

**KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY FACULTY OF
RENEWABLE NATURAL RESOURCES,
DEPARTMENT OF FISHERIES AND WATERSHED MANAGEMENT**

KNUST

**ASSESSMENT OF HEAVY METAL CONTAMINATION OF ROAD DEPOSITED
SEDIMENTS AND RIVER SEDIMENTS IN THE KUMASI METROPOLIS,
GHANA**



**BOAKYE-ACHEAMPONG, ENOCH
(BSc. HONS)**

OCTOBER, 2015

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GHANA**

**A THESIS SUBMITTED TO THE DEPARTMENT OF FISHERIES AND
WATERSHED MANAGEMENT, KWAME NKRUMAH UNIVERSITY OF
SCIENCE AND TECHNOLOGY IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE AWARD OF THE DEGREE OF MASTER OF
PHILOSOPHY (MPHIL) IN
AQUATIC RESOURCE MANAGEMENT**

**BOAKYE-ACHEAMPONG, ENOCH
(BSc. HONS)**

OCTOBER, 2015

Declaration

“I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the qualification of any other degree or diploma of a university or other institution of higher learning, except where due acknowledgement is made”

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Dedication

This work is dedicated to my Brother Kwadwo Owoahene Acheampong and my Uncles John Opoku Agyemang and Patrick Ofori Mensah for their financial support towards this programme of study.

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Abstract

This study was conducted to determine the levels of five (5) heavy metals (arsenic, cadmium, lead, copper and zinc) in and the effect of seasons on road-deposited sediments and river/ stream sediments of five major roads and adjacent water bodies in the Kumasi Metropolis. Samples were collected over two sampling periods that coincided with the rainy and dry seasons for heavy metal analysis. Road sediments along the sampled highways and major roads in Kumasi were highly contaminated with the studied heavy metals compared to background values, signifying an anthropogenic input most likely from the road-traffic environment. The ranges of the recorded heavy metal concentrations in the road-deposited sediments over the study period across the study sites were as follows; arsenic (3.30-87.80 mgkg⁻¹), cadmium (0.20-0.60 mgkg⁻¹), copper (0.16-630.10 mgkg⁻¹), lead (11.93-121.90 mgkg⁻¹) and zinc (11.80-160.30 mgkg⁻¹). The heavy metal concentrations in the river/stream sediments over the study period across the study sites were as follows; arsenic (46.73-298.40 mgkg⁻¹), cadmium (0.20-1.80 mgkg⁻¹), copper (11.80-1052.60 mgkg⁻¹), lead (0.20-620.20 mgkg⁻¹) and zinc (109.30-1045.10 mgkg⁻¹). The variations across the sites appear to be primarily due to site-specific attributes with the sites having higher traffic densities generally recording higher levels of the studied metals. The measured heavy metal levels of the road-deposited sediments and sediments from nearby rivers and streams showed a general trend; the concentrations were significantly higher ($p < 0.05$) in the river / stream sediments than in the road deposits. In terms of seasonality, higher metal concentrations were generally

recorded during the dry season than in the wet season. The calculated pollution load indices were generally indicative of sites with deteriorated quality as far as the studied metals are concerned. Frequent monitoring of road deposits and river sediments are necessary in order to detect and prevent cumulative consequences of heavy metal pollutants.

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List of Abbreviations and Units

AAS	Atomic Absorption Spectrophotometer
As	Arsenic
Cd	Cadmium
GESAMP	Group of Experts on Scientific Aspects of Marine Environmental Protection
H ₂ SO ₄	Sulphuric Acid
HCl	Hydrochloric Acid
HClO ₄	Perchloric Acid
HNO ₃	Nitric Acid
IQ	Intelligence Quotient
Pb	Lead
TOC	Total Organic Carbon
TN	Total Nitrogen
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
WHO	World Health Organisation
Zn	Zinc

CHAPTER 1

INTRODUCTION

1.1 Background

Pollution and contamination of the natural environment with heavy metals have become universal and continues to be on the increase. Consequently, heavy metal contamination has gained attention from both governmental and non-governmental organisations in order to reduce or prevent pollution of the different ecosystems. In cases where pollution has already occurred, the research focus has been on finding suitable and efficient methods of remediation (Pereira *et al.*, 2007).

Even when pollution is in terrestrial or aerial ecosystems, these pollutants sometimes find their way into aquatic ecosystems especially through surface runoff (Storm water). One of the important sources of contamination in the aquatic environment is from contaminants that are adsorbed to roadside sediments. Urban storm water quality might be heavily affected by sediments deposited along roads and polluted by these heavy metals (Saeed and Shaker, 2008). Contaminants can persist for many years in sediments in both freshwater and marine systems where they hold the potential to affect human health and the environment (Mackevičienė *et al.*, 2002).

Sediment and dust have been documented to contain high contaminants such as heavy metals as well as organic compounds (Chung and Lee, 2006). Catchments vary significantly in heavy metal concentrations and this might be

from natural sources or may include materials transported by water from surrounding soils, pollutants from dry and wet atmospheric deposition and biological materials from vegetation (Ewe *et al.*, 2006). Road deposited sediments can be examined by the equation of continuity, i.e. inputs, outputs, storage changes and their associated processes. Road surface sediment inputs may be from extrinsic sources including: biological inputs from leaf-fall, water transport material from surrounding soils, slopes by inter-rill, rill erosion process, dry and wet atmosphere depositions (Pal *et al.*, 2011). The rest could also be partially due to intrinsic sources including road surface and road paint degradation, vehicle wear (i.e. tyres, brake linings), vehicle fluids and particulate emissions (Sutherland and Tolosa 1999).

Sediments and dust transported and stored in the urban environment have the ability to provide considerable loadings of heavy metals to receiving waters and water bodies, particularly, with changing environmental conditions (Pereira *et al.*, 2007; Yisa, 2010). Sediments and dust with concentrated heavy metals could affect entire ecosystems (Lough *et al.*, 2005; Steiner *et al.*, 2007); high levels of heavy metal contamination also threatens ecosystem components or are likely to have long-term adverse effects on animals, plants and human beings (Barua *et al.*, 2011).

Environmental changes can be attributed to factors including urbanisation. Urbanisation is considered as one of the environmental changes confronting developing countries (Ramsar Convention Secretariat, 2007). As urban areas become densely populated, the environmental quality of the urban soil becomes

related to human health (Herath *et al.*, 2013). Heavy metal contamination and pollution in urban areas have for long been of concern to environmentalists and governments, due to their long biological half-lives and their non-biodegradable nature resulting in low rates of elimination from the human body. Particularly, increasing vehicular emissions due to rapid urbanisation and growth have become a major issue to deal with and its mobilisation into the biosphere has also become a vital process of geological recycling (Radha *et al.*, 1997). Odat and Alshammari (2011), Binggan and Linsheng (2010) and Prabal *et al.* (2011) all reported that, road deposited sediments come as a result of reactions between climates, anthropogenic activities by man, mother rock and formed under specific topographic and weather conditions within a certain time and affect the accumulation of heavy metals. That is, sediments containing these heavy metals can be highly influenced by certain factors including topographic and weather conditions. Moreover, the structure as well as the floristic composition of this road deposits sediment may also be influenced by various climatic conditions (Fagbote and Olanipekun, 2010).

1.2 Research Justification

Roads that do experience intense vehicular traffic and are lined with fuel filling stations have the potential to produce discharges of lead and cadmium beyond the minimum threshold of UNEP (2002) in road deposited sediment. Moreover, discharges from roads that also experience high vehicular traffic and with tyre repair shops and auto mechanic shops along the road also have the tendency to produce zinc, copper and lead above acceptable limits set by the UNEP (2002) in

urban soils, and urban road deposits (Binggan and Linsheng, 2010). Various studies have been done in Ghana including Addo *et al.* (2012) which found arsenic and lead to be higher than the background values of GESAMP (1982).

A lot of research has been conducted on heavy metals in Kumasi; mostly on some streams, in groundwater and in food. Principal streams such as Subin, Sisa and Aboabo produced lead and iron above the acceptable limit of WHO (1973) in the survey of water quality for irrigation and its implication for human health (Cornish, 1999). Agyemang *et al.* (2006) found lead, copper, zinc and cadmium were also above the minimum threshold of WHO (1973) in the surface water of Akyeamponmene at the Suame Magazine area of Kumasi, while Obiri-Danso *et al.* (2008) also established that, lead was above the minimum limit of WHO (2006) in groundwater at Boadi. Zelda (2009) and Darko (2010) have also reported lead and cadmium levels in food seasonings in Kumasi markets were higher than the acceptable threshold of WHO (2002).

Although, these researches have been conducted on heavy metals in Kumasi and its environs, there is a dearth in knowledge on heavy metals in road deposits and rivers sediments. No research has been conducted on the contribution of the transport sector to heavy metals deposits in roadside sediments and their relative contribution to heavy metal concentrations in streams and rivers. Principal roads within Kumasi Metropolis include Dr. Kwame Antwi Avenue, Dr. Osei Tuffour bypass, Osei Tutu II Blvd, Santasi-Bekwai and Maakro-Offinso roads. These have been lined up with tyre repair shops, auto mechanic shops, fuel filling

stations and also experience intense vehicular traffic and could be an important source of these contaminants in road-deposited sediments. Rivers such as Akos, Washi, Susuanso, Kwadaso and Bonkumfour are traversed by these roads. There is the likelihood of runoffs from road deposits with heavy metals contaminating these rivers and streams. Ghana Water Company Limited supplies most of the inhabitants of Kumasi and environs with water. Rivers and streams within Kumasi drain into the various reservoirs that Ghana Water Company Limited uses for drinking water production. Moreover, inhabitants of communities at the different portions of some of these rivers do fishing from these water bodies. Therefore, this research provides vital information on the heavy metals in road deposits and river/stream sediments within the Kumasi Metropolis of the Ashanti Region, Ghana.

1.3 Research Goal

This research seeks to contribute knowledge on the types and quantities of heavy metal deposition on the road side and in river sediments and provide information for best management of the environment in Kumasi. Moreover, this research will form the initial basis for development of an information base on road sediments quality within the Kumasi Metropolis.

1.4 Research Objectives and Hypotheses

1. To determine the levels of some heavy metals (arsenic, cadmium, copper, lead, zinc) in road deposited sediments and river sediments in the Kumasi Metropolis.

H₀: Concentrations of heavy metals in road and stream sediments within the Kumasi Metropolis are not greater than the natural sediment concentration.

2. To determine the seasonal variations in heavy metal concentrations in road deposited sediments and river sediments in the Kumasi Metropolis.

H₀: There are no seasonal differences in the concentration of heavy metals in road deposited sediments and in stream sediments within the Kumasi Metropolis



CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals and Sources

Metals exist naturally in the earth's crust, but the environmental concentrations are also affected heavily by man's activities. Sutherland and Tolosa (1999), Pagotto *et al.* (2001) and Yisa (2010) have all reported that, significant quantities of particulate matter can be attributed to anthropogenic sources such as abrasion of vehicular components and their exhaust emissions, foundry operations, industrial processes, incinerators- tyre and road surface wear and power plants. Moreover, other possible sources includes industrial effluents containing metals (Phuong *et al.*, 1998) industrial and municipal landfills leachates (Moodley *et al.*, 2007), and wastewater arising from settlements (Yisa *et al.*, 2011) and fuel filling stations (Shriadah, 1998). Another significant source of pollution is storm water runoff which removes large quantity of road deposits and its associated metals causing pollution threat to surface and sub-surface water resources (Singh, 2009). According to Santos *et al.* (2005), the most significant anthropogenic sources include industrial and petroleum sources.

Natural biological systems are increasingly affected by anthropogenic activities. It is difficult to find a river or any other water body whose natural regime has not been modified by man's activities. According to Ramsar Convention Secretariat (2007), urbanisation is identified as one of the environmental challenges confronting developing countries. Urbanisation, industrial activities as well as

higher exploitation of cultivable land have brought about an increase in the quantity of effluents and diversification in types of pollutants that reach rivers and other aquatic environments.

2.1.1 Environmental Pollution by Heavy Metals

Heavy metal pollution has become a persistent problem in many urban cities in the world today. As a result, large populations of people living in urban centres and its environs are exposed to an unnatural and unhealthy environment which may cause serious threats to human health as well as the environment. With the exception of natural and bedrock sources, most heavy metal pollutants are anthropogenic in origin (Kim *et al.*, 1998). When environmental pollution becomes visible, it often becomes too late to prevent chronic toxic effects; the initial stage of the process becomes impossible to notice and is later manifested after many years according to Alloway and Ayres (1998). Moreover, the introduction of toxic chemical substances into the environment may be transported by the air, water and living organisms and consequently become a part of the natural biogeochemical cycle and accumulate in the food chain (Gadzała-Kopciuch *et al.*, 2004).

The changes in the natural environment as a result of constant technological inputs results in deteriorating environmental quality and negatively affects ecosystem interactions. Some organisms are affected by these heavy metals at even at low concentrations. However, some heavy metals are very essential to the proper functioning of the human body. Uptake of essential elements by organisms from the environment is normally homeostatically-controlled, and

based on nutritional demand. The effects of heavy metals on organisms are manifested when regulating mechanisms break down as a result of either excess levels or insufficiency according to Duffus (2002).

2.1.2 Pollution of the Aquatic Environment with Heavy Metals

According to Rashed (2004), the main factor controlling the health and disease state of aquatic organisms is the quality of the aquatic environment. Heavy metals which enter the aquatic environment form ions which can react with constituents in the water or react and settle to the bottom with the sediments.

Water pollution is associated with discharge of effluents from agricultural drainage systems, municipal drains, factories to rivers, streams and sewage treatment plants. When the heavy metal concentrations are low, the aquatic systems are able to recover from any effects that occur, however, there are great hazardous effect to man and the ecosystem when there is accumulation of these heavy metals. In considering these sources of metals that flow into water bodies, the sources of heavy metals into aquatic ecosystems can be grouped under the following categories:

- **Natural Sources:** Heavy metals are found throughout the earth in rocks and soil and introduced into the water body through natural processes such as weathering and erosion (Prabal *et al.*, 2011).
- **Domestic Sources:** Usually domestic wastewater contains substantial quantities of metals which are often overlooked (Ewen *et al.*, 2006).

- **Agricultural Sources:** These include discharges from farmed lands/systems that contains fertilizer and pesticide residue which contain metals.
- **Industrial Sources:** These are effluents resulting from the processing of metal ores, finishing and plating of metals, manufacturing of metallic objects (Rashed, 2004).
- **Atmospheric Pollution:** Can be made up of particulate matter or acid rains containing metals (Binggan & Linsheng, 2010).
- **Mine runoff and solid waste disposal leachate** (Rashed, 2004).

2.1.3 Pathways of Distribution of Heavy Metals in Aquatic Environment

Once in the aquatic environment, metals are partitioned among the various aquatic compartments (i.e. biota, sediments, suspended solids, and water) and can occur in the complex, dissolved or particulate form (Hannany, 2009).

The main processes governing distribution and partitioning are dilution, dispersion, sedimentation and adsorption/desorption; nonetheless, some chemical processes could also occur. The removal of metals from water is usually through adsorption and followed by the other processes. Metals in the aquatic environment can permanently or temporarily be stored in the sediments or biota (Atiemo *et al.*, 2011).

2.2 Toxic Effects of Heavy Metals to the Human Body

When organisms are exposed to very low concentrations, some metals have the capacity to accumulate in tissues over time and become very harmful to the

human body (Nevin, 2000). These heavy metals usually cause damage to some organs in the human body resulting in increased mortality rates in some populations.

Heavy metals also have adverse sub-lethal effects on the human body including intelligent quotient deficits in children; therefore have effects on their psychological and social outputs (Nevin, 2000) behavioural and cognitive changes, and may also result in higher risks of cardiovascular attacks and strokes in adults (Chapman, 1996). Abdominal cramps, dyspnea and muscular weakness, nausea, vomiting can also be attributed to some heavy metals including cadmium and lead (Chapman, 1996; Bearer, 2000; Duruibe *et al.*, 2007). Sections 2.2.1 to 2.2.5 review the harmful effects of heavy metals (Pb, Cd, As, Zn and Cu), with emphasis on the studied metals on the environment and mankind.

2.2.1 Lead

Lead is one of the elements in nature, usually found in combination with other elements to form different minerals. There are so many sources of lead in our environment. Major sources of lead exposure include lead in paint, gasoline, water distribution systems, food and lead used in hobby-related activities. Emissions from automobiles were a major lead exposure source prior to 1996 (UNEP, 2002). Lead poisoning is an environmental and public health hazard of global proportions. Children and adults in virtually every region of the world are being exposed to unsafe levels of lead in the environment (Duruibe, 2007). In

fact, children are exposed to lead from different sources, such as paint, gasoline and solder. (Chapman, 1996).

Lead is considered a harmful, toxic metal with no biological relevance to most biological organisms including aquatic organisms and human beings and accumulates with time in organisms exposed to it (USEPA, 1986; Lenntech, 2008). Lead enters the human body through the digestion of contaminated food (Bhaskaram, 2001) including fishes or plants or through other pathways such as air, water, dust and soil. Aerial deposition and contaminated food are considered to be the vital source of exposure (Bhaskaram, 2001). Herath *et al.* (2013) established that, the urban environment is being burdened with lead pollution and this is strongly related to heavy vehicular traffic when lead gasoline is in use. Chapman (1996) also found out that, lead levels in roadside vegetation linearly increased with increased vehicular traffic density. Generally, vehicular emission in the urban environment is generally higher than that in rural areas (Yisa *et al.*, 2011).

Meilke (1999), Bearer (2000) and Dietert *et al.* (2000) all established that, children are vulnerable to environmental lead hazards which results in neurological disorders especially in the fetus, and decreased intelligence. Children between 12-24 months are usually prone to lead exposure through hand to mouth environmental attitude (Calabresse *et al.*, 1997; Manton *et al.*, 2000).

According to Gulson *et al.* (1998), pregnant women who are usually exposed to lead during their childhood can transfer it to their foetus during delivery and nursing; thus being transferred from one generation to another with its associated problems (Meilke *et al.*, 2005).

2.2.2 Cadmium

Cadmium occurs as a minor component in most zinc ores and therefore is a by-product of zinc production. It was used for a long time as a pigment and for corrosion-resistant plating on steel, whereas cadmium compounds were used to stabilize plastic. Cadmium has been widely dispersed into the environment through the air by its mining and smelting as well as by other man-made routes: usage of phosphate fertilizers, presence in sewage sludge, and various industrial uses such as plating, pigments, plastics and paints (ATSDR 1999).

Naturally a very large amount of cadmium is released into the environment, about 25,000 tons a year. About half of this cadmium is released into rivers through weathering of rocks and some cadmium is released into air through forest fires and volcanoes. The rest of the cadmium is released through human activities, such as manufacturing (Lenntech, 2008).

Cadmium has a wide range of sources entering into the aquatic environment as well as the entire environment. Some of the sources include: effluents from industrial and domestic bodies, run-off from road deposits, agricultural run-off. Corrosion protection of alloy or metal electroplating also, contributes to the industrial quota; tyre wear and exhaust emission are some common sources. Cadmium is usually bio-accumulative and persistent (Chapman, 1996). Cadmium gets into the human body through food including fishes. WHO (2006) established that, cereals irrigated with water polluted with cadmium, and crustaceans and fishes from polluted cadmium waters had elevated levels of cadmium. In addition, organs such as liver and kidney of mammals are found to be highly contaminated

with cadmium when they consume food contaminated with cadmium. Hannany (2009) established that, fertilizers made from municipal sewage sludge can also be of vital source of cadmium. However, Robinson *et al.* (2013) also point out that, atmospheric sources as well as road deposit sources affect crops and plants grown near them; the chloro-complexation available through uptake of cadmium ions from soil solution by the plant makes it choosy to control cadmium when especially grown in the saline area (Smolders and McLaughlin, 1996).

Cadmium introduced in the human body causes tubular proteinuria (WHO, 2004) renal dysfunction, skeletal defects related to calcium loss which results in osteomalacia and osteoporosis (WHO, 1989). Abdominal cramps, dyspnea and muscular weakness, nausea, vomiting can be attributed depending on the degree of exposure (Duruibe *et al.*, 2007). Further problems attributed to cadmium include pulmonary effects with sub-chronic inhalation (Chapman, 1996).

2.2.3 Arsenic

Arsenic is found in the natural environment in some abundance in the Earth's crust and in small quantities in rock, soil, water and air. It is present in many different minerals. About one third of the arsenic in the atmosphere comes from natural sources, such as volcanoes, and the rest comes from man-made sources. Due to natural geological contamination, high levels of arsenic can be found in drinking water that has come from deep drilled wells (Nwadinigwe *et al.*, 2014).

Industrial processes such as mining, smelting and coal-fired power plants all contribute to the presence of arsenic in air, water and soil. Environmental contamination also occurs because it is used in agricultural pesticides and in chemicals for timber preservation. Much of the arsenic in the atmosphere comes from high-temperature processes such as coal-fired power plants, burning vegetation and volcanic activity. The arsenic is released into the atmosphere primarily as arsenic trioxide where it adheres readily onto the surface of particles. These particles are dispersed by the wind and eventually fall back to the earth due to their weight or during rain (Chapman, 1996).

