

**ASSESSING HEAVY METAL LOAD OF FISH AND
SHOREBIRDS IN THE DENSU DELTA RAMSAR SITE,
GHANA**

THIS THESIS IS SUBMITTED TO THE UNIVERSITY OF GHANA,
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BY

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DECLARATION

This thesis is the result of a research undertaken by me, Anthony Awuku Addo, Department of Marine and Fisheries Sciences, University of Ghana, under the supervision of Dr. Angela Lamptey, Dr. Erasmus Owusu, and Dr. Lailah Akita as advisor.

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DEDICATION

This work is dedicated to God Almighty, my wife (Sheila Akaluti), children (Nicolena and Jesse), siblings, Dad, mum, and all the family.



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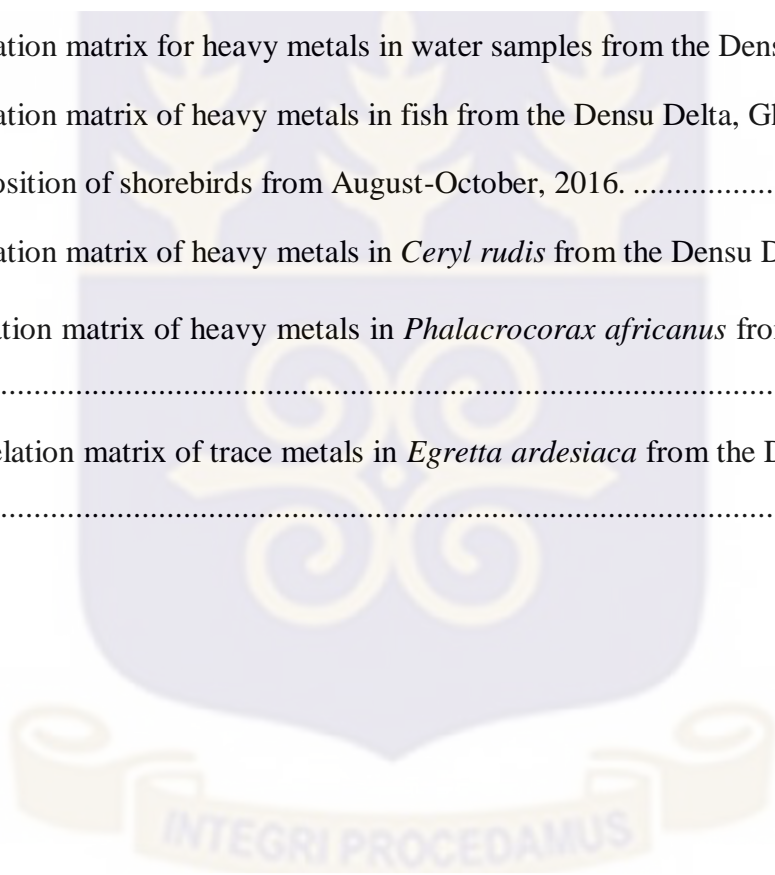
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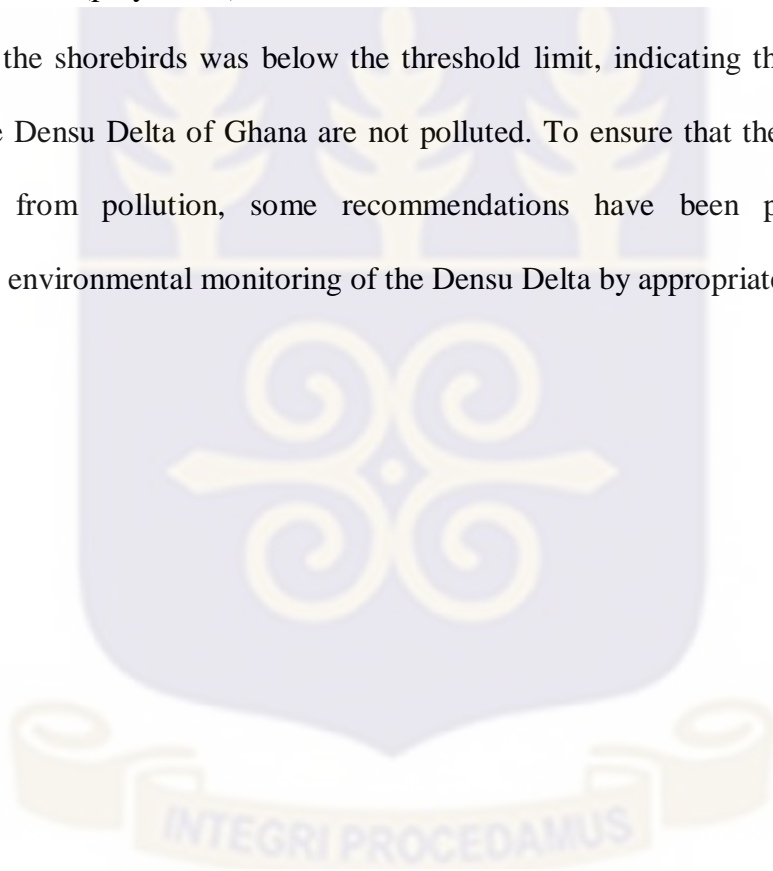
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ABSTRACT

