SA3	(4º 51' 50.742"N, 2º 14' 17.185"W)
SA4	(4º 51' 44.705"N, 2º 14' 10.395"W)
SA5	(4º 51' 44.003"N, 2º 14' 10.481"W)
SN1	(4º 47' 51.510"N, 1º 56' 57.0.02"W)
SN2	(4º 47' 51.842"N, 1º 56' 52.182"W)
SN3	(4º 47' 51.821"N, 1º 56' 38.642"W)
SN4	(4º 47' 51.862"N, 1º 56' 52.886"W)
SN5	(4º 47' 51.018"N, 1º 56' 52.006"W)

Appendix 2 Summary of heavy metals concentration in soil at 0-15 cm

Communities	Descriptive statistics	As	Cu	Pb	Zn	Se	Hg
				(mg/kg)			
EA	Min	0.42	1.34	11.19	14.28	0.19	BDL
	Max	1.39	11.13	25.12	74.95	0.22	0.0049
	Mean	1.00	4.59	20.10	48.65	0.21	0.0013
	SD	0.36	3.64	5.23	21.13	0.01	0.002
JH	Min	0.46	0.33	11.07	22.36	0.18	ND
	Max	2.57	1..91	40.85	38.66	0.22	ND
	Mean	1.29	0.86	18.98	26.39	0.20	ND
	SD	0.71	0.57	11.15	6.18	0.016	ND
NL	Min	.2.29	0.05	20.40	44.64	0.21	BDL
	Max	3.91	46.51	27.97	65.87	0.24	0.004
	Mean	3.03	12.10	24.25	54.29	0.22	0.0012
	SD	0.71	17.38	2.70	8.95	0.012	0.0016
AD	Min	0.52	0.048	12.74	19.87	0.196	BDL
	Max	2.85	4.05	19.05	83.13	0.204	0.002
	Mean	1.64	1.64	16.14	57.51	0.199	0.001
	SD	0.88	1.55	2.59	20.65	0.003	0.0008
SA	Min	1.04	0.42	14.52	10.09	0.06	BDL
	Max	7.97	9.99	32.82	42.09	0.32	0.0006
	Mean	4.43	6.89	21.79	27.29	0.18	0.0003
	SD	3.01	3.34	7.58	12.61	0.10	0.0002
SN	Min	0.39	9.46	10.43	11.21	BDL	ND
	Max	2.09	21.18	65.80	76.86	0.10	ND
	Mean	0.97	13.20	28.28	35.71	0.06	ND
	SD	0.62	4.49	19.60	23.89	0.04	ND

Appendix 3 Summary of heavy metals concentration in soils at15-30 cm

Communities	Descriptive statistics	As	Cu	Pb (mg/kg)	Zn	Se	Hg
EA	Min	0.44	0.35	9.71	13.38	0.18	BDL
	Max	2.80	8.75	25.90	63.04	0.26	0.006
	Mean	1.25	3.91	18.78	38.18	0.20	0.002
	SD	0.81	2.81	5.52	20.11	0.03	0.001
JH	Min	0.74	0.44	12.95	22.82	0.19	ND
	Max	5.44	85.75	34.48	33.09	0.21	ND
	Mean	2.11	19.52	22.28	37.12	0.20	ND
	SD	1.71	33.26	9.51	12.91	0.006	ND
NL	Min	1.74	0.06	14.51	37.87	0.19	BDL
	Max	4.03	12.22	33.28	73.47	0.24	0.0008
	Mean	2.92	5.19	24.12	56.10	0.22	0.0002
	SD	0.95	5.43	7.09	13.27	0.02	0.0003
AD	Min	0.53	1.26	13.71	18.91	0.18	BDL
	Max	2.12	14.41	18.82	42.92	0.22	0.003
	Mean	1.01	4.56	15.89	30.52	0.20	0.001
	SD	0.58	4.99	1.87	8.16	0.015	0.0009
SA	Min	0.75	1.80	14.63	16.94	0.04	BDL
	Max	6.18	15.54	26.51	48.85	0.20	0.00030
	Mean	2.86	9.70	19.08	28.26	0.10	0.00013
	SD	2.46	5.30	4.41	11.18	0.07	0.00011
SN	Min	0.63	10.77	11.06	16.52	BDL	ND
	Max	2.09	19.97	63.39	64.27	0.14	ND
	Mean	1.30	15.23	29.08	40.46	0.08	ND
	SD	0.47	3.88	18.80	16.74	0.05	ND

Appendix 4 Summary of heavy metal concentration in plant samples

Communities	Descriptive statistics	As	Cd	Cu (mg/kg)	Pb	Zn	Se
EA	Min	0.85	12.21	0.69	80.02	7.89	1.42
	Max	24.74	21.12	5.83	95.64	10.65	1.69
	Mean	5.61	18.36	2.80	87.30	9.08	1.57
	SD	7.18	2.35	1.59	4.83	0.85	0.08
JH	Min	0.69	15.64	1.35	77.74	6.85	1.46
	Max	26.94	18.80	3.57	93.06	17.90	1.64
	Mean	6.31	17.89	2.59	87.27	9.51	1.56
	SD	8.06	1.03	0.73	4.64	3.02	0.06
NL	Min	0.87	14.46	1.87	75.46	7.84	1.25
	Max	2.63	19.78	6.72	99.52	12.73	1.67
	Mean	1.65	16.65	4.03	85.56	9.75	1.49
	SD	0.53	1.99	1.34	8.18	1.44	0.12
AD	Min	0.51	15.25	0.85	90.12	9.12	131
	Max	24.44	19.11	8.42	110.88	13.77	1.55
	Mean	3.58	16.89	3.30	100.91	10.89	1.42
	SD	6.99	1.12	2.15	7.02	1.31	0.08
SA	Min	0.55	17.47	1.30	86.76	9.25	1.35
	Max	2.67	20.88	3.57	98.90	11.89	1.64
	Mean	1.68	19.06	2.49	92.35	10.79	1.54
	SD	0.67	1.01	0.69	3.80	0.90	0.08
SN	Min	0.005	10.52	1.97	88.64	7.82	1.47
	Max	12.30	17.77	6.05	110.16	10.98	1.60
	Mean	4.19	16.04	3.79	97.02	9.22	1.54
	SD	3.40	2.04	1.21	5.84	1.06	0.04