Natural, low-temperature biological reactions involving microbes also release arsenic into the atmosphere. Microbes acting on arsenic in soils and sediments generate arsine gas or other volatile arsenic compounds. Arsine reacts with oxygen in the air and is converted back to non-volatile forms of arsenic, which settle back to the ground (Inengite *et al.*, 2010).

Chapman (1996) established that, the aquatic environment as well as the entire environment is polluted by atmospheric deposition of combustion products, nonferrous smelters, metallic alloys and run-off from fly-ash storage near power plants. According to WHO (1992), higher contamination levels of arsenic were recorded in water near exploration areas of mines. Agricultural applications of fertilizers also contribute to arsenic pollution of the environment and the inorganic arsenicals (arsenic acid, arsenic trioxide) arsenates of calcium, copper and lead have been used as algacides, desiccants, herbicides and insecticides (Chapman, 1996; WHO, 2002). According to David *et al.* (2011), elevated arsenic

levels in soils can also be attributed to the ore processing operations as well as coal burning power plant and cannot be destroyed once it gets into the environment, but only change form, separated from the particle or join their respective particles.

Arsenic affects the gastrointestinal system, lungs and the skin in humans. Abdominal pain, cancer (especially lung and skin), diarrhoea, nausea and neuritis can also be attributed to arsenic when the human body is exposure to it and when exposed to the human body also causes abnormal rhythmic heartbeat and diarrhoea. Vascular collapse, macrocytosis, neuropathy and skin lesion can also be caused by arsenic when gets to the human body (Chapman, 1996; WHO, 1992). So arsenic in any form is hazardous to the human body. In addition, arsenic in its minute concentration to the human body is very toxic and can cause ulceration in skin folds, increased skin pigmentation, soles, rashes, atrophy and muscular paralyses (Chapman, 1996).

2.2.4 Zinc

Zinc is one of the most common elements in the earth's crust. It is found in air, soil, and water, and is present in all foods. Pure zinc is a bluish-white shiny metal. Zinc has many commercial uses as coatings to prevent rust, in dry cell batteries, and mixed with other metals to make alloys like brass, and bronze. A zinc and copper alloy is used to make pennies in the United States. Zinc combines with other elements to form zinc compounds. Common zinc compounds found at hazardous waste sites include zinc chloride, zinc oxide, zinc

sulfate, and zinc sulfide. Zinc compounds are widely used in industry to make paint, rubber, dyes, wood preservatives, and ointments (Chapman, 1996).

Olivet *et al.* (2011) established that, enzyme involved catalytic functions require zinc to function optimally; zinc also has a regulatory function and is required for structural stability maintenance. Zinc plays vital roles in the development and responses of the immune system as well as reproduction and the neurological system development. Holum (1998) points out that, zinc also serves as co-factor in carbonic anhydrase as well as enzymes dehydrogenation. Protein structures stabilize cell membrane, bind and affect transcription of genes (King and Cousins, 2006) cell signalling and transmission of impulse nerves (Chapman, 1996). It also forms retinol-binding protein in transporting vitamin A and also converts vitamin A to retinal (Christian and West, 1998). Nolan (2003) reported that, zinc balances with copper in the human body especially in men and enhances reproductive activity. Food containing concentrations of zinc a little above the acceptable threshold can causes acute and chronic effects including abdominal cramps, diarrhoea, nausea, vomiting, and appetite loss and reduced levels of lipoprotein in higher concentrations. Lower concentrations of zinc exposed through food (including fishes) in accumulation causes anorexia, defects of the neural tube, lung cancer and slower growth in humans (ATSDR, 2005).

2.2.4 Copper

Copper is a very common substance that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely

use copper. For instance it is applied in the industries and in agriculture. The production of copper has lifted over the last decades. Due to this, copper quantities in the environment have increased (Chapman, 1996).

Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. A few examples of human activities that contribute to copper release have already been named. Other examples are mining, metal production, wood production and phosphate fertilizer production. Copper is released both naturally and through human activity it is very widespread in the environment. Copper is often found near mines, industrial settings, landfills and waste disposals (Nwadinigwe *et al.*, 2014).

Most copper compounds will settle and be bound to either water sediment or soil particles. Soluble copper compounds form the largest threat to human health. Usually water-soluble copper compounds occur in the environment after release through application in agriculture (Chapman, 1996).

Plants and animals including *Homo sapiens* tissues also contain some copper. Özçelik *et al.* (2002) established that, metalloproteinase which is significant in cell function in biological systems are also formed from copper. Copper plays a vital role in metabolism resulting in proper transport of oxygen and iron absorption as well as its utilization. Moreover, the maintenance, growth and development of the connective tissues of the brain, heart and other organs within the human body needs the assistance of copper (WHO, 1992; WHO, 2004). In addition, Wardlaw (2003) also shows that, the human brain and the nervous

system are strongly protected against certain radicals and therefore serves as antioxidants.

Despite the importance of this metal, it gets accumulated over time and this can threaten the health of man when above the acceptable threshold (WHO, 1992; WHO 2004). Pamphlett *et al.* (1997) reported that, the central nervous system and kidneys can be totally damaged with copper when also exposed to mercury; copper above the acceptable threshold gets accumulated in the human liver (Yisa *et al.*, 2011).

2.3 Synergistic and Additive Effects of Heavy Metals

Metals get accumulation over time in road deposits and water bodies sediments (Chapman, 1996). Cadmium can mainly be found in the earth's crust. It always occurs in combination with zinc. Cadmium also consists in the industries as an inevitable by-product of zinc, lead and copper extraction. After being applied it enters the environment mainly through the ground, because it is found in manures and pesticides (Nwadinigwe *et al.*, 2014). According to Wah and Chow (2002), high level of cadmium shows the presence of lead and zinc since they are the by-product of cadmium.

2.4 River/Stream Quality and Contamination

Inland water bodies (rivers, streams, lakes) have been affected by heavy metals around the globe as confirmed by several studies under the tropics. High dissolved cadmium, lead and zinc concentrations are exhibited in these catchments, basically been impacted from atmospheric fallout, industrial

activities, sewage treatment plants (Robson and Neal, 1997; Rees *et al.*, 1998; Neal *et al.*, 2000).

Heavy metal concentrations in impacted water bodies always exceed environmental quality standards; lead and cadmium are often removed by precipitation and sorption from the water column especially carbonate-rich geology river drainages (Gunawaradana *et al.*, 2013). Areas that have been influenced by anthropogenic activities like mining with higher heavy metal concentrations influences water bodies heavily than areas that have not been tempted). Heavy metals become enriched in water bodies through a number of processes (Figure 2.1) and metal-bearing sulphide minerals resulted from high metal concentrations of drainages especially pyrite which host elements like arsenic, cadmium, copper, lead and zinc (Younger *et al.*, 2002). The pH of most drainage waters depends on factors including:

- Carbon and oxygen supply (as fixed or bicarbonate)
- The grain size and composition of the pyrite or metal sulphides
- Iron- and sulphur-oxidising bacteria presence
- Temperature

Acid reaction solutions can be neutralized with carbonate minerals such as calcite and dolomite, and silicate minerals (Rose and Cravotta, 1998).

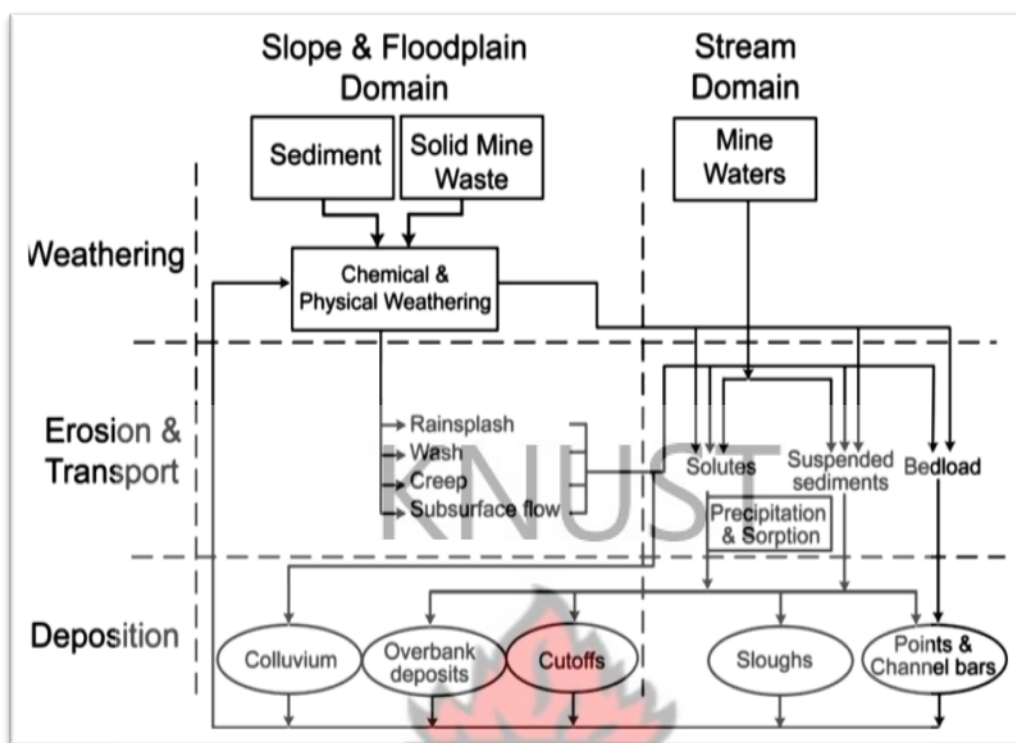


Figure 2.1: Model for the dispersal and storage of particulate and dissolved heavy metals mining wastes (Lewin et al., 1977).

In situ chemical weathering of contaminated soils, road deposit sediments and other mining activities happen to be another process by which heavy metals enter into water bodies (Figure 2.1). Changes in pH and redox potential (oxidation or reduction) may be accelerated through the weathering process and acid rain or breakdown of organic matter and its formation of organic acids resulted in low pH which can also resulted metal-bearing silicate solute phase metals are released at last. The breakdown of metal bearing iron can be reduced as a result of oxidization conditions and the water-table levels also do fluctuate as a result of reduction (Hudson-Edwards, 2003). Rivers and streams channel sediments forms of insoluble metal sulphides (Cd, Cu, Pb and Zn) and aquatic life is been reduced by their toxicity (Hudson-Edwards, 2003). Dispersal of metal-

rich sediment during events of high flow happens to be another way of polluting aquatic bodies. Erosion by high flow and heavy rainfall with contaminated materials of heavy metals pollutes aquatic bodies. Aquatic life is temporarily affected by the oxidization of sediments containing metal sulphide when released into solutions (Gozzard *et al.*, 2006). However, further work is needed to comprehend if acute toxicity is also caused by these metallic sulphides.

2.5 Sediment Quality and Contamination

Contaminated sediments in the aquatic environment are temporary or permanent stores of several contaminants. They are of vital significance around the globe and have the potential to accumulate and cause harmful effects on the environment and human health (Mackevičienė *et al.*, 2002). The long-term impact of heavy metals on river and stream systems is significant and suspended particles and sediment may be contaminated with some heavy metals including cadmium, copper, lead and zinc; however, metalloid element arsenic is also recognized as contaminant (Dennis, 2005). Sediments are influenced by allochthonous influence made of anthropogenic and natural effects and autochthonous influences including enrichment of organism, organometallic complexation during sedimentation and precipitation.

According to Gunawardana *et al.* (2013), sediment analysis is very useful in studying aquatic pollution with heavy metals. Biota, sediments and water are basically the three reservoirs of metals in the aquatic environment. Complex dynamic equilibrium governed by various biological, chemical and physical dominates the reservoirs which contain the metals. Heavy metals have affected

ivers, streams, lakes and sediment quality worldwide and maximized concentration in sediments occurred in the late nineteenth century (Hudson-Edwards *et al.*, 1999a). Highly contaminated material can be dispersed and remobilized in downstream during major flood periods. Heavy metals in riparian vegetables cause phytotoxic effects on the vegetables and thereby affect many river systems (Dennis *et al.*, 2003).

Five components were considered in a comprehensive sediment assessment approach according to Ulrich (2001). They include (1) benthic community structure, (2) laboratory bioassays for evaluating the toxicity of in-place pollutants, (3) bioaccumulation information, (4) knowledge of site stability, and (5) physicochemical properties (Ulrich, 2001). Bioavailability and contaminant concentrations are required to evaluate sediment contamination toxicity potential as well as food chain transfer. The benthic invertebrate bioavailable fraction could be analysed and collected by direct measurement which contributes the least uncertainty to the exposure estimates. Time, personnel or finances of sampling support could affect direct measurement of concentration in biota and therefore estimation becomes the only alternative (United States Department of Energy, 1998).

Variety of methods can be used to estimate contaminant concentration with complex mechanism process models inclusion; however, it gives accurate estimates and requires information which risk assessment doesn't require.

Sediment enrichment assessment with elements can be carried out using the index of geoaccumulation (Muller, 1979) and enrichment factors. The index of

geoaccumulation (I_{geo}) has been used as a measure of bottom sediment contamination since the 1970s. It determines contamination by comparing current metal contents with pre-industrial levels. The background is multiplied each time by the constant 1.5 in order to take into account natural fluctuations of a given substance in the environment as well as very small anthropogenic influences. The geoaccumulation (I_{geo}) is calculated as: $I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n}$ (Muller, 1979).

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2.6 Vehicular Traffic Density and Heavy Metal Pollution

Several researchers have found severe health problems are associated with heavy metals even at low concentrations; although, certain amounts of these elements are vital in plant nutrition. Vehicular traffic density is one of the important sources of heavy metal pollution. Gunawardana *et al.* (2013) reported that, the urban environment is polluted with lead as a result of intense vehicular traffic density when gasoline containing lead is been used. He also found out that, lead levels in vegetation linearly increased with intense vehicular traffic density. Higher concentrations of heavy metals (i.e. Pb, Cd and Zn) above UNEP (2002) were identified in samples of plants with intense vehicular traffic (Buszewski *et al.*, 2000). In addition, vehicular emissions in the urban environment and its environs are higher than rural areas (Chapman, 1996).

Paint particles and some metal particles are also released during the intense vehicular traffic (Chapman, 1996). Sediments deposition along roads are influenced by the distance from traffic, season as well as the topography. Nabulo (2004) also reported that, heavy metal concentrations decreased with increased

distance from the roads. Sediments deposited along roads are affected by the distance from the road and decreases in concentration of the metal like cadmium and lead were (Chapman, 1996).

2.7 Review of Heavy Metals in the African Aquatic Environment

Africa is a continent naturally endowed with natural resources and rich in diversity including aquatic organisms, amphibians, birds, reptiles and mammals (Chapman, 1996). As a result Africa has attracted a lot of exploration companies into the continent resulting in the introduction of heavy metals like arsenic, mercury, cadmium, chromium (Yisa, 2010). Although, there is relatively low industrial activities in the African sub region there is also the need create the awareness for best management practices on our natural resources including aquatic resources, mineral resources (Obirikorang, 2010). However, serious concern has been raised about the environmental pollution caused by these domestic and foreign mining organizations and their significant deterioration of the rich content Africa (Duruibe *et al.*, 2007). Pollution of our environment as a result of economic development has introduced various degree of contamination by heavy metals (Rashed, 2004; Norman *et al.*, 2007; Yisa *et al.*, 2011).

Distribution and fate of metal contaminants from anthropogenic sources and terrestrial sources into water bodies and other ecosystems need to be understood for the development of best management practices and effective pollution control of our natural resources. This has led to the initiation of various research works in various academics institutions.

2.8 Heavy metals pollution in Ghana

Ghana is a country within the sub-Sahara endowed with natural resources. Heavy metals are introduced into the country through different sources. Some sources are natural as well as anthropogenic activities and include: natural resources (minerals) exploration, vehicular emissions, agricultural activities (Addo *et al.*, 2012). The Ghanaian environment is gradually getting polluted by heavy metals especially in the communities being explored by major mining organizations and illegal mining activities by the local indigenes (Armah *et al.*, 2010). However, urban environment pollution is also becoming alarming due heavy vehicular traffic (Addo *et al.*, 2012). Road deposits that accumulate in urban environments in Ghana have the potential to contribute heavy metals loading to receiving waters and water bodies (Armah *et al.*, 2010). Sediments and dust with high levels of heavy metal could affect entire ecosystems (Agyemang *et al.*, 2006). Due to the harmful effects of heavy metals and the reported cases of harmful effects by the Ministry of Health, there is the need to conduct more research on heavy metal contamination to provide information and advice for best management practices.

2.9 Seasonal Dynamics of Heavy Metal Pollution

The seasonal dynamics of heavy metals pollution in both water bodies and sediment is largely determined by the hydrodynamic characteristics of the water body. The water quality varies in three dimensions which are further modified by the flow direction, discharge and time. Consequently, season dynamics cannot

usually be measured in only one location and at a time (Chapman, 1996; (Nwadinigwe *et al.*, 2014).

2.10 Factors affecting dynamics of heavy metals in the aquatic environment

There are several factors that drive heavy metal dynamics in the environment. Some include; pH, conductivity and organic matter. The vital part of dynamic hydro-geochemical system in the cycling of elements, the accumulation and store of heavy metals in sediments or the release of heavy metals and other toxic elements into the aquatic environment depends of certain conditions including pH, conductivity, organic matter, redox potential and grain size distribution of the sediment (Nwadinigwe *et al.*, 2014). Heavy metals accumulation from the overlying water to the sediment is based on a number of external environmental factors such as pH, electrical conductivity and the available surface area for adsorption caused by the variation in grain size distribution (Inengite *et al.*, 2010).

2.10.1 pH

The pH of sediment can vary significantly - from acidic in the coniferous forest or on peat bog, to basic on karst terrain (Nabulo *et al.*, 2006). The pH of sediment changes ability of aquatic plants to take nutrients from the ground and also the ability of some aquatic organisms to tolerate some habitat. Thus some aquatic plants will not grow well in acidic or basic sediment and other organisms including some fishes cannot tolerate acidic or basic regions. The measurement of sediment pH is very important - but in no way it is easy (Chapman, 1996).

2.10.2 Conductivity

Conductivity in water is affected by the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, and phosphate anions (ions that carry a negative charge) or sodium, magnesium, calcium, iron, and aluminium cations. Conductivity in streams and rivers is affected primarily by the geology of the area through which the water flows. Streams that run through areas with granite bedrock tend to have lower conductivity because granite is composed of more inert materials that do not ionize (dissolve into ionic components) when washed into the water (Chapman, 1996). On the other hand, streams that run through areas with clay soils tend to have higher conductivity because of the presence of materials when washed into the water and high conductivity levels leads to high metals accumulation over time Helmreich *et al.*, 2010). Ground water inflows can have the same effects depending on the bedrock they flow through.

Discharges to streams can change the conductivity depending on their make-up. A failing sewage system would raise the conductivity because of the presence of chloride, phosphate, and nitrate; an oil spill would lower the conductivity (Inengite *et al.*, 2010).

Studies of inland fresh waters indicate that streams supporting good mixed fisheries have a range between 150 and 500 $\mu\text{hos/cm}$. Conductivity outside this range could indicate that the water is not suitable for certain species of fish or macro invertebrates (USEPA, 1986).

2.10.3 Organic Matter

Organic matter in sediment consists of carbon and nutrients in the form of carbohydrates, proteins, fats and nucleic acids. Bacteria quickly eat the less resistant molecules, such as the nucleic acids and many of the proteins. Sediment organic matter is derived from plant and animal detritus, bacteria or plankton formed *in situ*, or derived from natural and anthropogenic sources in catchments (Inengite *et al.*, 2010). Sewage and effluent from food-processing plants, pulp and paper mills and fish-farms are examples of organic-rich wastes of human origin (Chapman, 1996); high organic matter levels leads to high metals contamination (Sansalone *et al.*, 1996; Kim and Sansalone, 2008).

Total Organic Carbon (TOC) refers to the amount of organic matter preserved within sediment. The amount of organic matter found in sediment is a function of the amount of various sources reaching the sediment surface and the rates at which different types of organic matter are degraded by microbial processes during burial.

Sediment organic matter can be a source of 'recycled nutrients' for water column productivity (including algal blooms) when it degrades. Dissolved oxygen concentrations are usually lowered when organic matter is degraded by aerobic bacteria, and anoxic & hypoxic conditions may develop under stratified conditions (Inengite *et al.*, 2010).

Organic matter is also a source of food and energy, and plays an important role in material flow through ecosystems. Decomposition rates of organic matter

increase as nitrogen and phosphorus contents increase and as TOC/TN and ratios decrease. 'Labile' is the term used to describe organic matter with low TOC: TN ratios (e.g. phytoplankton) that breaks down easily, whereas 'refractory' organic compounds (woody debris made of lignin and cellulose) have very high TOC: TN ratios and are highly resistant to degradation. Organic matter with very high TOC:TN ratios consumes more dissolved oxygen, supports less denitrification and releases fewer nutrients to the water column when it breaks down than organic matter with low TOC:TN ratios (Inengite *et al.*, 2010). The decomposition of organic matter with very high TOC:TN ratios can even be nutrient-controlled meaning that it can cause the uptake of dissolved inorganic nitrogen (DIN) from the water column. Sediments with high TOC:TN ratios (and lower N contents) tend to support a lower biomass of benthic invertebrates.