The study aimed at assessing the impact of pollution on shorebirds at Densu Delta in Ghana. In view of this study, data on trace metals in water, sediment and biotic factors (fish and shorebirds) were collected and analyzed from August 2016 to February 2017 in four sampling stations within the Densu Delta. The trace metals assessed from the study were copper, zinc, cadmium, arsenic and mercury. From the study, the dominant trace metals assessed in water, sediment, fish and shorebirds were copper and zinc. From the wet season, the average concentration of copper and zinc in sediments was 6.68 ± 0.24 mg/kg and 28.99 ± 0.95 mg/kg respectively. For the dry season, the average concentration of copper and zinc in sediments was 6.01 ± 0.21 mg/kg and 30.02 ± 0.99 mg/kg respectively. Regarding water samples, the average concentration of copper and zinc was 1.54 ± 0.11 mg/kg and 2.98 ± 0.38 mg/kg respectively during the wet season while in the dry season, the mean concentration of copper and zinc was 1.11 ± 0.07 mg/kg and 13.04 ± 0.4 mg/kg correspondingly. Mean concentrations of these dominant trace metals between the dry and wet seasons were significantly different ($p < 0.05$). Concerning fish samples, the mean concentration of copper and zinc was 0.14 ± 0.17 mg/kg and 5.35 ± 0.81 mg/kg correspondingly for *Sarotherodon melanotheron* (Blackchin tilapia) while for *Coptodon zillii* (formerly known as *Tilapia zillii*) (Red belly tilapia) the mean concentration of copper and zinc was 0.11 ± 0.09 mg/kg and 4.20 ± 0.56 mg/kg correspondingly. However, the variation in dominant trace metals for both fish species was not significantly different ($p > 0.05$). Regarding shorebirds, the study focused on three main species including *Cerylerudis* (Piedkinfisher), *Phalacrocorax africanus* (Longtail Cormorant) and *Egretta ardesiaca* (Black Heron). The mean concentration of

copper was 1.57 ± 0.24 mg/kg, 6.16 ± 0.55 mg/kg and 11.89 ± 0.15 mg/kg correspondingly for *Cerylerudis* (Piedkinfisher), *Phalacrocorax africanus* (Longtail Cormorant) and *Egretta ardesiaca* (Black Heron) while for zinc, the respective concentrations were 4.36 ± 0.75 mg/kg, 12.41 ± 0.01 mg/kg and 17.58 ± 0.16 mg/kg. The variation in concentration of the trace metals for the shorebirds was significant ($p < 0.05$). Correlation analysis in terms of trace metals revealed a strong association ($R^2 = 0.81 - 0.93$) with fish (prey items). From the results, the concentration of the dominant trace metals in the shorebirds was below the threshold limit, indicating that these shorebirds within the Densu Delta of Ghana are not polluted. To ensure that these bird species are protected from pollution, some recommendations have been provided including consistent environmental monitoring of the Densu Delta by appropriate authorities.