Organic matter has a high affinity for fine-grained sediment because it adsorbs onto mineral surfaces. The adsorption process helps to preserve the organic matter and gives rise to a generally positive correlation between TN or TOC. Sites of organic matter accumulation in coastal waterways are therefore controlled to a large extent by processes that govern the transport and deposition of fine sediment (Chapman, 1996).

CHAPTER 3

MATERIALS AND METHODS

3.1 Study Area

Kumasi is the regional capital of the Ashanti Region and among the largest metropolitan areas of Ghana. Kumasi is the commercial, industrial and cultural capital of Ashanti Region.

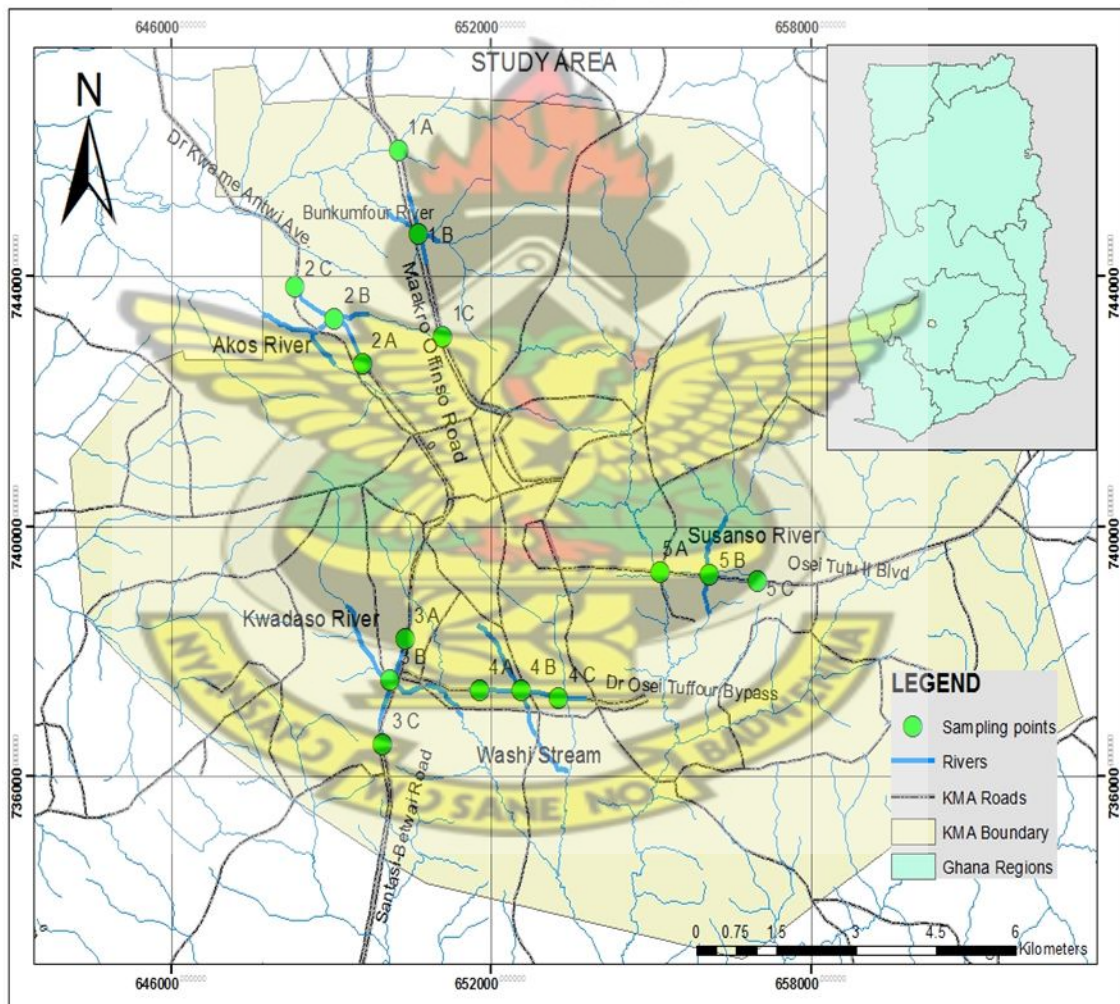


Figure 3. 1: The map of the study area showing the sampling points of each site marked by green dots.

Kumasi is about 270 km north of the national capital, Accra and a transitional forest zone of Ghana. It is between latitude 6.35° – 6.40° and longitude 1.30° – 1.35° , with an elevation which ranges between 250 – 300 metres above sea level and an area of about 24,389 square kilometres (Ghana Statistical Service, 2010).

Many water bodies flow through Kumasi and there are several major roads within the metropolis (Figure 3.1). Some principal roads within Kumasi Metropolis include Dr. Kwame Antwi Avenue, Osei Tutu II Blvd, Dr. Osei Tuffour Bypass, Santasi-Bekwai and Maakro-Offinso Roads. Rivers such as Akos, Susuanso, Washi, Kwadaso and Bonkumfour are the water bodies that flow under these roads (Ghana Statistical Service, 2010).

3.1.1 Climatic Conditions

Temperature and Humidity

The wet sub-equatorial region is the area where Kumasi Metropolis can be found with the average maximum and minimum temperatures of 30.7°C and 21.5°C respectively. The average humidity at 09:00 GMT and 15:00 GMT is about 84.16% and 60% respectively (Ghana Statistical Service, 2010) with moderate temperature and humidity having direct effect on the environment and population growth (Ghanadistricts.com, 2006).

Rainfall

The double maxima rainfall regime of the study area (214.3 mm in June and 165.2 mm in September) has direct effect on the environment and population

growth (Ghana Statistical Service, 2010). The major rainy season occurs between March/April to July and September to October as the minor rainy season. In addition, between November to early February, Kumasi experiences dry season which affects small streams to dry up.

3.1.2 Conditions of the Natural Environment

Kumasi is drained by a number of streams/rivers including Akos, Susuanso, Owabi, and Subin; and lies within the moist semi-deciduous section of the South East Ecological Zone. As a results of increasing population growth, people within Kumasi have encroached upon the green reserves and the water bodies have also been gradually polluted by anthropogenic activities (Ghanadistricts.com, 2006). In addition, the few green patches along the waterways have been cleared for agricultural purposes leading to siltation. Occasional flooding occurs within Kumasi Metropolis as a results of some developers who have built along and across watercourses (Ghanadistricts.com, 2006).

The Kumasi Metropolis has in recent times been experiencing both human and vehicular traffic congestion, particularly in the Central Business District (CBD). This has resulted in the dominance of the distributive trade in the city's economy and hawkers taken over the principal streets (Ghanadistricts.com, 2006).

The Kumasi Metropolis has in recent times been experiencing both human and vehicular traffic congestion, particularly in the Central Business District

(CBD). As a result of the dominance of the distributive trade in the city's economy, the CBD and all the principal streets have been taken over by hawkers (Ghanadistricts.com, 2006).

3.2 Site Selection and Coding

Roads that experience different levels of vehicular traffic, have tyre repair shops, auto mechanic shops and fuel filling stations were selected as sampling sites within the Kumasi Metropolis. Another criterion for the selection of the sampling locations along these major roads was proximity to surface water bodies. The selected sampling locations for this study together with their allocated codes are shown in Table 3.1. In general, for each location, Sites A and C are the sites for collection of roadside deposits and locations B are sites for collection of stream sediments.

Table 3. 1: The sampling sites of the study area.

Sites	Location
Sites 1 A & C	Maakro-Offinso Road
Site 1 B	Bonkumfour River
Sites 2 A & C	Dr. Kwame Antwi Avenue
Site 2 B	Akos River
Sites 3 A & C	Santasi-Bekwai Road
Site 3 B	Kwadaso River
Sites 4 A & C	Dr. Osei Tuffour Bypass
Site 4 B	Washi Stream
Sites 5 A & C	Osei Tutu II Blvd
Site 5 B	Susuanso River

3.3 Sample Design and Duration

A Garmin Map 62 Geographical Position System (GPS) receiver was employed to record the geographical positions of the selected sampling locations to ensure traceability. Sampling for this study was designed to coincide with the rainy (July) and dry (January) seasons to collect sediments from all fifteen sites. The sediments were analysed for the following heavy metals: arsenic, cadmium, copper, lead, and zinc and the following physicochemical characteristics: pH, conductivity and organic matter were measured. Contamination levels were also assessed using three different criteria: the index of geoaccumulation, contamination factor, and pollution load index.

3.4 Sediment Sampling

Thirty (30) sediment samples were collected in all. Samples (road sediments) were collected within 1m from the edges of the road along a 100 m stretch by gently sweeping the road deposited sediments with a brush into a plastic dustpan. Stream/River bank sediments (0 to 10 cm deep) were also collected 10cm from the stream into the water with the aid of a pre washed plastic trowel. Samples collected were stored in sealed polythene bags and transported to the FRNR-KNUST laboratory for pre-treatment and analyses.



Plate 1: Roadside deposit collection along Site 2 (Dr. Kwame Antwi Avenue)

3.5 Sediment Processing

The sediments were air dried at room temperature, ground using a mortar and a pestle and then sieved using laboratory test sieve of 125 μ m diameter mesh size before they were digested for analyses. One gram (1g) of each sediment sample was taken to which was added concentrated diacid made of HNO₃ and HClO₄ in the ratio of 9:4. The samples were boiled at 150°C for 15 minutes until the liquid turned colourless. The colourless liquids were then filtered to get rid of any solid matter using 0.5 μ m pore size membrane filter paper after digestion. The clear filtrates were collected in beakers and the volume topped up with distilled water up to 20ml. The extracts were then transported to AngloGold Ashanti laboratory and the heavy metals (arsenic, cadmium, copper, lead and zinc) were analysed by Atomic Absorption Spectrophotometer (AAS). Sediment organic matter, pH and electrical conductivity were respectively determined by gravitational ignition

method and with the aid of a digital pH and EC metres (AOAC International, 2002).

3.6 Analytical Determination of Metal Concentrations

Samples (filtrates from 3.5) were aspirated through a nebulizer and then sprayed as fine aerosol to the mixing chamber of the AAS where there was a mixture of the sample aerosol and fuel, oxidant gas and then carried to a burner head. The sample aerosol was atomized in the flame. There was a drain where excess sample solution was removed. Light of selected wavelength falling on the atoms in the free ground state were absorbed by the atoms and entered the excited state in a process known as atomic absorption absorbance. Absorbance is linearly proportional to concentration of the analytes up to a certain concentration limit (Beer Lambert law). An absorbance was measured and quantified by comparing to that of the standard solution according to AOAC International (2002).

3.7 Assessment of Contamination in the Road Deposited Sediments and River Sediments

The index of geoaccumulation (I_{geo}), contamination factor (CF), as well as pollution load index (PLI) was applied to assess heavy metal (As, Cu, Cd, Pb, and Zn) distribution and contamination in the road deposited sediment and the nearby river sediment samples.

3.7.1 Index of geoaccumulation (I_{geo})

The index of geoaccumulation index (I_{geo}) was originally used with bottom sediment by Müller (1969). This contamination assessment index has been cited by many researchers in environmental studies (Loska *et al.*, 2004; Abraham and Parker, 2008; Lu *et al.*, 2009) and is defined by the equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5 \cdot B_n}$$

Where:

C_n - is the measured concentration of element n in tested sediment (road and river sediments)

B_n - is the geochemical background value for the element n .

1.5 - constant introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments.

Müller (1979) proposed seven sediment quality classes associated with the geoaccumulation index as shown in table 3.2:

Table 3. 2: Classes of the Geoaccumulation Index used to define sediment quality

I_{geo} value	I_{geo} Class	Quality of Sediment
< 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly to extremely polluted
> 5	6	Extremely polluted

(Müller, 1979)

3.7.2 Contamination factor (CF)

The geochemical background values in continental crust averages of the trace metals under consideration reported by Taylor and McLennan (1985) were used as background values for the metals (Hakanson, 1980; Nasr *et al.*, 2006; Mmolawa *et al.*, 2011). CF is expressed as:

$$CF = C_{\text{metal}} / C_{\text{background}}$$

Where:

CF- is the contamination factor,

C metal- is the concentration of pollutant in sediment,

C background- is the background value for the metal and

The CF was classified into four groups as expressed in table 3.3 below:

Table 3.3: Categories on basis of contamination factor

CF value	CF category	Contamination extent
<1	0	Low contamination
1≤CF<3	1	Moderate contamination
3≤CF≤6	2	Considerable contamination
>6	3	Very high contamination

(Hakanson, 1980; Nasr *et al.*, 2006 & Mmolawa *et al.*, 2011)

3.7.3 Pollution Load Index (PLI)

The PLI is an indicator of site quality and for each metal the contamination factor (CF) was first determined for use in calculating the PLI. All roadway deposit samples and river sediments were evaluated for the extent of metal pollution by

employing the pollution load index (PLI) developed by Thomilson *et al.* (1980) as follows:

$$PLI = n\sqrt{(CF1 \times CF2 \times CF3 \times \dots \times CFn)}$$

Where:

N - is the number of metals studied (As, Cd, Cu, Pb and Zn) and

CF - is the contamination factor calculated as described in 3.7.2.

The PLI provides simple but comparative means for assessing the quality of a site, where value of $PLI < 1$ denotes perfection, $PLI = 1$ denotes that only baseline levels of pollutants are present and $PLI > 1$ indicates deterioration of site quality (Thomilson *et al.*, 1980).

3.8 Data Analyses

Normality tests for all the variables in the dataset were performed prior to further analyses using the Shapiro-Wilk test. As the data did not follow Gaussian distribution, the Kruskal -Wallis test, which represents a nonparametric version of one-way ANOVA, was used to determine whether significant differences existed in metal concentrations and physicochemical measures among sampling sites. The Mann-Whitney test was used to determine whether significant differences existed for metal concentrations and physicochemical parameters between the sampling periods (rainy and dry season). Data in this study were presented graphically as means \pm SD. All descriptive statistics and graphs were executed using the GraphPad Prism 5 Software. In all cases, differences were considered significant at $p < 0.05$.

CHAPTER 4

RESULTS

4.1 Physicochemical Parameters the Road-deposited Sediments and River Bottom Sediments

The measured physicochemical parameters of the road-deposited sediments of the major vehicular highways in the Kumasi Metropolis and the bottom sediments of nearby rivers and streams showed a general trend of higher levels in the bottom sediments of the studied water bodies. Below are the spatial variations of the assayed physicochemical parameters over the sampling duration.

4.1.1 pH of Sediments at the Sampling Areas

Overall, there were no significant differences ($p > 0.05$) in pH levels of the road-deposited sediments of the highways and the bottom sediments of their respective nearby surface water bodies at all the sampling locations (Figure 4.1). The pH of the road-deposited sediments over the sampling period ranged from 5.46 (Site 3) to 7.10 (Site 5). The pH of the streams/ rivers sediments ranged from 5.34 (Site 5) to 7.89 (Site 3).

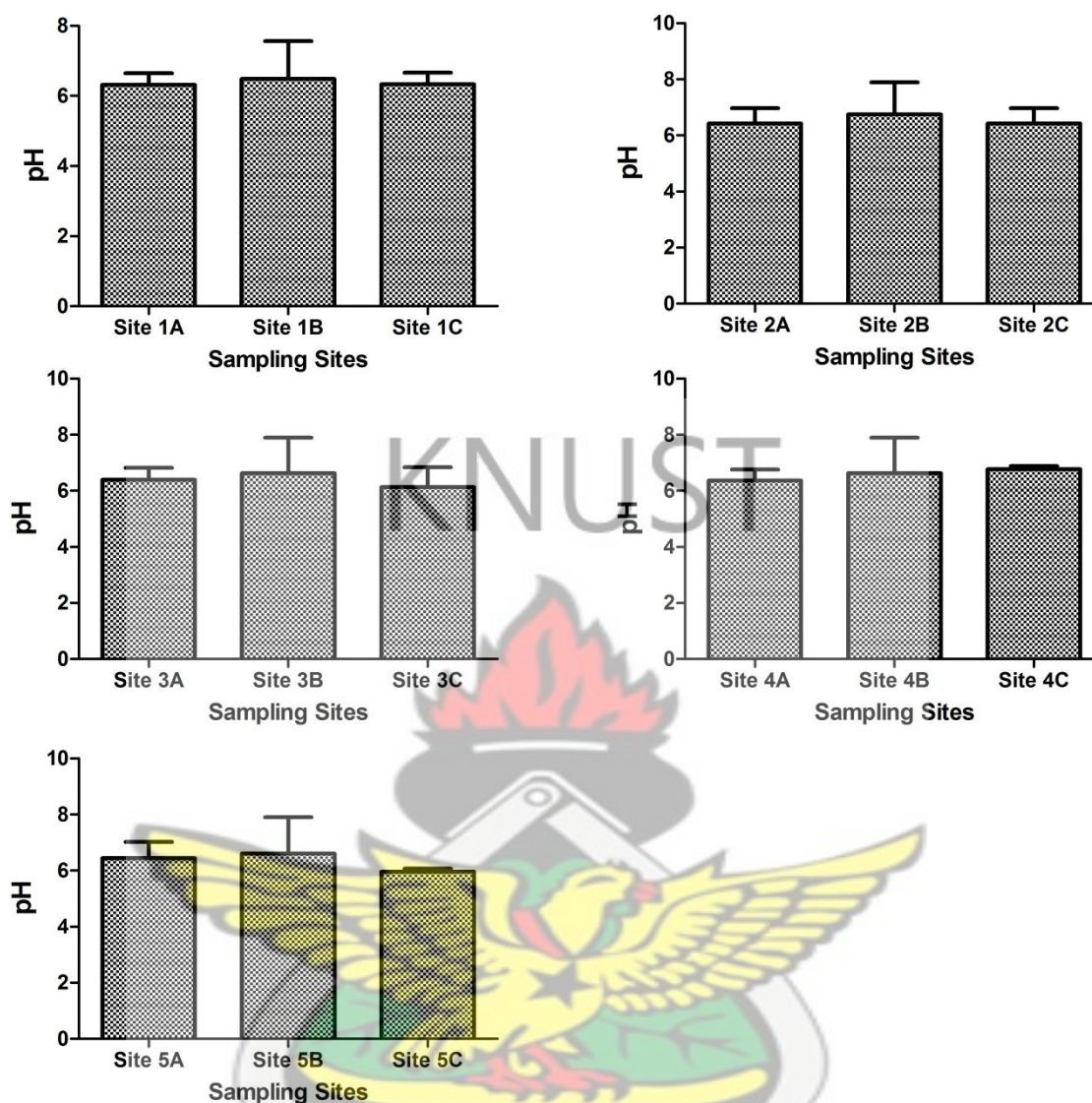


Figure 4. 1: Variations in the pH of the sediments of the different sampling locations

4.1.2 Conductivity

The conductivity levels of each road-deposited sediment of the five sampled highway locations were significantly lower ($p < 0.05$) than each bottom sediment of their respective nearby surface water bodies (Figure 4.2). Comparison of the conductivity levels of the road-deposited sediment of the 5 sampled highways indicated that Site 5 recorded the highest mean level of $625.00 \pm 2.00 \mu\text{Scm}^{-1}$

with Site 1 recording the lowest mean level of $175.00 \pm 3.00 \mu\text{Scm}^{-1}$. Overall, the conductivity of the bottom sediments of the sampled water bodies ranged from a lowest mean level of $250.00 \pm 5.00 \mu\text{Scm}^{-1}$ at Site 3 to a highest of $949.66 \pm 1.53 \mu\text{Scm}^{-1}$ at Site 5. Figure 4.2 shows the mean \pm SD of the conductivity levels recorded at the different sampling sites over the 2 seasons.

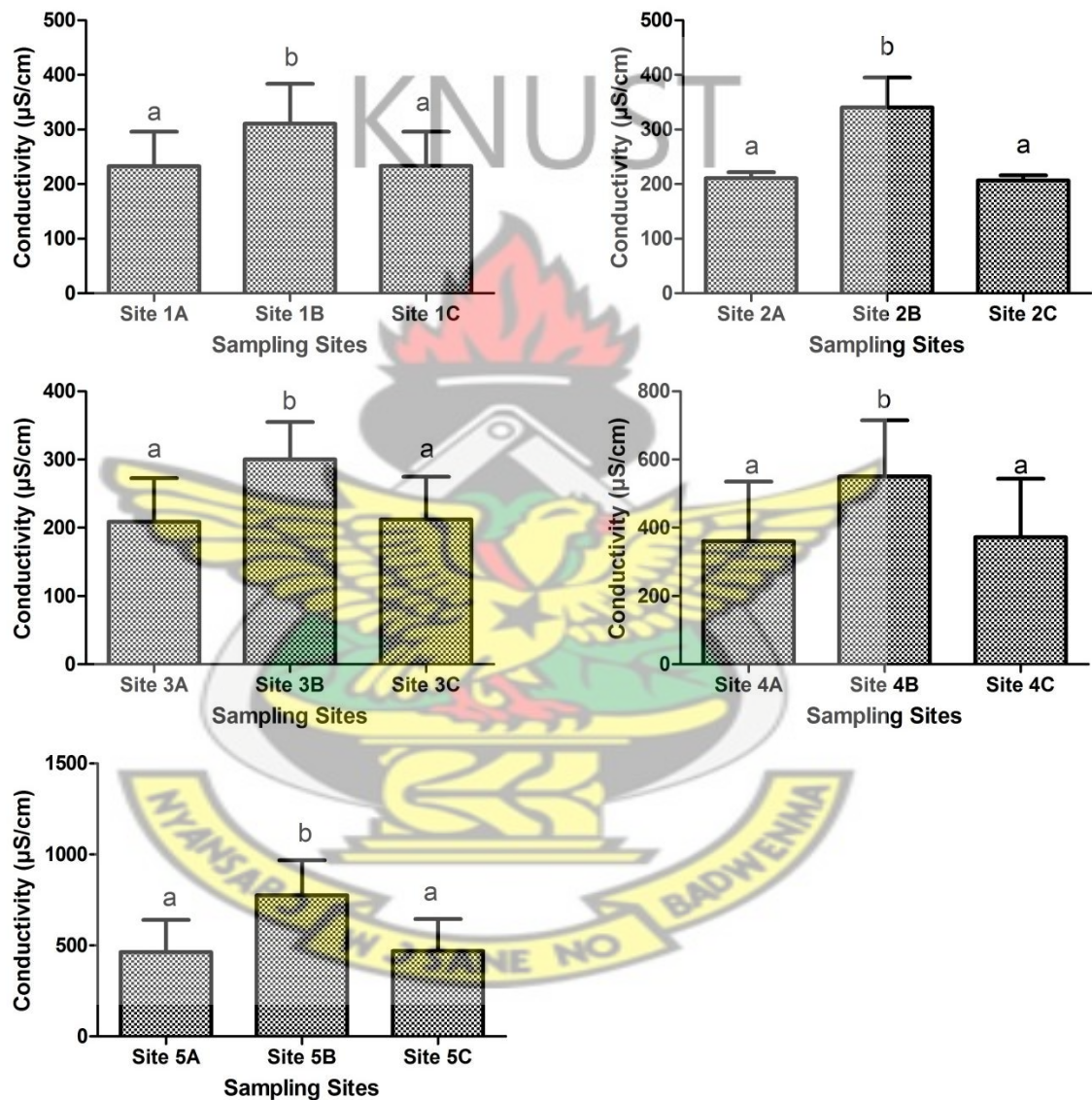
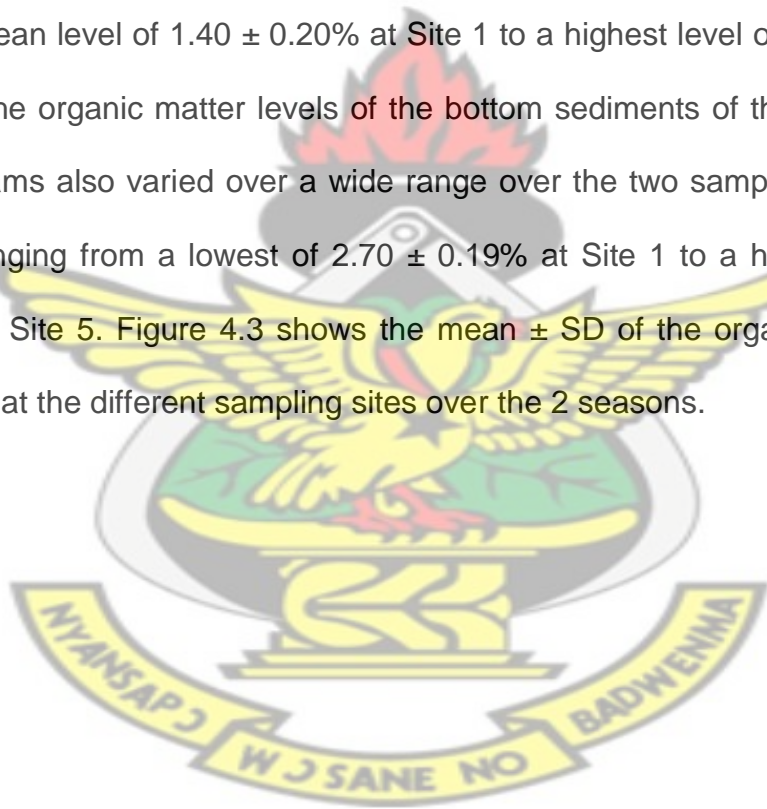


Figure 4. 2: Variations in the conductivity levels of the sediments of the different sampling locations.

4.1.3 Organic Matter

Similar to the conductivity trend, the organic matter levels of each road-deposited sediment of the 5 sampled highway locations were significantly lower ($p < 0.05$) than that of each bottom sediment of their respective nearby surface water bodies (Figure 4.3). The organic matter levels of the bottom sediments of the sampled water bodies were on average two-fold higher than the levels recorded for the road-deposited sediments. Mean organic matter levels of the road-deposited sediments of the 5 sampled vehicle highways in Kumasi ranged from a lowest mean level of $1.40 \pm 0.20\%$ at Site 1 to a highest level of $8.80 \pm 0.20\%$ at Site 5. The organic matter levels of the bottom sediments of the sampled rivers and streams also varied over a wide range over the two sampling seasons with levels ranging from a lowest of $2.70 \pm 0.19\%$ at Site 1 to a highest of $17.10 \pm 0.21\%$ at Site 5. Figure 4.3 shows the mean \pm SD of the organic matter levels recorded at the different sampling sites over the 2 seasons.



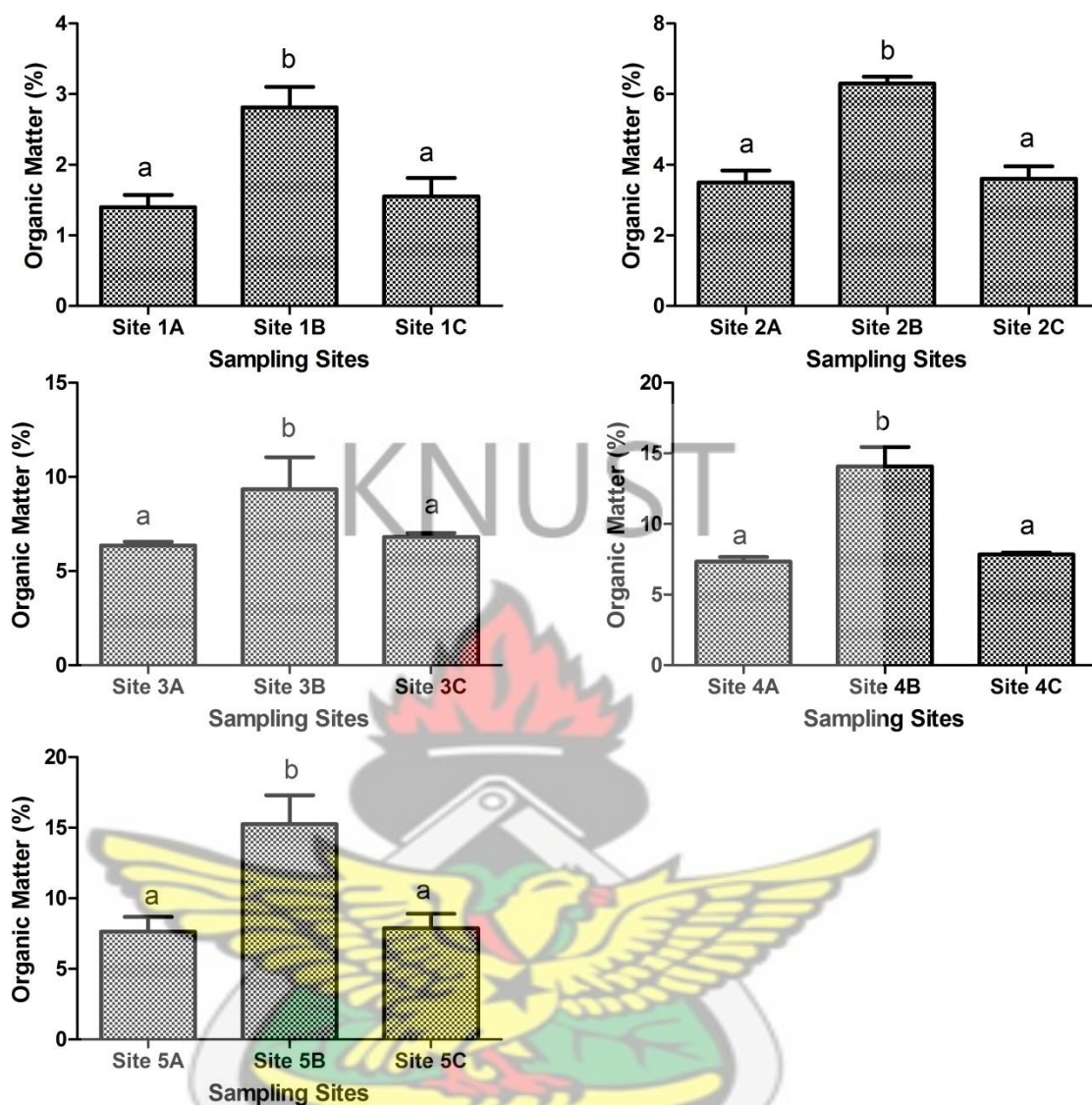


Figure 4. 3: Variations in the organic matter levels of the sediments of the different sampling locations.

4.2 Heavy Metal Concentrations in the Road-deposited Sediments and River Bottom Sediments

Similar to the trend observed for the physicochemical parameters, the measured heavy metals levels of the road-deposited sediments of the 5 sampled highways and the bottom sediments of nearby rivers and streams showed a general trend of significantly higher levels ($p < 0.05$) in the bottom sediments of the surface water bodies. The spatial variations of the studied heavy metals at the various sampling locations in this study are outlined below.

4.2.1 Arsenic

The arsenic levels of the road-deposited sediments of five sampled highway locations were highly variable and found to be significantly lower ($p < 0.05$) than that of the bottom sediments of their respective nearby surface water bodies (Figure 4.4). The measured levels of Arsenic in the bottom sediments of the sampled water bodies were found to be between 1.4 and 15 times higher than the levels recorded for their respective road-deposited sediments. Mean arsenic concentrations of the road-deposited sediments of different sampling sites ranged from a lowest level of 3.30 mgkg^{-1} at Site 1 to a highest level of 87.80 mgkg^{-1} at Site 2. With respect to the bottom sediments of the sampled rivers and streams, arsenic levels also varied over the two sampling seasons with levels ranging from a lowest of 46.73 mgkg^{-1} at Site 5 to a highest of 298.40 mgkg^{-1} at Site 4. Figure 4.4 shows the mean \pm SD of the arsenic concentrations recorded at the different sampling sites over the two seasons.

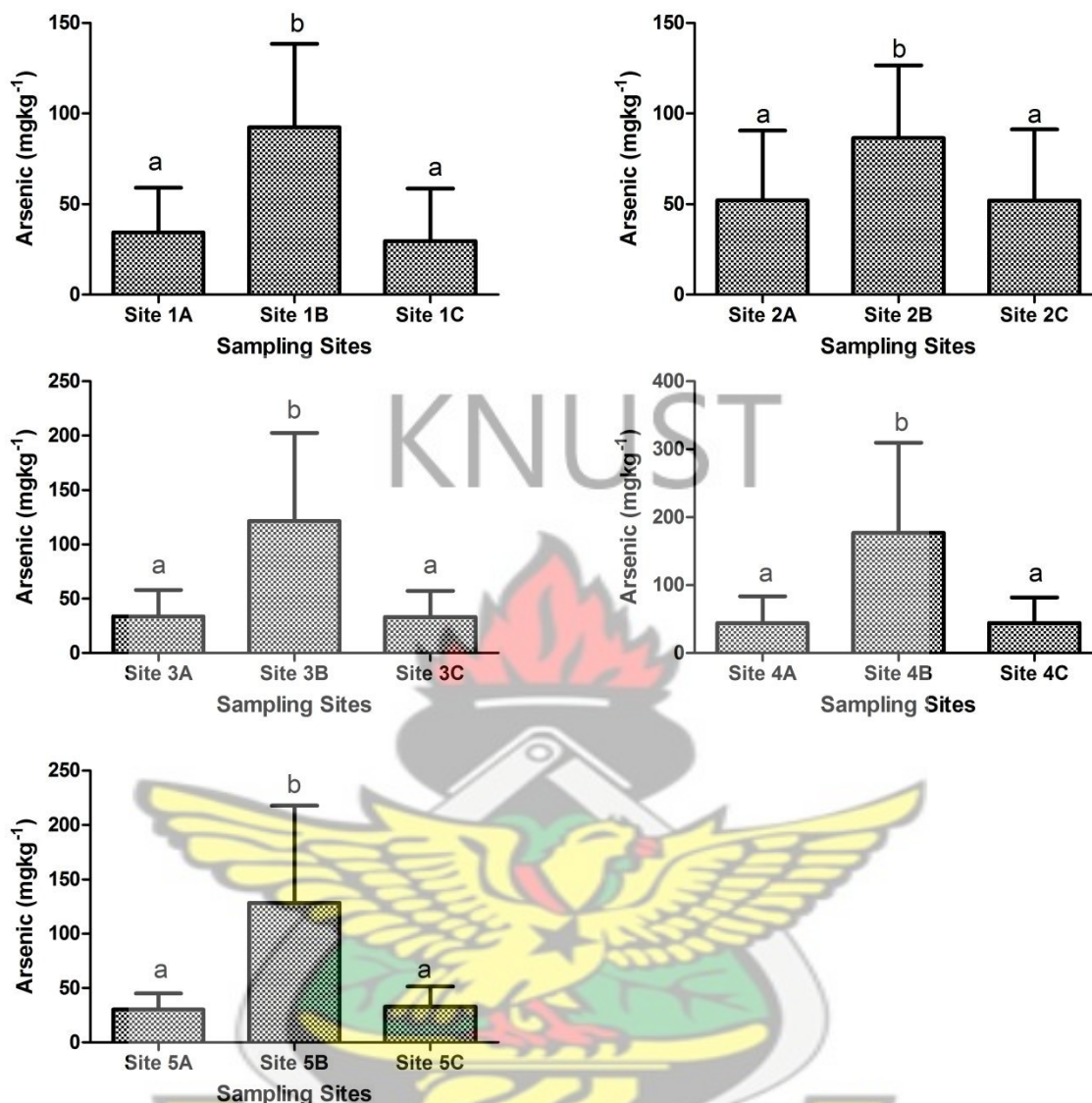
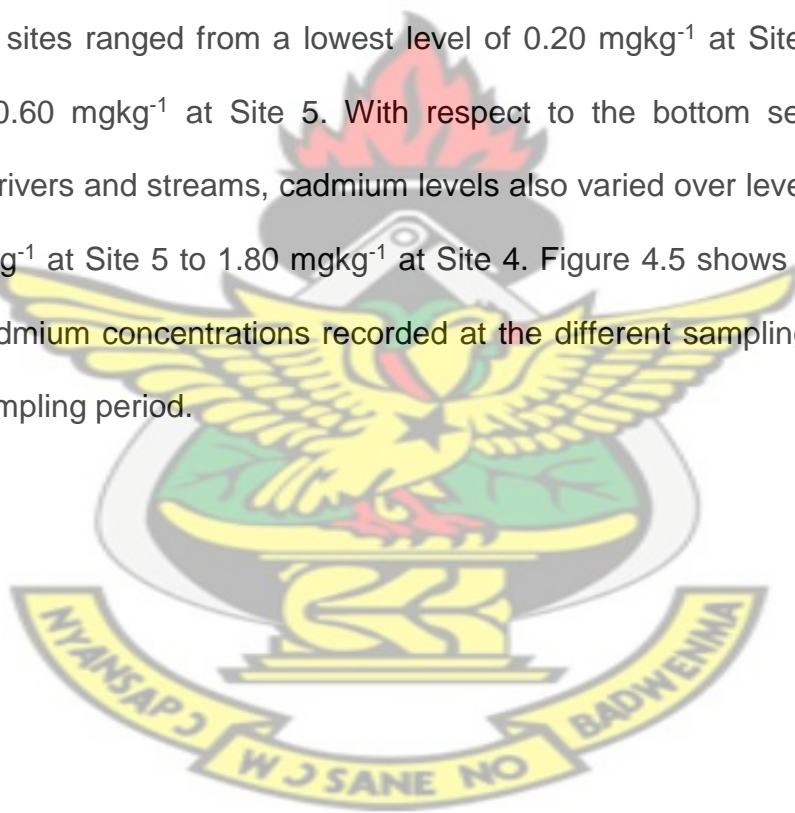


Figure 4. 4: Variations in the arsenic concentrations of the sediments of the different sampling locations.

4.2.2 Cadmium

Recorded cadmium levels of the road-deposited sediments at the different sampling locations were highly variable and also found to be significantly lower ($p < 0.05$) than that of the bottom sediments of their respective nearby surface water bodies (Figure 4.5). The measured levels of cadmium in the bottom sediments of the sampled water bodies were recorded to be at least two-folds higher than the levels recorded for their respective road-deposited sediments. Mean cadmium concentrations of the road-deposited sediments of different sampling sites ranged from a lowest level of 0.20 mg kg^{-1} at Site 3 to a highest level of 0.60 mg kg^{-1} at Site 5. With respect to the bottom sediments of the sampled rivers and streams, cadmium levels also varied over levels ranging from 0.20 mg kg^{-1} at Site 5 to 1.80 mg kg^{-1} at Site 4. Figure 4.5 shows the mean \pm SD of the cadmium concentrations recorded at the different sampling sites over the whole sampling period.



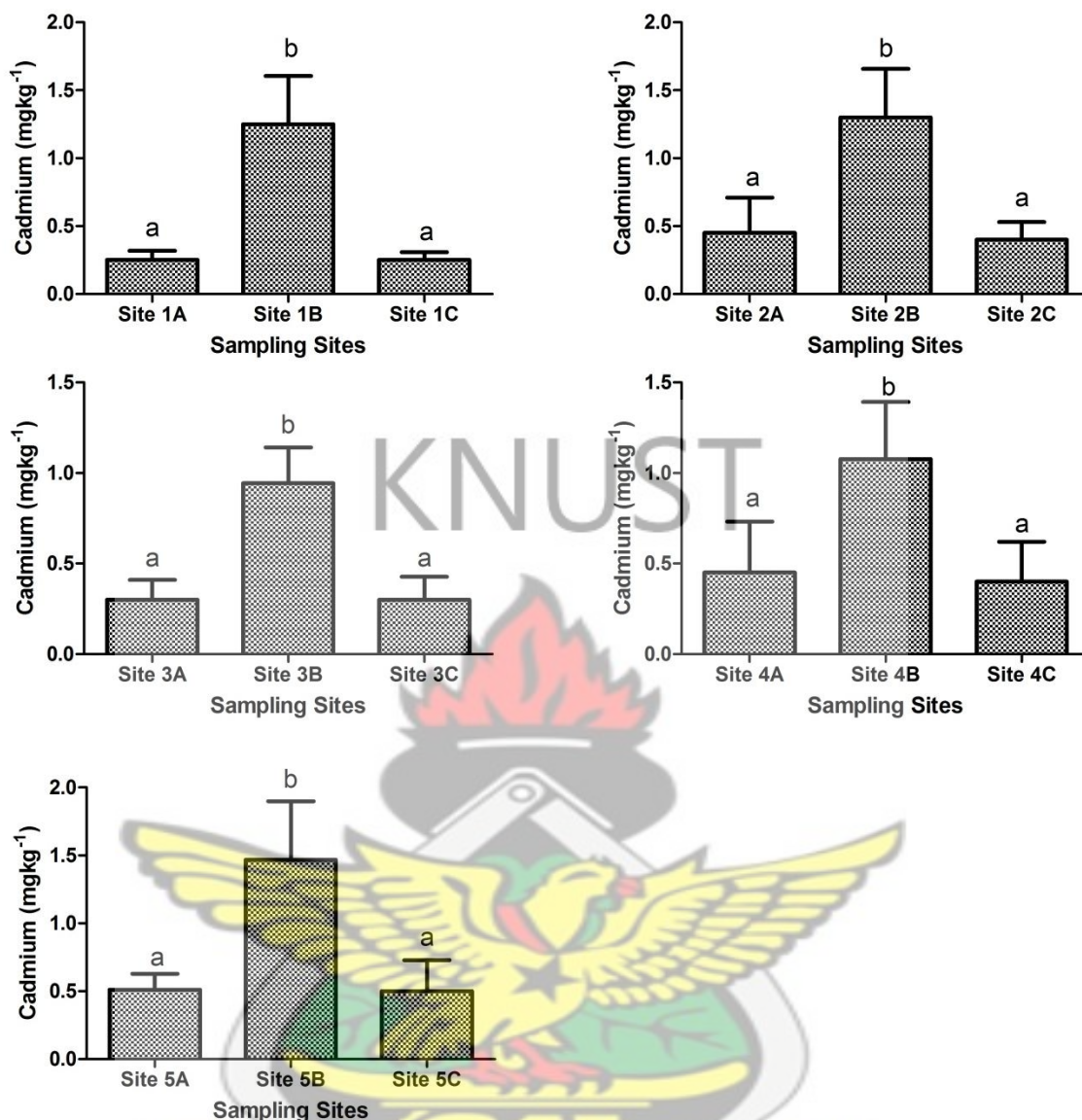


Figure 4. 5: Variations in the cadmium concentrations of the sediments of the different sampling locations.