CHAPTER ONE

INTRODUCTION

1.1 Background

The pollution of aquatic systems with heavy metals is a major worldwide problem due to their lasting nature and toxic impacts on organisms (MacFarlane and Burchett, 2000). Heavy metals among others are of great interest due to their ability to bioconcentrate in cells of organisms in aquatic food chain (Censi *et al.*, 2006).

Wetland ecosystems plays significant economic, social and environmental roles such as filtration of pollutants, provision of nursery sites and regulating atmospheric carbon dioxide (Russi *et al.*, 2013). However, human activities on wetland ecosystems have resulted in poor water quality, reduced biodiversity, and loss of aquatic habitats (Morales-Ojeda, 2009). Urbanization, industrialization and other anthropogenic activities have put undue pressure on the resources of all wetlands in Ghana resulting in recent calls for the need to protect these wetlands from the effects of anthropogenic land use (Yeboah *et al.*, 2013). Ghana being part of the signatory to numerous conservation codes including United Nations Convention on Biological Diversity, Convention on Wetlands of International importance, and African Convention on the Conservation of Nature and Natural Resources, has the duty to ensure the conservation and the sustainable utilization of wetlands to the benefit of humanity (Abdul Razark, 2012).

The coast of Ghana falls within the boundary of two major shorebird migration corridors, The East Atlantic and the Mediterranean flyways (van de Kam *et al.*, 2004), and receives greater number of shorebirds than most wetland sites in West Africa (Piersma and Ntiamoa-Baidu, 1995). Fifteen species of internationally important shorebirds populations occur in Ghana (Ntiamoa-Baidu *et al.*, 2001), however, the degradation of shorebirds habitats in wetlands along flyways have partly caused their decline (UNEP/AEWA., 2013). There exists thirteen key wetlands along the coast of Ghana of which five of them: Keta Lagoon, Songhor, Sakumo II lagoon, Densu Delta and Muni-Pomadze, were designated as Ramsar Sites in 1992 for their protection under the Ghana Coastal Wetland Management Project.

The Densu Delta Ramsar Site is one of the designated Ramsar Sites in Ghana which is associated with the Densu River estuary. It is an important nestling site for local and migratory shorebirds (Ntiamoa-Baidu *et al.*, 1998). The Densu Delta Ramsar Site, has undergone several forms of transformations in land use in the past decades. It experiences annual flooding which brings in lots of sediments, garbage, and pollutants directly or indirectly from household and industrial developments, farming and fishing activities (Kudu *et al.*, 2012). The accumulation of pollutants and heavy metals largely impact negatively on organisms especially those that depend extensively on resources within the Delta (Osei *et al.*, 2010).

However, threats from housing development, overfishing, dumping of refuse near and into the wetland, changing wetland habitat into saltpans, overgrazing, farming associated with the use of pesticides/herbicides, implicate the health of the Densu Delta Ramsar Site (BirdLife International, 2018; Ntiamoa-Baidu, 1991). Wetlands and lagoons have a limited water circulation to compensate for changes in water quality and as such, are prone to anthropogenic pollution (Johnson *et al.*, 2007).

Accordingly, the city of Accra have detrimental effects on the quality of water and sediments as well as other aquatic fauna in surrounding riverine systems (Sayadi *et al.*, 2010). The disposal of urban wastes, untreated discharges from industries and agrochemicals in the nearby aquatic environments is alarming with the potential for continually increasing concentrations of trace metals, and deteriorating water quality (Fatma, 2008). Transformations in coastal ecosystems as a result of anthropogenic influence of trace metals pollution is a major worldwide concern, because heavy metals are not biodegradable (Tessier and Turner, 1995). Urbanization, industrialization and other forms of modernization have changed the productive capacities of coastal aquatic systems threatening their existence to sustainable limits (Hothem, 2002).