4.2.3 Copper

With the exception of Site 1, fairly high concentrations of copper were recorded at all the other sampling sites. The copper concentrations recorded in the road-deposited sediments as well as the river bottom sediments of Site 1 ranged between 0.6 and 20 mgkg⁻¹ over the study period. For the other sampling sites,

recorded copper concentrations fell between 18.4 to 1052.6 mgkg^{-1} . Similar to the trend for arsenic and cadmium, the copper concentrations of the bottom sediments of the surface water bodies were significantly higher ($p < 0.05$) than that of the road-deposited sediments at all the sampling sites. The mean \pm SD of the copper concentrations recorded at the different sampling sites over the whole sampling period of this study is shown in the plots (Figure 4.6).

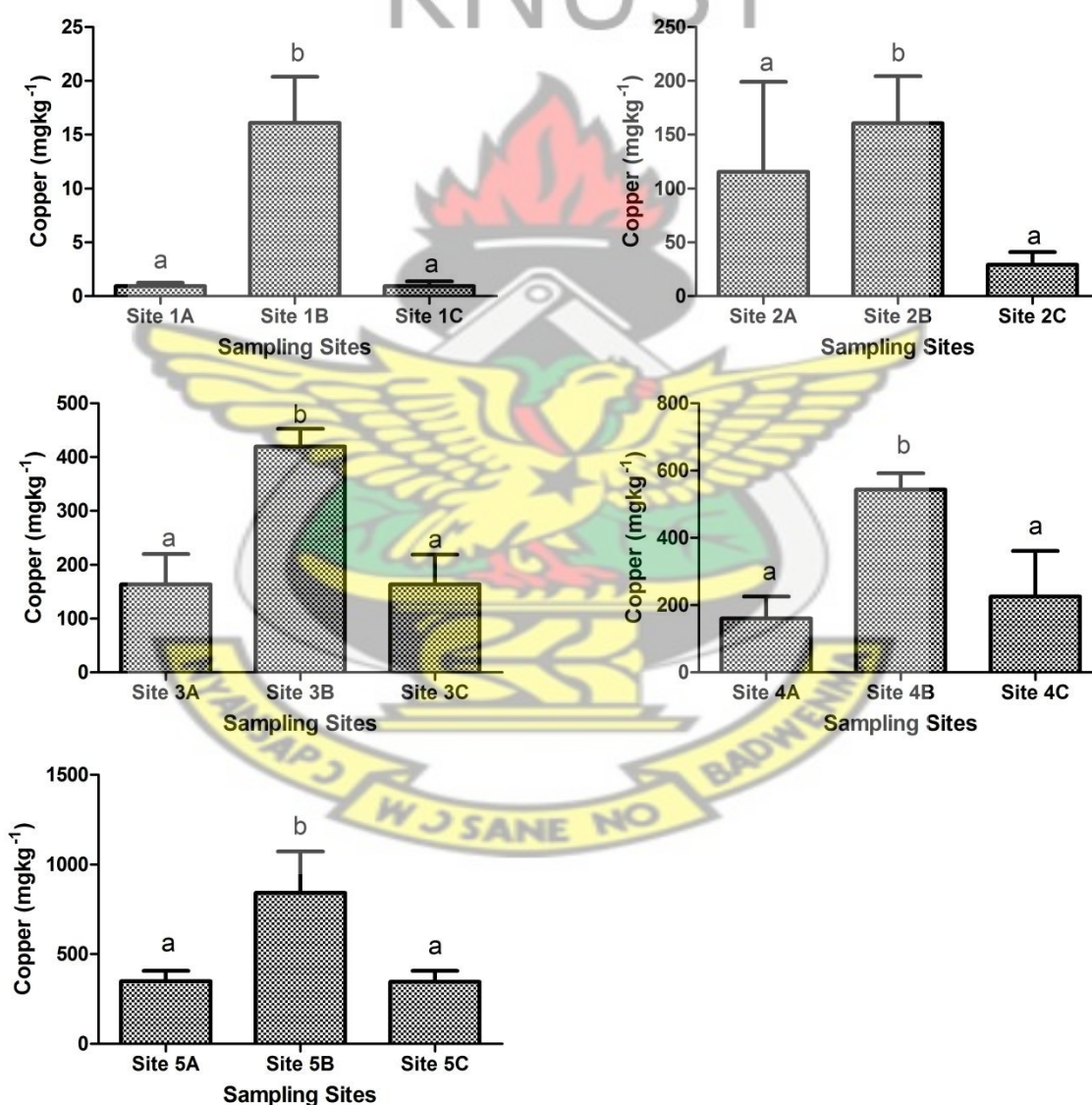
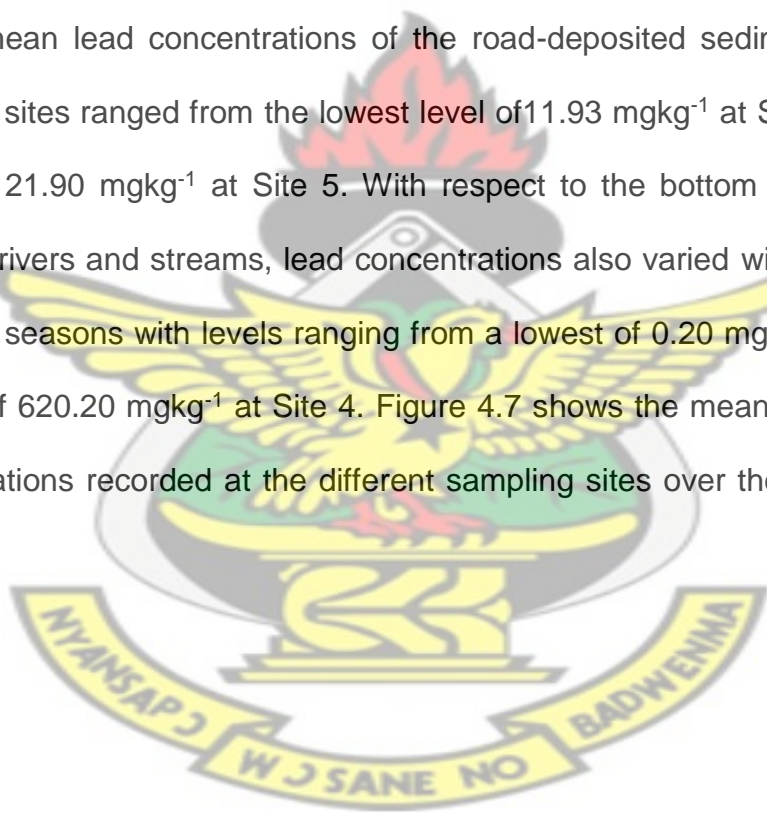


Figure 4. 6: Variations in the copper concentrations of the sediments of the different sampling locations.

4.2.4 Lead

Similar to the accumulation trends observed for all the other metals, the lead levels of the road-deposited sediments at the different sampling locations were highly variable and also found to be significantly lower ($p < 0.05$) than that of the bottom sediments of their respective nearby surface water bodies (Figure 4.7). The measured levels of lead in the bottom sediments of the sampled water bodies were recorded to be between 4 to 14 times higher than the levels recorded for their respective road-deposited sediments. Over the sampling period, mean lead concentrations of the road-deposited sediments of different sampling sites ranged from the lowest level of 11.93 mgkg^{-1} at Site 1 to a highest level of 121.90 mgkg^{-1} at Site 5. With respect to the bottom sediments of the sampled rivers and streams, lead concentrations also varied widely over the two sampling seasons with levels ranging from a lowest of 0.20 mgkg^{-1} at Site 5 to a highest of 620.20 mgkg^{-1} at Site 4. Figure 4.7 shows the mean \pm SD of the lead concentrations recorded at the different sampling sites over the whole sampling period.



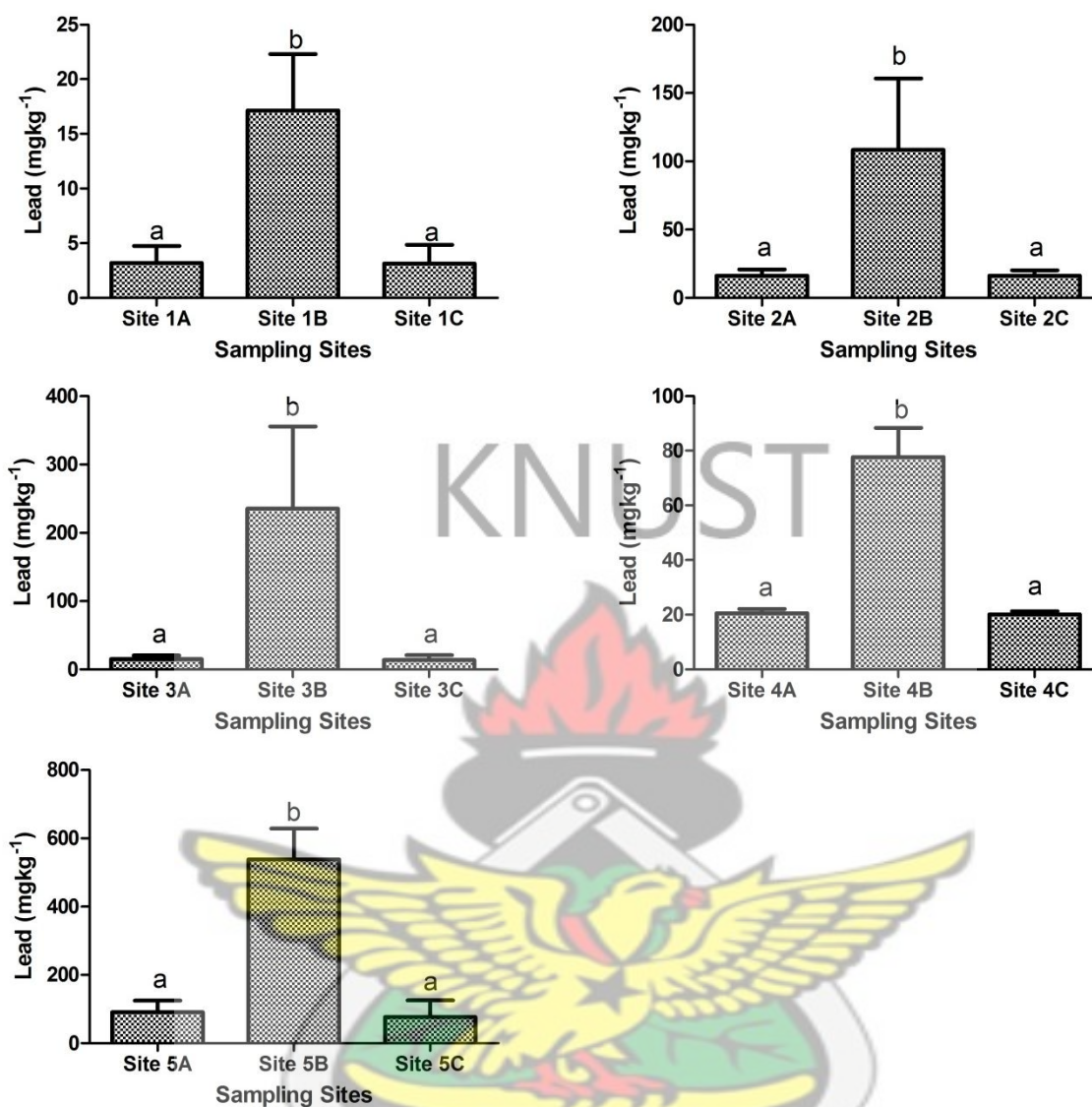


Figure 4. 7: Variations in the lead concentrations of the sediments of the different sampling locations.

4.2.5 Zinc

Zinc concentrations of the road-deposited sediments of the five sampled highway locations were highly variable like all the other assayed metals and found to be significantly lower ($p < 0.05$) than that of the bottom sediments of their respective nearby surface water bodies (Figure 4.8). The measured levels of zinc in the bottom sediments of the sampled water bodies were found to be between 6 and 13 times higher than the levels recorded for their respective road-deposited

sediments. Mean zinc concentrations of the road-deposited sediments of different sampling sites ranged from a lowest level of 11.80 mgkg^{-1} at Site 3 to a highest level of 160.30 mgkg^{-1} at Site 5. With respect to the bottom sediments of the sampled rivers and streams, the recorded zinc levels ranged from a lowest of 109.30 mgkg^{-1} at Site 2 to a highest of $1045.10 \text{ mgkg}^{-1}$ at Site 5. Figure 4.8 shows the mean \pm SD of the zinc concentrations recorded at the different sampling sites over the two seasons.

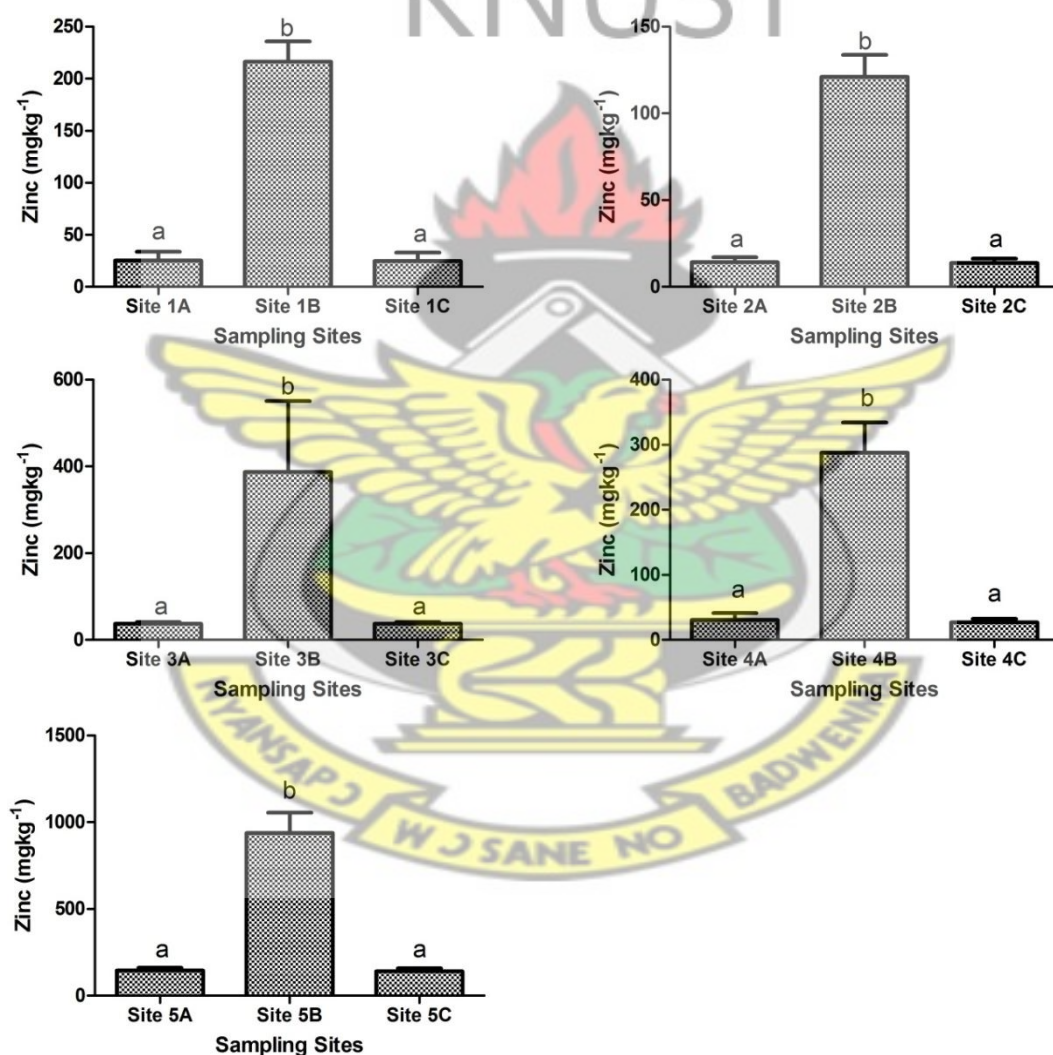


Figure 4. 8: Variations in the zinc concentrations of the sediments of the different sampling locations.

4.3 Seasonal Variations in Physicochemical Parameters and Heavy Metals Concentrations of the Road-deposited Sediments and the River Bottom Sediments

The effect of season on the recorded physicochemical parameters and on heavy metal accumulation was apparent over the sampling period. The recorded levels of the physicochemical parameters were generally higher during the rainy season. An opposite trend was recorded for the heavy metals where higher concentrations were generally recorded during the dry season sampling period. Below are the detailed results of the temporal variations in the levels of the physicochemical parameters and heavy metals recorded in this study.

4.3.1 pH of Sediments at different seasons

The recorded pH levels were generally higher during the rainy season for the different sampling sites. With the exception of Site 3, significant seasonal differences ($p < 0.05$) in pH were only observed for the bottom sediments of the sampled rivers and streams (Figure 4.9). The pH of the bottom sediments were slightly basic during the rainy season and slightly acidic during the dry season.

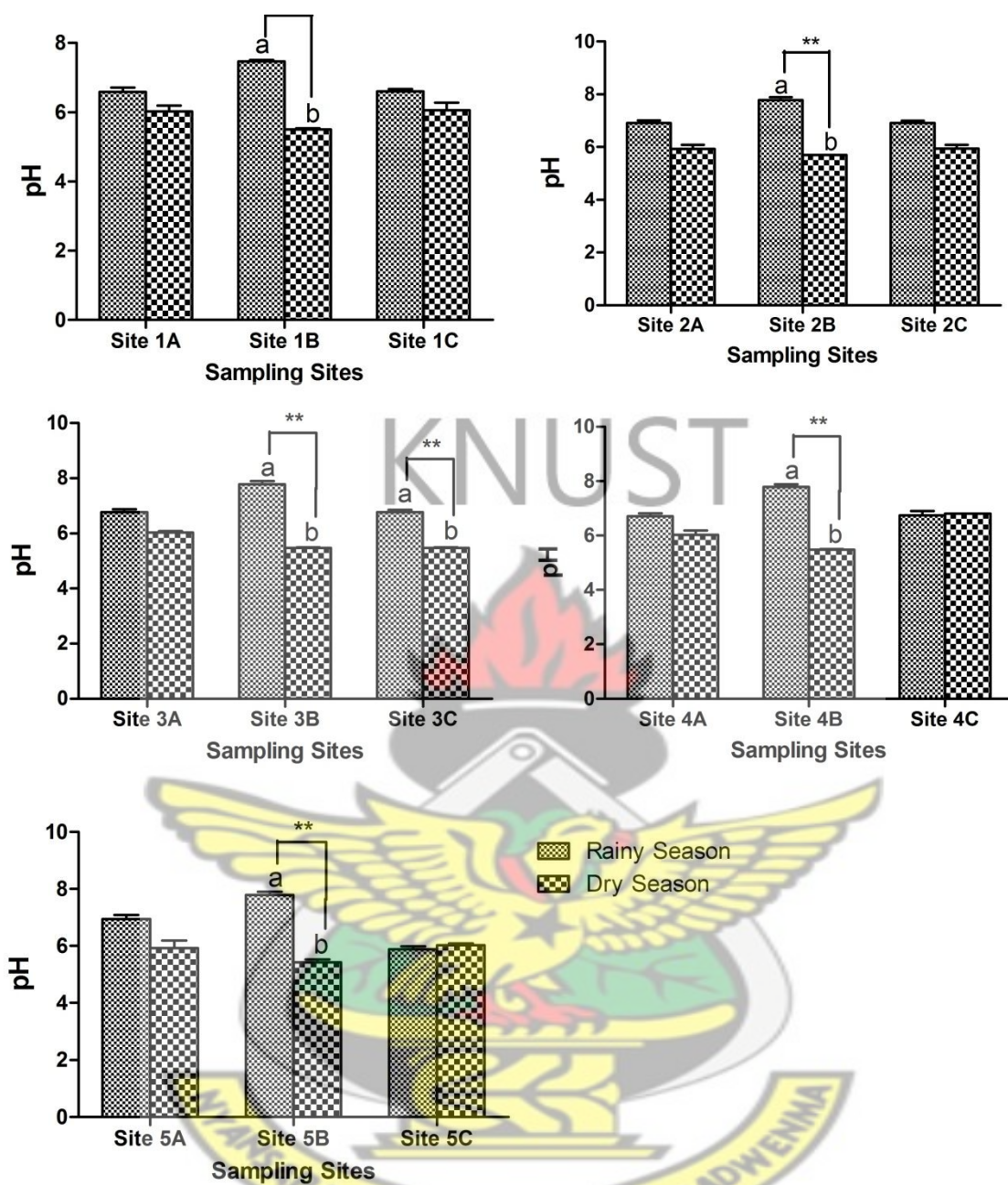


Figure 4. 9: Seasonal variations in pH levels of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars).

4.3.2 Conductivity

Similar to the trend observed for pH, conductivity of the road-deposited sediments and the bottom sediments were higher during the rainy season compared to the dry season. With the exception of Site 2 where significant seasonal differences ($p < 0.05$) were observed for only the river bottom sediments, all the other sampling sites recorded significant variations in conductivity levels for both the road-deposited and the bottom sediments (Figure 4.10).



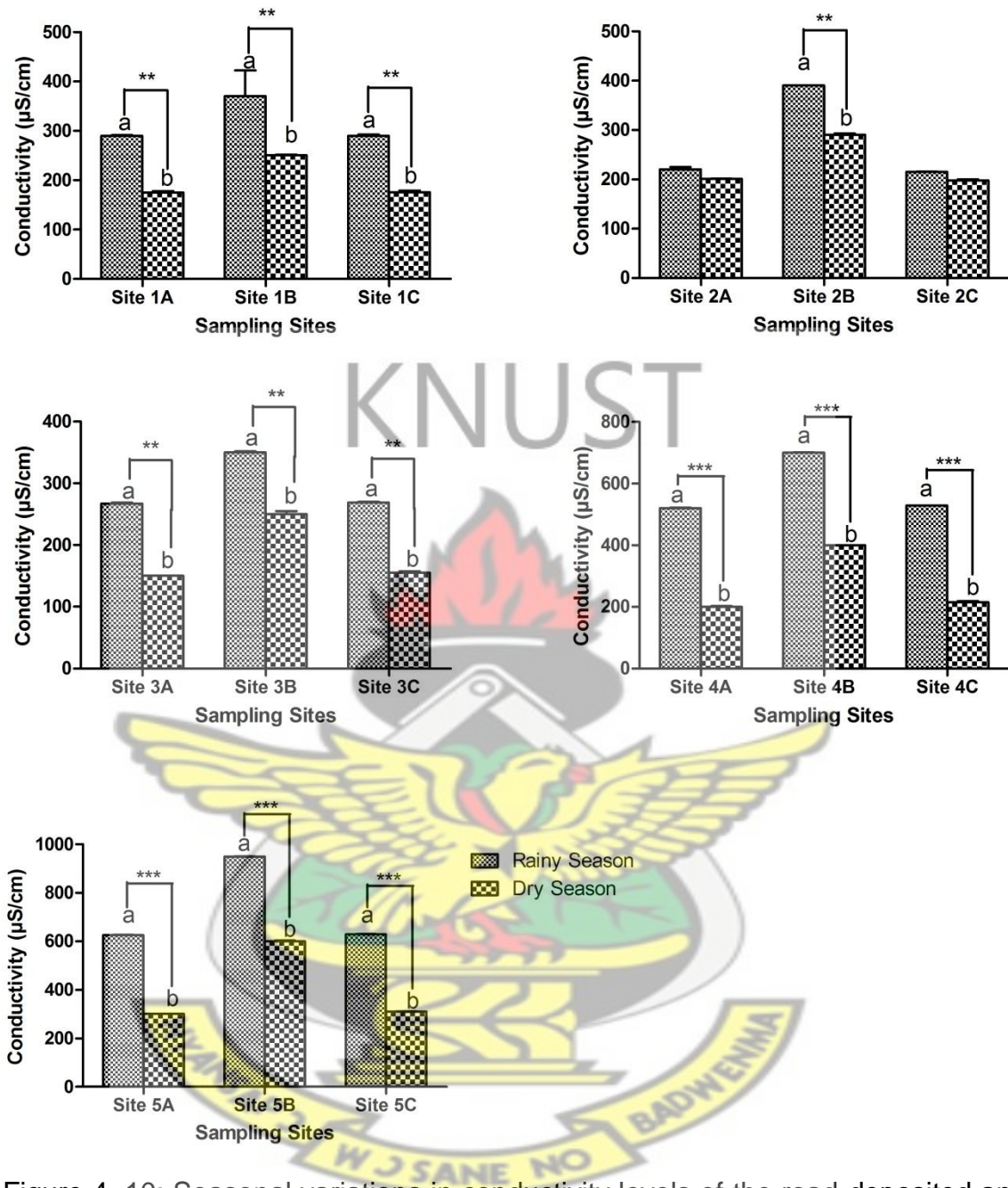


Figure 4. 10: Seasonal variations in conductivity levels of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars).

4.3.3 Organic Matter

The only significant seasonal variations ($p < 0.05$) in organic matter levels over the study period were recorded for the river bottom sediments of Sites 3, 4 and 5. Organic matter levels were fairly similar in the road-deposited sediments over the two seasons with no significant differences ($p > 0.05$) at all the sampling sites over the study period (Figure 4.11).

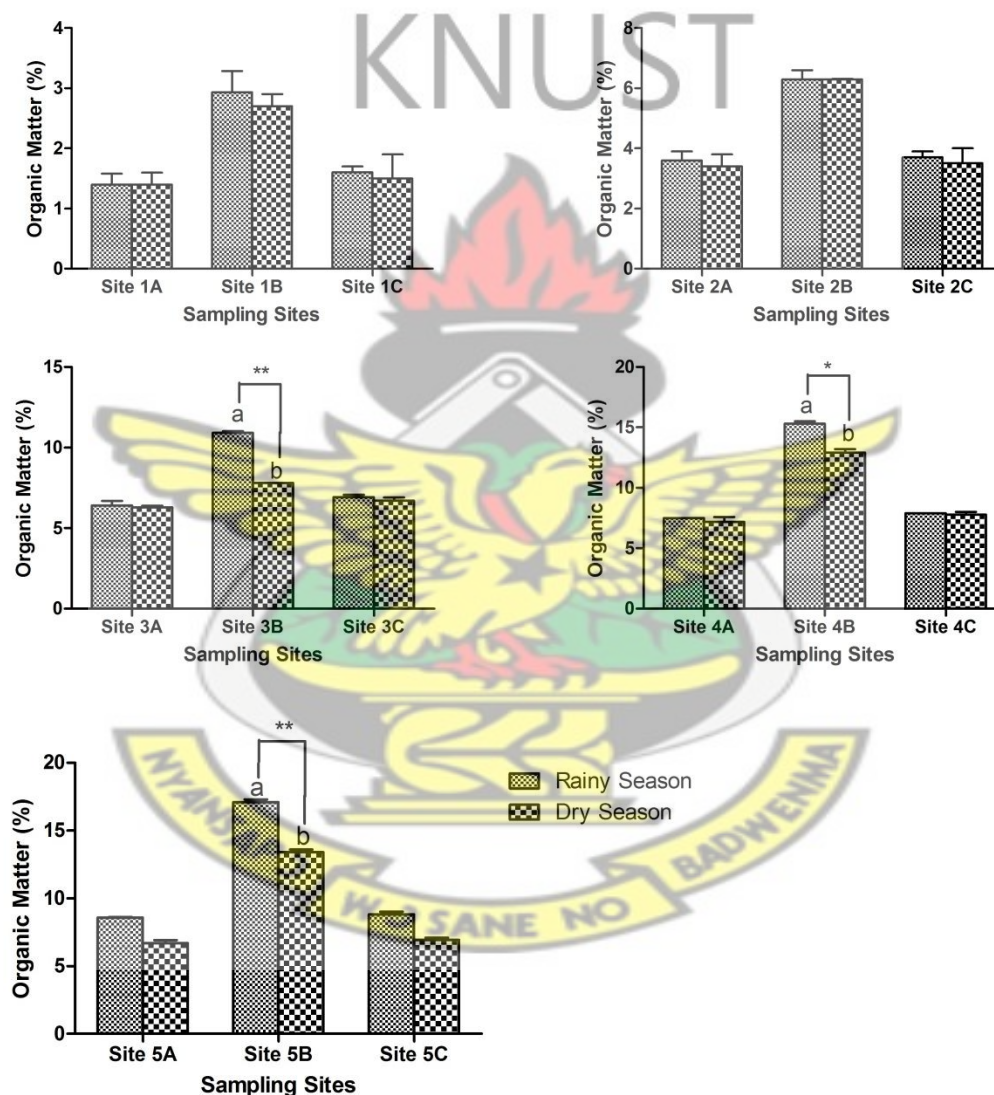


Figure 4. 11: Seasonal variations in organic matter levels of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars).

4.3.4 Arsenic

Arsenic levels in the road-deposited sediments and the bottom sediments of the surface water bodies were significantly affected by season over the study period. Levels of arsenic in the road-deposited and bottom sediments were significantly higher ($0 < 0.05$) during the dry season compared to the rainy season at all the sampling sites. The elevations in arsenic concentrations during the dry season were between 2.5 and 8 times higher than their respective rainy season levels.



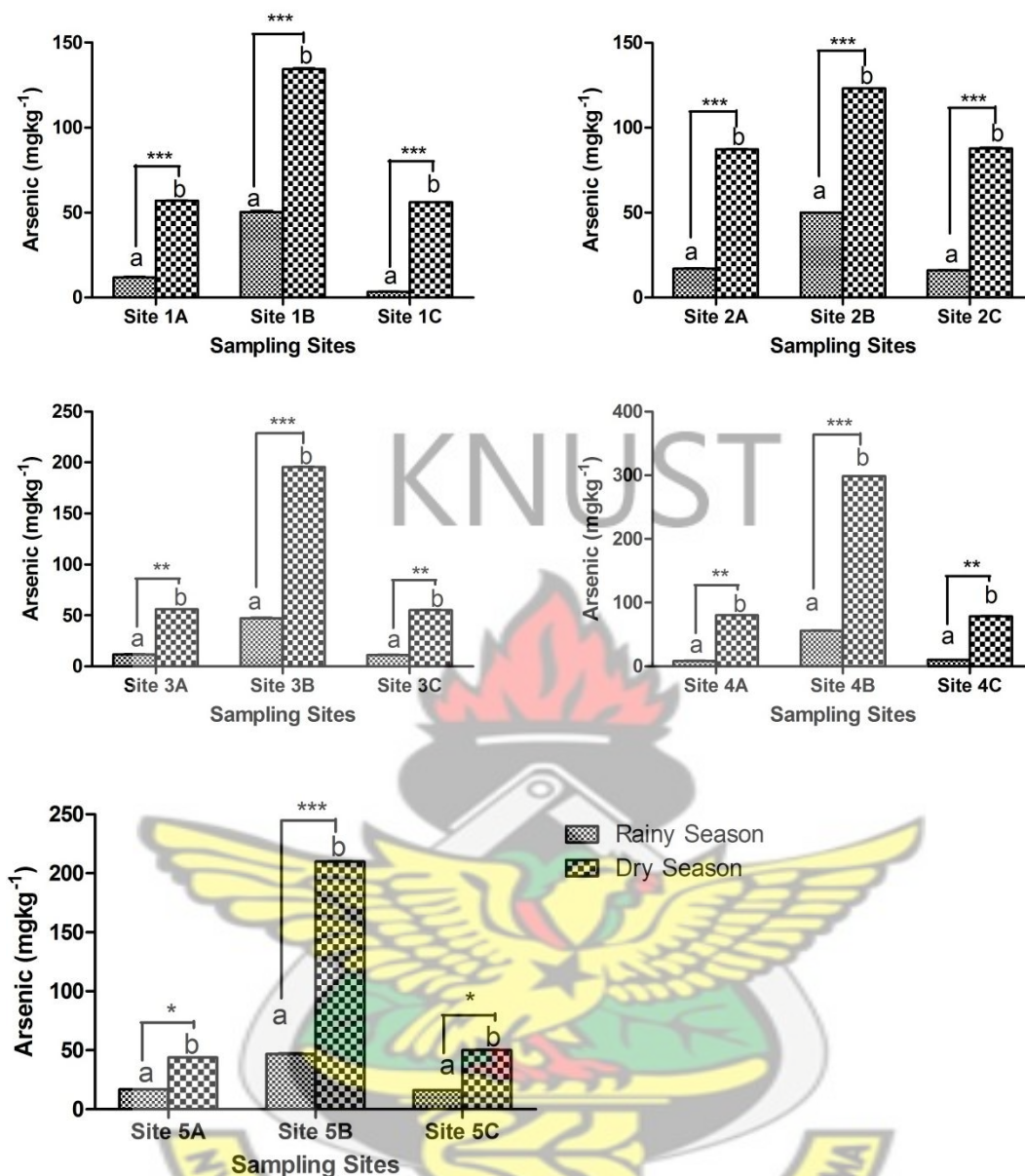
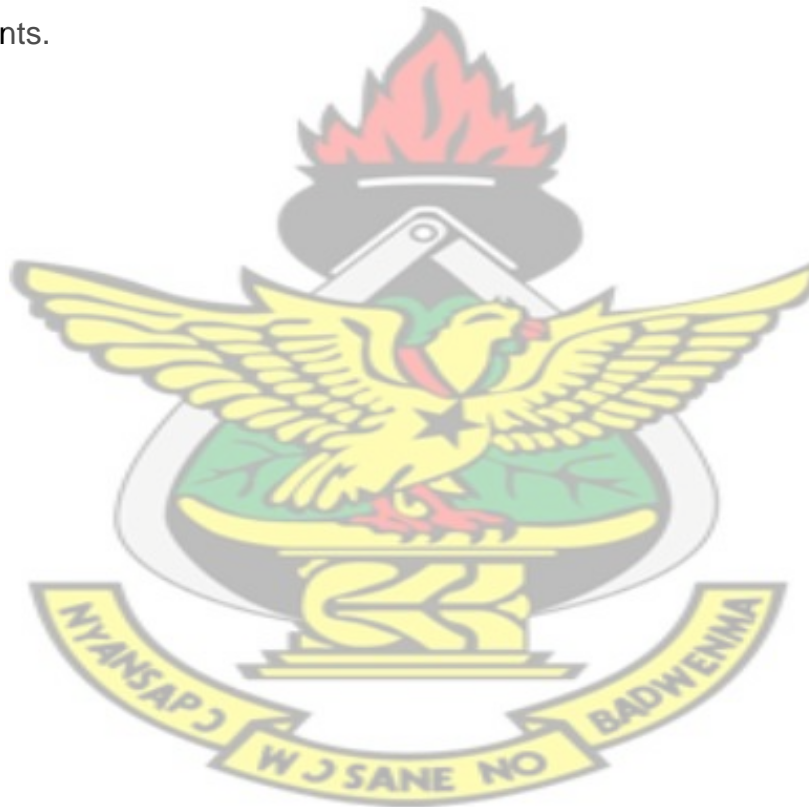


Figure 4. 12: Seasonal variations in arsenic concentrations of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars).

4.3.5 Cadmium

The recorded cadmium concentrations in the road-deposited sediments and the bottom sediments of the surface water bodies were significantly affected by season over the study period. Except at Site 1 where significant seasonal

variations ($p < 0.05$) were recorded for only the bottom sediments, the cadmium concentrations in the road-deposited and bottom sediments were significantly different ($0 < 0.05$) at all the other sampling sites. There was a general trend of higher cadmium concentrations in the road-deposited bottom sediments during the dry season except for Site 5 where a reverse trend was observed. With the exception of Site 4 where the dry season cadmium concentrations were more than 3 times higher than the rainy season concentration, all the other seasonal differences recorded at the other sampling sites were less than 2-fold increments.



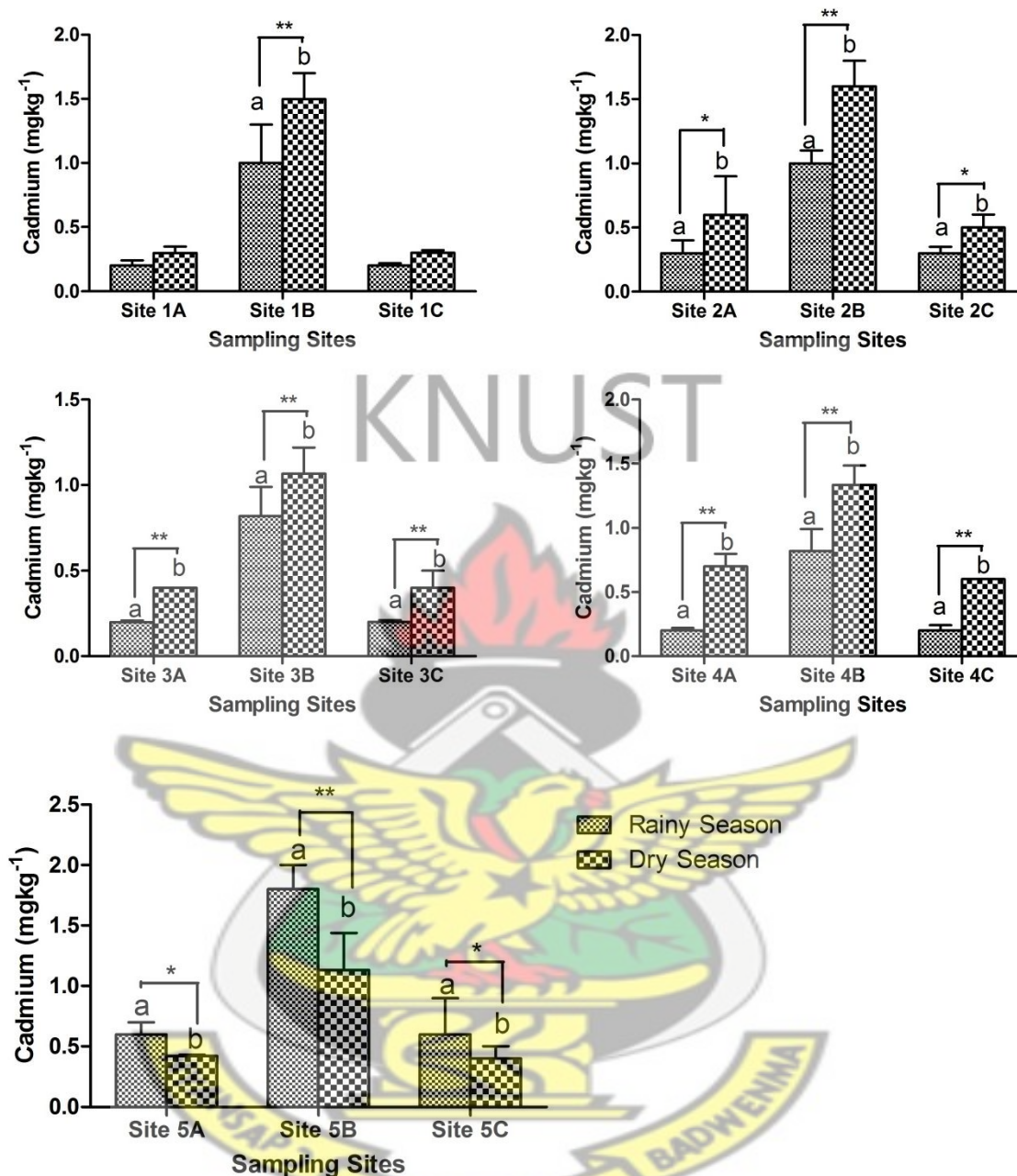
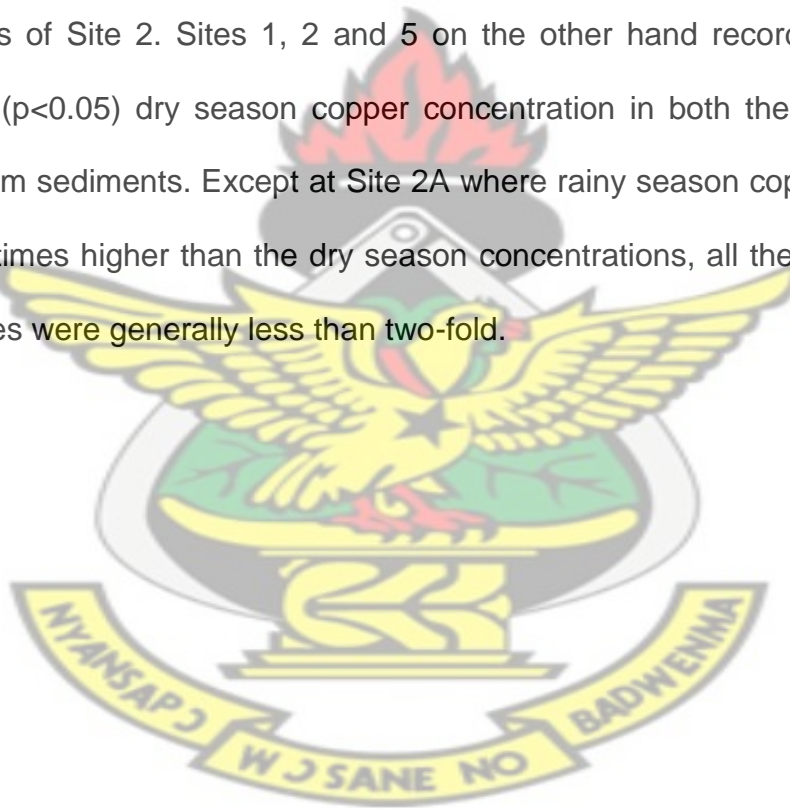


Figure 4. 133: Seasonal variations in cadmium concentrations of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars.

4.3.6 Copper

Seasonal variations in copper concentrations did not follow defined trends with the different sampling sites recording elevated copper levels at different times. This notwithstanding, the recorded copper concentrations in the road-deposited sediments and the bottom sediments of the surface water bodies were significantly affected by season over the study period (Figure 4.14). Significantly higher ($p < 0.05$) rainy season copper concentrations in both the road-deposited bottom sediments were recorded at Sites 3 and 4 and also in the road-deposited sediments of Site 2. Sites 1, 2 and 5 on the other hand recorded significantly elevated ($p < 0.05$) dry season copper concentration in both the road-deposited and bottom sediments. Except at Site 2A where rainy season copper levels were nearly 5 times higher than the dry season concentrations, all the other seasonal differences were generally less than two-fold.