Land development for infrastructure and agriculture have increased erosion in uplands areas resulting in sedimentation in lowland wetlands, altering the hydrologic status of wetlands in a relatively shorter time (Bellio and Kingsford, 2013). In addition, waste water from irrigated agricultural fields greatly affect the composition and abundance of shorebird communities in wetlands (Bellio and Kingsford, 2013). The interactions of

heavy metals in aquatic systems are extremely complex due to variations in sources, physicochemical properties and the influence of numerous in situ physical, chemical and biological processes. These influences are particularly dramatic in coastal zones where processes are accelerated by natural events such as storms, river runoff and human activities such as domestic and industrial discharge, deforestation and erosion (Bellio and Kingsford, 2013).

Heavy metals introduced into wetlands either associate with colloids and fine particles, or undergo biological uptake. These colloids and fine particles remain in suspension to be chemically altered, or undergo aggregation and sedimentation, or are taken up by biota (Bellio and Kingsford, 2013).

In the same vein, bioaccumulation of pollutants and its effects have been documented for wetlands receiving non-point source run-off (Garcia-Hernandez *et al.*, 2001). Effects of this documentation regarding the integrity of the wetlands include toxicity to algae and aquatic plants, fish, amphibians, and shorebirds resulting in simplification of the food chain (Adamus *et al.*, 2001). These effects have been shown for heavy metals such as Mercury, Zinc, Copper and Cadmium (Campbell, 1994).

Investigating the impacts of contaminants in individual shorebirds provides key information as to if specific contaminants pose a threat to endangered species (Adams *et al.*, 2001). Oxidative stress in some shorebirds have been attributed to high levels of

heavy metal concentrations (Lucia *et al.*, 2009). Cellular damages in shorebirds due to high heavy metal levels are practically unexplored in Ghana (Adams *et al.*, 2001).

Heavy metal concentration in organs and tissues of fish and other aquatic vertebrates are determined by the level of heavy metals concentration of the water and sediment, and so indicative of the level of metal pollution in the aquatic system (Farkas *et al.*, 2000).

Besides, maintaining healthy wetland ecosystems to protect the organisms living within, requires information of how stressors vary in these ecosystems (Chen *et al.*, 2008). The deterioration of water quality may have negative effects on wetland ecosystem directly or indirectly (Nyame *et al.*, 2012), and understanding the impacts of trace metals in wetlands to provide early diagnosis of changes of any potential adverse effect is very necessary (Dauwe *et al.*, 2004). Therefore, regular monitoring of metal pollutants in wetland ecosystems is critical in trying to protect ecological risk (Nyame *et al.*, 2012). Polluted sediments do not always remain at the bottom but re-suspends whenever the water stirs up. When this happens all organisms in the water and not just the bottom-dwelling organisms will be exposed to contaminants (Nyame *et al.*, 2012). To maintain sustainable wetlands and lagoon ecosystems which are greatly impacted by various human activities, it is vital to monitor both water and sediments (Fulweiler *et al.*, 2007). It is also to provide an estimate of heavy metals level contamination in the shorebird's food chain. This will provide key information to formulate any conservation interventions required by the principle of sustainable use as enjoined by the Ramsar Convention

1.2 Rationale

The Densu Delta Ramsar Site is composed of lagoons, salt pans, scrubs, which provide feeding, roosting and nesting grounds for shorebirds, and economically supports large number of the inhabitants through fishing, salt extraction and water supply for agriculture (EPA Ghana, 2006). Salt mining, fishing and tourism are some anthropogenic activities around the Densu Delta Ramsar Site which subjects the wetland to pollution from storm water runoff, agriculture, industrial and household sewage from the surrounding communities, and land-based mining through the Densu River discharge (Osei *et al.*, 2010). This has the potential of increasing bioaccumulation of pollutants in the macrofaunal community (Bustamante and Miramand, 2005). Accumulation of high levels of pollutants like heavy metals even in small amounts could have a devastating impacts on the health of all life form which depends exclusively on the Densu Delta Ramsar Site.