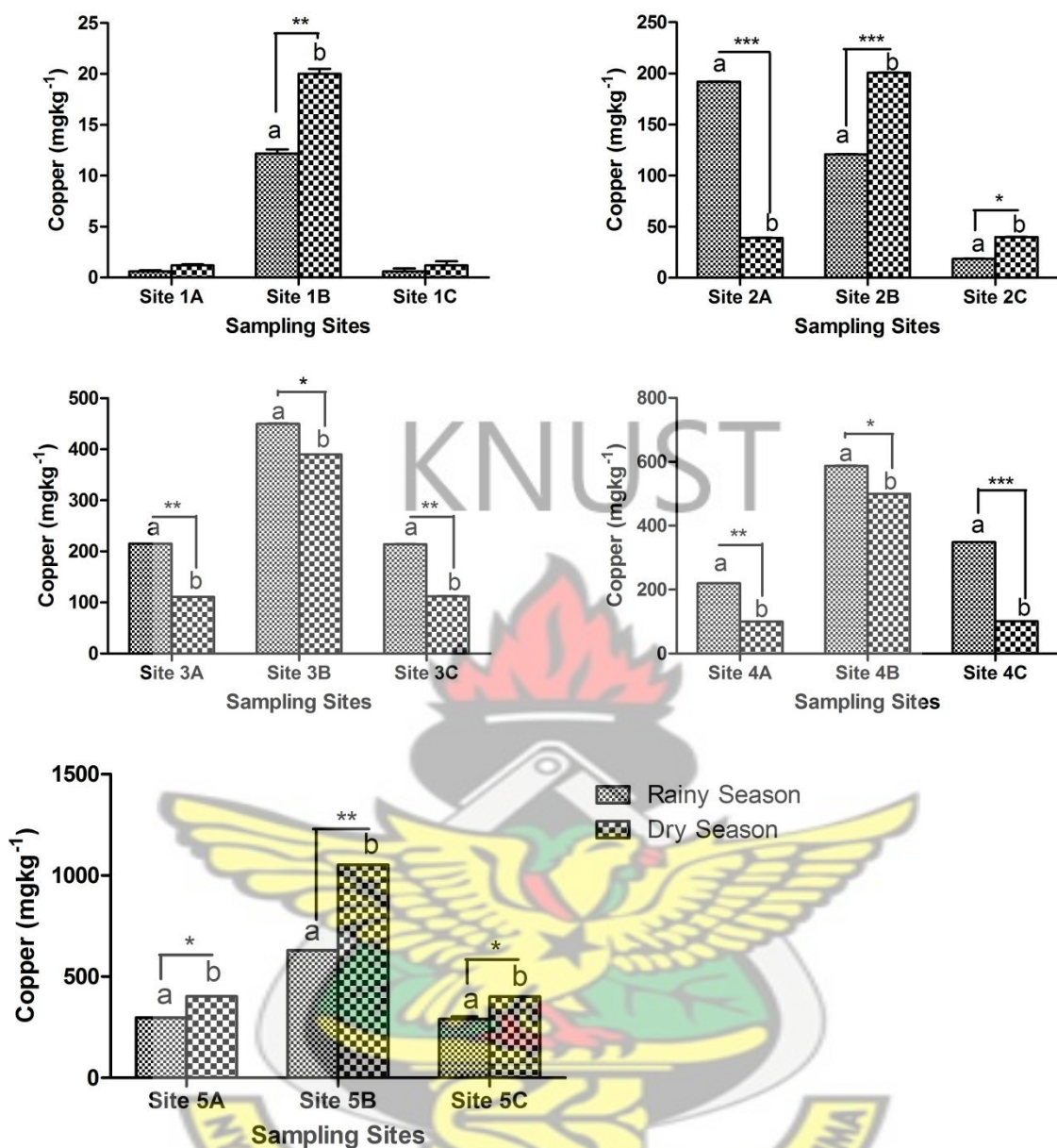


Figure 4. 144: Seasonal variations in copper concentrations of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars.

4.3.7 Lead

Similar to the seasonal arsenic trend, the recorded lead concentrations in the road-deposited sediments and the bottom sediments of the surface water bodies were significantly affected by season over the study period with the dry season recording higher lead levels. The seasonal variations in the recorded lead levels in the bottom sediments of the sampled rivers were significant ($p < 0.05$) at all the sampling sites. Significant seasonal variations in lead concentrations ($p < 0.05$) of the road-deposited sediments were recorded at Sites 1 and 5. All the other 3 sampling sites recorded no significant ($p > 0.05$) influence of season on road-deposited sediment lead concentrations.



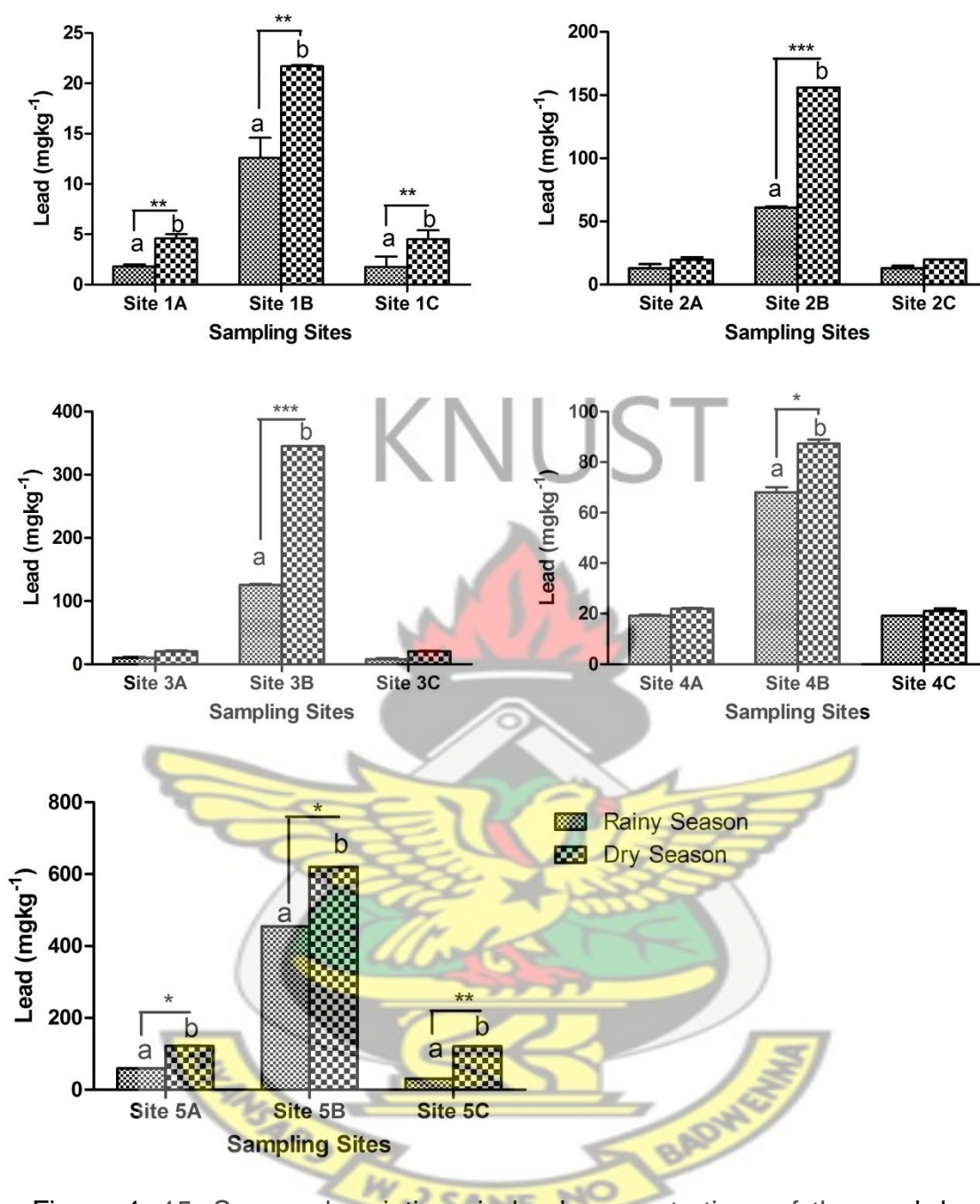


Figure 4. 15: Seasonal variations in lead concentrations of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars).

4.3.8 Zinc

Similar to the seasonal arsenic and lead trends, the recorded zinc concentrations in the road-deposited sediments and the bottom sediments of the surface water bodies were significantly affected by season over the study period with the dry season recording higher zinc concentrations. The variations between rainy and dry season zinc concentrations of the bottom sediments of the sampled rivers were significant ($p < 0.05$) at all the five (5) sampling sites. Significant seasonal variations in the zinc concentrations ($p < 0.05$) of the road-deposited sediments were recorded only at Sites 1. All the other 4 sampling sites recorded no significant ($p > 0.05$) influence of season on road-deposited sediment as far as zinc concentrations are concerned.



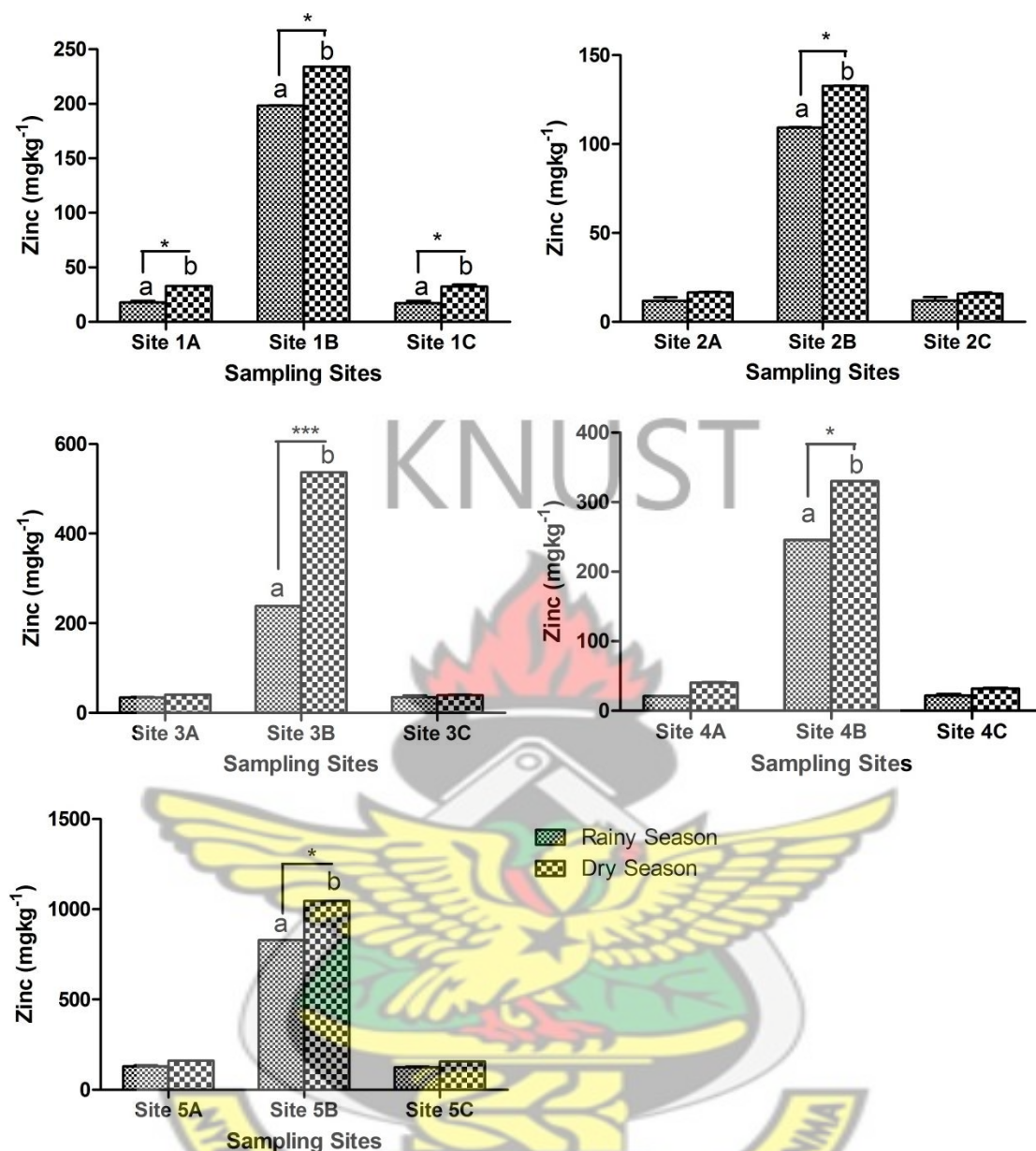


Figure 4. 16: Seasonal variations in zinc concentrations of the road-deposited and bottom sediments different sampling sites of the study. (Bars with different letters indicate significant differences ($p < 0.05$). Absence of letters indicate no significant differences ($p > 0.05$) between compared bars.

4.4 Sediment Pollution Analysis

The concentrations of the five metals in the sediment samples were subjected to various calculations to ascertain the extent of metal pollution in the road-

deposited sediments and the bottom sediments of their respective surface water bodies. Below are the detailed results for the sediment contamination assessments using the different indices.

4.4.1 Geoaccumulation Index

Based on the geoaccumulation index, it was realized that the road-deposited sediments from the various sampling locations were generally unpolluted (class 0) as far as rainy season arsenic concentrations are concerned. The bottom sediments of the various rivers and streams were generally unpolluted to moderately polluted (class 1) as far as rainy season arsenic levels are concerned. The dry season arsenic loads of the road-deposited sediments, also, indicated a situation of unpolluted to moderately polluted (class 1). During the dry season the bottom sediments of the surface waters all fell within the pollution category of moderately to strongly polluted (class 3). With the exception of road-deposited sediments of Site 5 which fell within the moderately polluted (class 2) category, all the road-deposited sediments of the other sampling sites were unpolluted to moderately polluted (class 1) as far as rainy season cadmium concentrations are concerned. The bottom sediments were generally moderately to strongly polluted (class 3) as far as the recorded rainy season cadmium concentrations are concerned. The bottom sediments of Site 5 were, however, strongly polluted (class 4) with respect to the rainy season cadmium concentrations. During the dry season the road-deposited sediments of all the sampling sites were moderately polluted (class 2) with respect to cadmium. The dry season cadmium concentrations of the bottom sediments fell in the

moderately to strongly polluted (class 3) and strongly polluted (class 4) categories. The pollution intensities of copper were highly variable among the sampling sites within the same sampling season. The road-deposited sediments of Sites 1 and 2 were unpolluted (class 0) as far as both rainy and dry season copper concentrations are concerned. All the other sites, however, recorded rainy season road-deposited sediment copper concentrations that indicated moderately to strongly polluted (class 3) pollution intensities. With the exceptions of Sites 1 and 2 which were unpolluted (class 0), the rainy season copper concentrations of the bottom sediments generally indicated a situation of strong pollution (class 4). Except for Sites 1 and 2, the road-deposited sediments were generally moderately polluted (class 2) at Sites 3 and 4 and strongly polluted (class 4) at Site 5 during the dry season. The bottom sediments were also moderately to strongly polluted (class 3) for Sites 2 and 3, strongly polluted (class 4) for Site 4 and strongly to extremely polluted (class 5) for Site 5 with respect to dry season copper concentrations. The rainy season lead concentrations of the road-deposited sediments for Sites 1, 2 and 3 indicated a situation of no pollution (class 0) with Sites 4 and 5 indicating pollution intensities of unpolluted to moderately polluted (class 1). The pollution intensities of the bottom sediments with lead were highly variable among the sampling locations and were as follows; Site 1 (unpolluted), Sites 2 and 4 (moderately polluted), Site 3 (moderately to strongly polluted) and Site 5 (strongly polluted). For the dry season, the road-deposited sediments at Sites 1, 2, 3 and 4 were unpolluted (class 0) as far as lead is concerned. The road-deposited sediments of Site 5 were moderately to strongly polluted (class 3) with lead during the dry season. The pollution

intensities of the bottom sediments with respect to lead were highly variable among the sampling locations similar to the rainy season trend and were as follows; Site 1 (unpolluted), Site 2 (moderately to strongly polluted), Site 3 (strongly polluted), Site 4 (moderately polluted) and Site 5 (strongly to extremely polluted). The road-deposited sediments of all the 5 sampling sites were unpolluted with respect to the recorded rainy season zinc concentrations. As far as rainy season zinc concentrations in the bottom sediments are concerned, the pollution intensities for the different sites were as follows; Sites 1, 3 and 4 (unpolluted to moderately polluted), Site 2 (unpolluted) and Site 5 (moderately to strongly polluted). With the exception of Site 5 (unpolluted to moderately polluted) all the other sites were unpolluted (class 0) as far as dry season zinc concentrations are concerned. As far as dry season zinc concentrations in the bottom sediments are concerned, the pollution intensities for the different sites were as follows; Site 1 (unpolluted to moderately polluted), Site 3 and 4 (unpolluted to moderately polluted), Site 2 (unpolluted), Sites 3 and 4 (moderately polluted) and Site 5 (moderately to strongly polluted). The results of the calculated geoaccumulation indices for the studied metals at all the sampling sites are shown in Tables 4.1 and 4.2.

Table 4. 1: Sediment Geoaccumulation Index of the studied metals on sampling sites for rainy season

	1A	1C	1B	2A	2C	2B	3A	3C	3B	4A	4C	4B	5A	5C	5B
Metals															
As	-1.346	-3.184	0.751	-0.827	-0.897	0.739	-1.346	-1.395	0.653	-1.836	-1.570	0.897	-0.827	-0.897	0.641
Cd	0.347	0.347	2.599	0.955	0.909	2.599	0.599	0.415	2.277	0.277	0.909	2.277	1.862	1.862	3.447
Cu	-6.366	-6.366	-2.020	-1.366	-1.427	1.288	2.118	2.112	3.183	2.152	2.817	3.569	2.582	2.585	3.670
Pb	-3.984	-4.017	-1.177	-1.143	-1.154	1.095	-1.468	-1.888	2.143	0.569	0.569	1.256	0.166	0.125	3.990
Zn	-2.992	-3.050	0.479	-3.594	-3.581	-0.382	-2.067	-2.033	0.740	-2.748	-0.813	0.787	-0.132	-0.193	2.542

Table 4. 2: Sediment Geoaccumulation Index of the studied metals on sampling sites for dry season

	1A	1C	1B	2A	2C	2B	3A	3C	3B	4A	4C	4B	5A	5C	5B
Metals															
As	0.923	0.903	2.163	1.539	1.549	2.036	0.900	0.879	2.704	1.415	1.387	3.314	0.545	0.736	2.806
Cd	1.203	1.084	3.184	2.021	1.862	3.277	1.447	1.277	2.862	2.084	1.862	2.977	1.347	1.277	2.862
Cu	-5.366	-5.366	-1.307	-0.343	-0.314	2.019	1.165	1.176	2.978	1.014	1.025	3.336	3.020	3.018	4.410
Pb	-2.631	-2.662	-0.393	-0.540	-0.532	2.452	-0.510	-0.503	3.597	-0.380	-0.440	1.610	2.096	2.087	4.443
Zn	-2.119	-2.150	0.715	-3.110	-3.172	-0.102	-1.804	-1.840	1.912	-1.814	-2.159	1.211	0.169	0.138	2.874

4.4.2 Contamination Factor

The contamination factors (CF) of the metal pollutants in the road-deposits as well as bottom sediments were also evaluated to contextualise the degree of anthropogenic contribution to the total heavy metal pollution. The results revealed varying degrees of pollution of the sampled sediments with respect to the 5 metals. The arsenic levels in the road-deposited sediments were similar to those found in areas of low contamination. During the dry season, however, the calculated arsenic contamination factors were similar to those of areas with moderate contaminated sediments. The contamination factors of the bottom sediments indicated pollution levels of moderate to high arsenic contamination in the two sampling seasons. Cadmium levels in the road-deposited and bottom sediments of the various sampling sites for the two seasons indicated contamination extents of moderate to very high contamination levels with the bottom sediments generally recording higher levels of contamination. The extent of copper contamination in the road-deposited and river sediments was highly variable among the different sampling sites ranging from low contamination (Site 1) to very high contamination levels at the remaining sites. The lead contaminations of the road-deposited sediments of all the sampling sites were similar to those of areas with low to moderate contamination extents. The bottom sediments, however, revealed considerable to very high contamination levels as far as lead is concerned. The road-deposited sediments of Sites 1, 2, 3 and 4 had low levels of zinc contamination with respect to their respective calculated contamination factors. The road-deposited sediments of Site 5 on the other hand

were moderately polluted with zinc. The bottom sediments of Sites 1, 2, 3 and 4 had moderate levels of zinc contamination with respect to their respective calculated contamination factors for the two seasons. The contamination factors of the bottom sediments of Site 5 on the other hand were similar to areas with very high zinc pollution. The results of the calculated contamination factors for the studied metals at all the sampling sites are shown in Tables 4.3 and 4.4.

4.4.3 Pollution Load Index (PLI)

The calculated pollution load indices were generally indicative of sites with deteriorated quality as far as the studied metals are concerned. Calculated PLIs were above 1 (deteriorated site quality) for all the samplings sites except for Sites 1 and 2 during the rainy season and Site 1 during the dry season. The calculated PLIs of the sampled sites in this study are shown in Table 4.5.