Similarly, the Atewa forest reserve which protects the headwaters of the Densu river and other rivers is also exposed to mining activities. However, the indiscriminate use of mercury (Hg) to amalgamate the gold by these illegal miners has in recent times resulted in environmental mercury pollution (Hilson and Pardie, 2006; Swain *et al.*, 2007). A research conducted by Oduro *et al.* (2012) found out that tributaries including Densu river has (27.59 ± 18.23 ng/ml) average dissolved Hg concentration which are far above the WHO guideline value of 1.0 ng/ml (Amankwah, 2013). Since river bodies flow from upstream to downstream, the pollutants travel downstream making it possible for shorebirds within the Densu Delta Ramsar Site to get polluted.

Added to this, the frequent use of heavy metals such as cadmium and lead in agricultural applications in and around the Densu Delta Ramsar Site, and due to their negative effects and stability has become a source of worry to many environmental enthusiasts. Shorebirds that brood and nest in this ecologically important wetland, could be exposed during feeding to non-essential metals such as cadmium and mercury, and essential metals such as copper and zinc, copper, and zinc which could be toxic at higher concentrations (Bennett, 2001).

Duly, the rapid alteration of the vegetation and land use is evidently pronounced in the Densu Delta (Ntiamoah-Baidu, 1991). Regular research are paramount to monitor water and sediment quality to understand the behaviour of heavy metals pollution in the Densu Delta Ramsar Site to assess any possible risk and also serve as a reference for management purposes.

Fish in the Densu Delta Ramsar Site also constitute an important source of protein for the inhabitants in and around the coastal community. There is therefore the need to ensure that fish products from the catchment are toxic free. It is envisaged that this study will generate credible baseline data on pollution status of the fisheries from the Densu Delta, the influence of human interventions and the health risk associated with contamination of the Densu Delta Ramsar site. However, correlation of heavy metals in fish and shorebirds to ascertain the level of toxicity in shorebirds have not been extensively studied from the aquatic systems in Ghana.

1.3 Aim

The primary aim of this study is to assess the levels of Cadmium (Cd), Copper (Cu), Zinc (Zn), Arsenic (As) and Mercury (Hg) as well as their accumulation in the tissues of two commercially important fish species and some resident shorebirds of the Densu Delta Ramsar Site, Ghana.

1.4 Specific Objectives

The objectives of the study are:

1. To determine the concentration of copper, zinc, arsenic, cadmium and mercury in sediments, surface waters, fish and shorebirds of the Densu Delta Ramsar Site, Ghana.
2. To determine the correlation of copper, zinc, arsenic, cadmium and mercury between shorebirds and their prey item (fish)
3. To determine the seasonal variations of copper, zinc, arsenic, cadmium and mercury in surface waters and sediments.

1.5 Hypotheses

For objective one,

Null hypotheses (H_0):- Estimated levels of heavy metals concentration (water, sediment, fish and shorebirds) do not pose toxicological threat to the Densu Delta ecosystem.

Alternate hypotheses (H_A):- Estimated levels of heavy metals concentration (water, sediment, fish and shorebirds) pose toxicological threat to the Densu Delta ecosystem.

For objective two:

Null hypotheses (H_0):- There is no significant relationship between shorebirds and prey items (fish) regarding trace metals concentration

Alternate hypotheses (H_A):- There is significant relationship between shorebirds and prey items (fish) regarding trace metals concentration.

For objective three:

Null hypotheses (H_0):- Variation in heavy metals concentration (water and sediments) during the wet season is the same during in the dry season.

Alternate hypotheses (H_A):- Variation in heavy metals concentration (water and sediments) during the wet season is not the same during in the dry season.

CHAPTER TWO

LITERATURE REVIEW

2.1 Heavy metal pollution in coastal environments

Heavy metals load in coastal environment are largely linked to metals with a specific gravity that is at least five times the specific gravity of water (Olatunji *et al.*, 2012). Most heavy metals have no beneficial functions to the body and can be highly toxic. If they enter into the body through inhalation, ingestion and skin they accumulate in the body tissue faster than the body's detoxification pathways can dispose of them (Ekpo *et al.*, 2008).

With heavy metals belonging to the group of elements whose hydro-geochemistry cycles have been greatly accelerated by man, the abundance, persistence and environmental toxicity of heavy metals has become a major problem of the world (Islam *et al.*, 2015a). Both natural and anthropogenic activities are the main agents for the abundance of heavy metals in the aquatic systems (Khan *et al.*, 2008). However, anthropogenic activities contribute to heavy metal pollution in sediment and water that pollute the water bodies (Sanchez-Chardi *et al.*, 2007). Heavy metals pollution is increasing as a result of the waste discharges from urbanization and industrialization (Martin *et al.*, 2015). The increasing pollution of water systems by heavy metals have adverse health effects for vertebrates and invertebrates (Martin *et al.*, 2015). These activities lead to imbalance the ecosystem and generate polluting elements that affect the quality of frail and precious areas (Lawani *et al.*, 2017). Omar *et al.*, (2014) reported that among metal polluting

substances, heavy metals are considered as dangerous for the aquatic environment, due to their persistence and their trend to the bioaccumulation of the aquatic organisms. Some heavy metals like iron and zinc are necessary to the growing and the well-being of the living organisms, including human being. They have toxic effects when the organisms are exposed to higher level of concentration than what is normally required. Other elements like lead, cadmium, arsenic are not necessary to the metabolic activities and reveal a poor measure of toxic properties (El Morhit, 2009).

The presence of metallic heavy elements in the coastal hydrosystems have received increasing interest in the last two to three decades due to the high biological importance of the aquatic ecosystems as they constitute shelter and vital feeding ground for migratory birds and a breeding ground for the fishes (Mohamed *et al.*, 2015). As a result, the behavior of these elements in lagoon areas including Ghana has broadly been discussed by scientists. For instance, researchers and other scientific groups such as the Environmental Management Associates have reported their concentrations in sediments and organisms. Also, studies done on heavy metals in aquatic bodies of Ghana such as Biney (1991; 1997), Armah and Nyarko (1995) and Okyere (2003) suggested that, there is the need for systematic monitoring of heavy metals in coastal waters of Ghana as part of developmental plans for coastal zone management. Armah and Nyarko (1995) in their studies on trace metals also submitted the use of biomonitors as a possible approach in monitoring trace metals pollution in coastal areas.

Nonetheless, studies on heavy metals within certain relevant wetlands in Ghana with global conservative status have been restricted to limited number of heavy metals as well as to sediments, water and fish, without particular attention to waterbirds or shorebirds. Even though shorebirds or water birds help maintain the ecological integrity of these aquatic ecosystems.

2.2 Heavy metals in sediments

Sediments are polluted with various kinds of hazardous and toxic substances, including heavy metals (Olatunji *et al.*, 2012). These accumulate in sediments via several pathways, including disposal of liquid effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban, industrial and agricultural activities, as well as atmospheric deposition. Sediments effectively sequester hydrophobic chemical pollutants entering water bodies such as lakes. Aquatic sediments provide a useful archive of information on changing lacustrine and watershed ecology (Golden *et al.*, 2003).

Heavy metals are contained in four media in the aquatic ecosystems; surface water, pore water, the suspended and bottom sediments. Once introduced into the water column, they may get accumulated in the sediments where they undergo physical, biological and chemical transformations that could have implications for living organisms (Erdogan, 2009). Concentrations of heavy metals in sediment do not vary to the same degree as surface waters. Sediments conserve past environmental history (VonGunten *et al.*, 1997), and are recognized as sources of contaminant in any aquatic system (Tessier *et al.*, 1994). Naturally, sediments act as the main sink for heavy metals due to characteristics such as

grain-size distribution, total organic carbon content, the redox state, and pH of pore waters (Szava-Kovats, 2008). Heavy metals are absorbed onto fine-grained sediments more readily than coarse-grained sediment (Blanton, 1995).