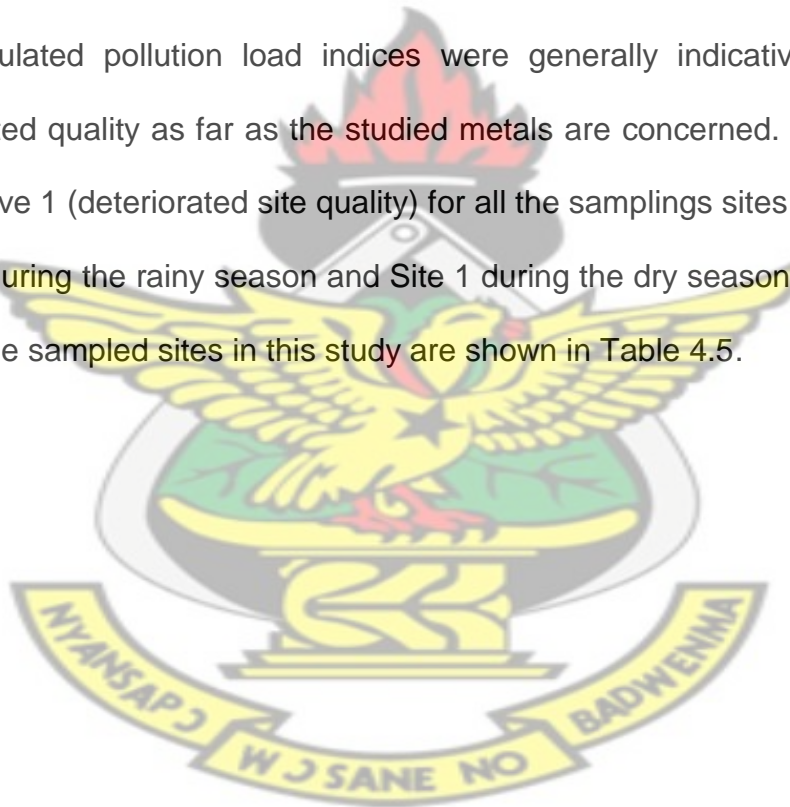


Table 4. 3: Sediment Contamination Factor of the studied metals on sampling sites for rainy season

Metals	1A	1C	1B	2A	2C	2B	3A	3C	3B	4A	4C	4B	5A	5C	5B
As	0.590	0.165	2.525	0.845	0.805	2.505	0.590	0.570	2.360	0.420	0.505	2.795	0.845	0.805	2.340
Cd	1.909	1.909	9.090	2.909	2.818	9.090	2.272	2.000	7.272	1.818	1.909	7.272	5.454	5.454	16.363
Cu	0.018	0.018	0.369	0.581	0.557	3.663	6.515	6.484	13.630	6.666	10.575	17.803	8.927	9.003	19.093
Pb	0.094	0.092	0.663	0.678	0.673	3.205	0.542	0.405	6.626	1.010	1.010	3.584	3.142	1.636	23.947
Zn	0.188	0.181	2.091	0.124	0.125	1.150	0.375	0.366	2.506	0.223	0.230	2.588	1.368	1.311	8.736

Table 4. 4: Sediment Contamination Factor of the studied metals on sampling sites for dry season

Metals	1A	1C	1B	2A	2C	2B	3A	3C	3B	4A	4C	4B	5A	5C	5B
As	2.845	2.805	6.720	4.360	4.390	6.155	2.800	2.760	9.780	4.000	3.925	14.920	2.190	2.500	10.495
Cd	3.454	3.181	13.636	6.090	5.454	14.545	4.090	3.636	10.909	6.363	5.454	11.818	3.818	3.636	10.909
Cu	0.036	0.036	0.606	1.181	1.206	6.081	3.363	3.390	11.821	3.030	3.054	15.154	12.175	12.154	31.896
Pb	0.242	0.236	1.142	1.031	1.036	8.210	1.052	1.057	18.157	1.152	1.105	4.578	6.415	6.415	3.642
Zn	0.345	0.337	2.463	0.173	0.166	1.396	0.429	0.418	5.647	0.426	0.335	3.473	1.687	1.651	11.000

Table 4. 5: Sediment Pollution Load Index of the studied metals on sampling sites for the rainy and dry seasons

	1A	1C	1B	2A	2C	2B	3A	3C	3B	4A	4C	4B	5A	5C	5B
Rainy Season	0.204	0.156	1.636	0.654	0.654	3.144	1.110	1.018	5.222	1.027	1.88	5.070	2.815	2.430	10.886
Dry Season	0.494	0.480	2.746	1.411	1.377	5.741	1.770	1.719	10.527	2.068	1.891	8.426	4.058	4.108	16.731



CHAPTER 5

DISCUSSION

5.1 Heavy Metal Sources in Road-Deposited and Bottom Sediments

In this study, the concentrations of pH in both the road deposited and bottom sediment water bodies sediment were fairly neutral and didn't pose any threat to the aquatic life in the water bodies. Moreover, the conductivity and the organic matter levels of the road deposited and river bottom sediments were minimal and did not cause any threat to living organisms in the water bodies. Although, high concentration of organic matter should result in high heavy metal concentrations, this study did not followed that pattern in some of the heavy metals concentrations measured in some of the sampling areas. In comparing with other studies conducted in Ghana and other countries, the data obtained were in agreement with Atiemo *et al.*, 2011; Herath *et al.*, 2013 which showed no high recorded physicochemical parameters (pH, conductivity and organic matter) in their studies of assessing heavy metals.

With regards to the heavy metal concentrations in the road deposited sediments, higher values were recorded indicating high pollution of the area. The specific sources of lead to road-deposited sediments include leaded fuels from vehicular exhaust, tyre wear, lubricating oil and grease, bearing wear. These findings agree with Atiemo *et al.*, (2011) in his study on heavy metals in Ghana. In addition, sources of copper to road-deposited sediments include metal platings in

vehicles, bearing and brushing wear, moving engine parts and brake lining wear. Cadmium in road-deposited sediments is mainly as a result of tyre wear. Moreover, zinc on the road deposited sediment could also be sourced from the metallic corroded parts of the vehicles falling on the road. In terms of spatial variation, Site 5 had the highest metal concentrations compared to the other sites. Studies have shown high contents of heavy metals in the road-deposited sediments at the traffic intersection where vehicles are typically decelerated (Ellis and Revitt 1982; Fergusson and Ryan 1984). Metals are found to be most detectable in the road-deposited sediments in busy traffic areas (Culbard *et al.* 1998; Leharne *et al.* 1992; Wong and Mak 1997). This possibly explains why the heavy metal concentrations of road-deposited sediments were generally highest along Site 5 (The Osei-Tutu II Boulevard) which has the intense vehicular traffic among the sampled sites.

Intensity of vehicle traffic, vehicle speed on roads, road geometry and surrounding road infrastructure may also affect the amount of heavy metal pollutant load. Based on Novotny *et al.* (1999), Hjortenkrans *et al.* (2006) and Ewen *et al.* (2009) studies, it can be presumed that the amount of abrasion products derived by traffic on roads is at a higher level near traffic signals and other traffic related bottlenecks, such as bridges and bends compared to straight road section sites with little stops. This agrees with the findings of this study where lower metal concentrations were recorded at Sites 1, 2 which had lower vehicular intensities and traffic hold-ups compared to Sites 3, 4 and 5. Considering Sites 3, 4, and 5, it is interesting to note that these sites experience

more frequent acceleration and deceleration activities dictated by traffic hold-ups, which possibly resulted in increased heavy metal loads in the road-deposited sediments along these roads. Vehicle acceleration and deceleration is known to be a key factor that enhances metal emissions (Charlesworth *et al.*, 2003; Ewen *et al.*, 2009).

According to research conducted in several countries like Venezuela (Machado, 2008), Spain (Zafra *et al.* 2007, 2011), Italy (Imperato *et al.*, 2003) and USA (Pal, 2012) heavy metals are found as a result of the mechanical action of the vehicles on urban roads, either by the interaction of tyres with the road surface or the wear of the brake and clutch. Tyre wear mainly results in zinc emissions while brake and road wear particularly asphalt roads mainly results in copper, cadmium and zinc emissions (Pal, 2012). Other possible sources of heavy metals to road-deposited sediments are the road markings or paintings. Wearing of road markings can serves as a source of copper and lead to road-deposited sediments (Pal, 2012).

With regards to the heavy metal concentrations in bottom sediments of the sampled surface water bodies, the highest concentration was recorded at Site 5 and the lowest at Site 1. The road runoff from auto mechanic shops, fuel filling stations, tyre repair shops has been identified as a significant source of pollution for receiving waters, and road traffic has been found to play an important role in generating such contamination in the water bodies' sediments. Moreover, in the present study the concentrations of the studied metals in the bottom sediments appeared to correspond to the levels found in the road-deposited sediments of

their respective nearby roads and the higher levels of heavy metals in the bottom sediments compare to the road-deposited sediments could possibly be as a direct result of accumulation of these metals over time. The findings of this study is in agreement with numerous research studies (Hoffman *et al.*, 1985; Lee *et al.*, 2004; Crabtree *et al.*, 2006) estimated that contamination of water bodies' sediments contributes between 35 and 75% of the total pollutant load to urban receiving waters in the UK and China; resulted from auto mechanics shops, fuel filling stations and tyre repair shops closed to water bodies and also along the road sides.

The calculated sediment quality indices (geoaccumulation index, contamination factor and pollution load index) appeared to be linked to the traffic densities, auto mechanics shops, tyre repair shops and fuel filling stations along the sampled roads and closed to the surface water bodies. Calculated PLIs were above 1 (deteriorated site quality) for all the samplings sites except for Sites 1 and 2 during the rainy season and Site 1 during the dry season. The Pollution Index may be used to evaluate the degree of metal contamination. A pollution index greater than 1 indicates that, on average, metal concentrations are above the permissible levels. An index below 1 indicates that average levels of metals are below the selected standards but does not necessarily indicate that there are no anthropogenic sources or other enrichment over the background levels (Nimick and Moore, 1991).

5.2 Seasonal Variation

In this study dry season heavy metal concentrations were generally higher than rainy season concentrations. This observation agrees with the findings of Pal (2012) who recorded lower metal concentrations during the rainy months compared to the months with less rain. A similar observation was reported by Robertson and Taylor (2007) from their study in Manchester, UK.

The antecedent dry days (ADD) or number of continuous days without precipitation is the major factor that accounted for the higher dry season metal loads in the road-deposited sediments. A common assumption is that the larger the ADD the higher is the sediment build-up on roads and consequently heavy metal build-up. It has been considered that the ADD has a positive linear or non-linear relationship with pollutant build-up (Sartor and Boyd, 2009; Hewitt and Rashed, 1998; Irish *et al.* 1998; Kim *et al.*, 2006). Considering the overall trend of the present study, the high metal concentrations in the dry season (January), for example, may be due to relatively long dry spells, while the low rainy season (July) concentrations may likely be linked to frequent rainfall during that period. A similar suggestion was made by Robertson and Taylor (2007) in their study in Manchester, UK. Furthermore, Fergusson and Kim (1991) noted that weather patterns had a significant influence on road-deposited sediments metal compositions stating that metal concentrations were significantly reduced after heavy rain, while warmer and drier periods promoted pollutant accumulation.

CHAPTER 6

CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

Road sediments along the sampled highways and major roads in Kumasi are highly contaminated by the studied heavy metals compared to their background values, signifying an anthropogenic input most likely from the road-traffic environment. With regards to the studied metals, the classifications of the quality of the sites' sediments ranged from unpolluted to strongly polluted with the intensity of vehicular traffic playing major roles. The calculated pollution load indices were generally indicative of sites with deteriorated quality or anthropogenic influence as far as the studied metals are concerned.

Although, there were variations among the sites, the physicochemical parameters and measured heavy metal concentrations were generally higher in the river/stream sediments than in the road deposited sediments. The variations across the sites appear to be primarily due to site-specific attributes with the sites having more vehicles plying the road or higher traffic densities generally recording higher levels of the studies metals.

The effect of season on the physicochemical parameters and heavy metal accumulation was apparent in this study; levels of the physicochemical

parameters were generally higher during the rainy season than in the dry season. An opposite trend was recorded for the heavy metals where higher concentrations were generally recorded during the dry season sampling period.

6.2 Recommendations

1. Further investigations or studies spanning over longer durations with more frequent sampling periods would be a useful extension to this work.
2. The evaluation of metal contamination along the sampled highways was based on simplified methods and only reports metal concentrations and levels of contamination. Further studies on the bioavailability of these metals can be carried out to ascertain the actual impact of these metals on receiving water bodies and the aquatic life in them.
3. Future studies on road-deposited sediments along highways can divide sediments based on grain size prior to metal analysis to investigate the influence of the different grain sizes on metal accumulation.

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APPENDIX

Appendix A: Wet season physicochemical parameters

Sampling Areas	pH			EC			OM		
Maakro-Offinso Road (A)	6.62	6.7	6.45	1.4	1.58	1.22	290	292	288
Bunkumfour River	7.5	7.42	7.48	2.9	2.6	3.3	400	309	401
Maakro-Offinso Road (C)	6.6	6.54	6.67	1.6	1.5	1.7	289	288	293
Dr. Kwame Antwi Avenue (A)	6.9	7.02	6.82	3.6	3.3	3.9	220	215	225
Akos River	7.8	7.88	7.68	6.3	6.6	6	390	390	390
Dr. Kwame Antwi Avenue (C)	6.9	6.84	7	3.7	3.5	3.9	215	216	214
Santasi-Bekwai Road (A)	6.8	6.86	6.66	6.4	6.1	6.7	267	265	269
Kwadaso River	7.8	7.67	7.89	10.9	10.8	11	350	352	348
Santasi-Bekwai Road (C)	6.8	6.84	6.68	6.9	6.8	7.1	269	268	270
Dr. Osei Tuffour Bypasss (A)	6.7	6.82	6.58	7.5	7.5	7.5	520	522	518
Washi Stream	7.8	7.69	7.87	15.3	15.1	15.5	700	701	699
Dr. Osei Tuffour Bypasss (C)	6.7	6.58	6.92	7.9	7.9	7.9	529	529	529
Osei Tutu II Blvd (A)	6.9	7.1	6.83	8.6	8.52	8.59	625	623	627
Susuanso River	7.8	7.9	7.66	17.1	17.3	16.9	950	951	948
Osei Tutu II Blvd (C)	5.9	5.98	5.78	8.8	8.6	9	629	628	630

Appendix B: Dry Season physicochemical parameters

Sampling Areas	pH			EC			OM		
Maakro-Offinso Road (A)	6	6.2	5.88	1.4	1.6	1.2	175	178	172
Bunkumfour River	5.5	5.54	5.48	2.7	2.5	2.9	250	251	252
Maakro-Offinso Road (C)	6	5.87	6.3	1.5	1.1	1.9	176	179	173
Dr. Kwame Antwi Avenue (A)	5.9	6.1	5.8	3.4	3	3.8	200	201	202
Akos River	5.7	5.7	5.7	6.3	6.29	6.31	290	293	287
Dr. Kwame Antwi Avenue (C)	5.9	5.8	6.1	3.5	3	4	198	196	200
Santasi-Bekwai Road (A)	6	5.98	6.1	6.3	6.2	6.4	150	150	150
Kwadaso River	5.5	5.47	5.46	7.8	7.8	7.8	250	255	245
Santasi-Bekwai Road (C)	5.5	5.46	5.47	6.7	6.5	6.9	155	157	153
Dr. Osei Tuffour Bypass (A)	6	5.88	6.2	7.2	7.6	6.8	200	203	197
Washi Stream	5.5	5.48	5.45	12.9	12.6	13.2	400	400	400
Dr. Osei Tuffour Bypass (C)	6.8	6.8	6.8	7.8	7.6	8	215	218	212
Osei Tutu II Blvd (A)	5.9	5.7	6.2	6.7	6.9	6.5	300	301	302
Susuanso River	5.4	5.34	5.54	13.4	13.2	13.6	600	604	596
Osei Tutu II Blvd (C)	6	6.1	5.98	6.9	6.8	7.1	310	312	308

Appendix C: Wet Season Heavy Metals Concentrations

Sampling Areas	As			Cd			Cu			Pb			Zn		
Maakro-Offinso Road (A)	11.8	11.6	12.2	0.2	0.24	0.16	0.6	0.5	0.7	1.8	1.6	2	17.9	16.6	19.2
Bunkumfour River	50.5	51	49.5	1	0.7	1.3	12.2	11.8	12.6	12.6	10.6	14.6	198.7	198.5	198.9
Maakro-Offinso Road (C)	3.3	3.1	3.5	0.2	0.18	0.22	0.6	0.9	0.3	1.76	2.78	0.74	17.2	15.1	19.3
Dr. Kwme Antwi Avenue (A)	16.9	16.6	17.2	0.3	0.2	0.4	192	191.8	192.2	12.9	9.5	16.3	11.8	9.8	13.8
Akos River	50.1	50.1	50.1	1	1.1	0.9	120.9	120.7	121.1	60.9	60.1	61.7	109.3	109.6	109
Dr. Kwme Antwi Avenue (C)	16.1	16	16.2	0.3	0.35	0.25	18.4	18.6	18.2	12.8	10.8	14.8	11.9	13.9	9.9
Santasi-Bekwai Road (A)	11.8	11.6	12	0.2	0.19	0.21	215	215	215	10.3	9.1	11.5	34	35	33
Kwadaso River	47.2	46.8	47.6	0.8	0.66	1	449.8	450	449.6	125.9	126.8	125	238.1	238	238.3
Santasi-Bekwai Road (C)	11.4	11.3	11	0.2	0.21	0.19	214	213.7	214.3	7.7	5.7	9.7	34.8	30.8	38.8
Dr. Osei Tuffour Bypasss (A)	8.4	8.1	8.7	0.2	0.18	0.22	220	219.5	220.5	19.2	19.6	18.8	21.2	21.1	21.3
Washi Stream	55.9	55.6	56.3	0.8	1	0.66	587.5	587	588	68.1	66.1	70.1	245.9	245.8	246.1
Dr. Osei Tuffour Bypasss (C)	10.1	10	10.2	0.2	0.16	0.24	349	349.3	348.7	19.2	19.2	19.2	21.9	19.9	23.9
Osei Tutu II Blvd (A)	16.9	16.8	17	0.6	0.5	0.7	296.4	296.8	296	59.7	59.6	59.8	130	135	125
Susuanso River	46.8	46.3	47.1	1.8	1.6	2	630.1	630	630.2	455	455	455	830	830	830
Osei Tutu II Blvd (C)	16.1	16	16.2	0.6	0.3	0.9	297.1	279.2	297	31.1	31	31.2	124.6	120.6	128.6

Appendix D: Dry Season Heavy Metals Concentrations

Sampling Areas	As			Cd			Cu			Pb			Zn		
Maakro-Offinso Road (A)	56.9	57.1	56.7	0.3	0.25	0.35	1.2	1.3	1.1	4.6	4.2	5	32.8	32.7	32.9
Bunkumfour River	134.4	134	134.8	1.5	1.7	1.3	20	20.5	19.5	21.7	21.6	21.8	234	234.1	233.9
Maakro-Offinso Road (C)	56.1	56.2	56	0.3	0.28	0.32	1.2	0.8	1.6	4.5	3.6	5.4	32.1	34.1	30.1
Dr. Kwame Antwi Avenue (A)	87.2	87	87.4	0.6	0.9	0.3	39	38.7	39.3	19.6	17.6	21.6	16.5	16.8	16.2
Akos River	123.1	123	123.2	1.6	1.4	1.8	200.7	200.5	200.9	156	156	156	132.7	132.9	132.5
Dr. Kwame Antwi Avenue (C)	87.8	87.3	88.3	0.6	0.5	0.4	39.8	40.2	39.4	19.7	19.6	19.8	15.8	15.1	16.5
Santasi-Bekwai Road (A)	56	56	56	0.4	0.4	0.4	111	111.2	110.8	20	21.5	18.5	40.8	40.9	40.7
Kwadaso River	195.6	195.3	195.9	1.2	1.1	0.9	390.1	390	390.2	345	345	345	536.5	536.3	536.8
Santasi-Bekwai Road (C)	55.2	55.1	55.3	0.4	0.3	0.5	111.9	111.4	112.4	20.1	19.1	21.1	39.8	39	40.6
Dr. Osei Tuffour Bypass (A)	80	79.8	80.2	0.7	0.6	0.8	100	100	100	21.9	21.6	22.3	40.5	40	41
Washi Stream	298.4	298.6	298.2	1.3	1.5	1.2	500.1	500	500.2	87	86	89	330	330	330
Dr. Osei Tuffour Bypass (C)	78.5	78.3	78.8	0.6	0.6	0.6	100.8	101.3	100.3	21	20	22	31.9	30.7	33.2
Osei Tutu II Blvd (A)	43.8	43.9	43.7	0.42	0.41	0.43	401.8	401.6	402	121.9	121.7	122.1	160.3	160	160.6
Susuanso River	209.9	209.7	210.2	1.2	0.8	1.4	1052.6	1052.3	1052.9	620.2	620	620.4	1045.1	1045	1045.2
Osei Tutu II Blvd (C)	50	50.3	49.7	0.4	0.5	0.3	401.1	401	401.2	121.2	121.3	121.1	156.9	156.8	157