The principal compartment of trace metals is a function of the suspended sediment composition and water chemistry in the natural water body (Mohiuddin *et al.*, 2012). During transportation of trace metals in the aquatic system, it may undergo frequent transformations due to dissolution, precipitation and sorption phenomena (Abdel-Ghani, 2007), which affect their bioavailability (Nouri *et al.*, 2011). The investigation of heavy metals in aquatic systems and sediments could be used to assess the anthropogenic and industrial impacts and risk posed by waste discharges on riverine ecosystems (Saleem *et al.*, 2015). Measuring levels of heavy metals in water and sediments of any contaminated, or potentially contaminated riverine ecosystem is critical (Nouri *et al.*, 2011). Obodai *et al.* (2011) reported that heavy metals largely get stored in bed sediments of water bodies or seep into the underground water, thus causing the water sources to be contaminated.

Many researchers including marine geochemists in Ghana have studied the pollution history of aquatic ecosystem using aquatic sediments (Karbassi *et al.*, 2005, Lopez & Lluch 2000, Mohamed 2005). Many researchers have used sediment to study the behaviour of metals (Bellucci *et al.*, 2003, Bertolotto *et al.*, 2003, Borretzen & Salbu 2002, Lee & Cundy 2001, Windham *et al.*, 2001). For example, Darko *et al.* (2008) used studies on heavy metals in sediments to ascertain the vulnerability status of the Densu

Delta, Ghana. Mahu (2014) applied sediments studies focused on heavy metals to evaluate the ecotoxicological threats to some brackishwater systems in Ghana. Awuah (2016) documented that heavy metals such as Arsenic and Mercury levels in both Tano and Ankobra Ghana, were above the WHO recommended levels for pristine freshwater ecosystems and may therefore poses a threat to aquatic wildlife and human health. In view of the above mentioned statements on sediments role in heavy metals pollution, sediments are widely used as indicators of trace metals pollution assessments in natural waters (Islam *et al.*, 2015c). However, to date there has not been a dual study on the sediments and the fish in the Densu Delta of Ghana, correlations between these heavy metals in the sediments and fish have also not been studied extensively.

2.3 Heavy metals in fish

Bioaccumulation of heavy metals in living organisms and biomagnification describes the processes and pathways of these pollutants from one trophic level to another thereby exhibiting an elevated concentration in higher consumers (Bosch *et al.*, 2016). Thus, the concentration of heavy metals in the aquatic ecosystem at any given time reflects the current pollution levels while that found in the organisms show a continuum of bioaccumulation from the time of birth (Ravera *et al.*, 2003). Trace metals impact on human health due to their rapid uptake into the food chain and bioaccumulation in living tissues and organs (Tyokumbur and Umma, 2017).

Fish as major source of affordable protein for the ever-growing human population in the developing countries of Africa, Asia and South America, is increasingly faced with the challenge of heavy metals contamination (Eroglu *et al.*, 2015).

Long exposure to water pollutants even in very low concentrations have been reported to induce morphological, histological and biochemical alterations in the tissues which may critically influence fish quality (Desta and Weldermarim, 2013). Fish, which usually occupies the last levels of aquatic food chains, are considered as the main aquatic pathway for heavy metals transferred into humans (Svensson *et al.*, 1992).

Biological and ecological factors such as ecological needs, habitat, feeding habits have significant influence on heavy metals bioaccumulation, bioavailability and therefore on their transference (Hosseini *et al.*, 2014). Fish absorb heavy metals from the surrounding water through their gills which are the primary route for the uptake of water borne pollutants and accumulate them in their tissues (Allen and Wilson, 1991). The fish diet is another source of these pollutants in the tissues. WHO (1996) reported that copper toxicity in fish is taken up directly from the water via gills and stored in the liver. However, feeding habit plays a significant role in the accumulation of pollutants in organism's tissues (Bustamante *et al.*, 2003). Therefore, tissues are the most indicative factor for the estimation of pollution and risk potential of human consumption (Authman *et al.*, 2008; Ekeanyanwu *et al.*, 2011). The freshwater fish species are exposed to continuous wastewater and industrial effluents discharged into the aquatic systems (Ekeanyanwu *et al.*, 2011).

Due to the toxicity and accumulation of heavy metals in biota, determining the levels of heavy metals in commercial fish species have received considerable attention in different countries including Ghana (Kalfakakon and Akrida-Demertai, 2000; Papagiannis *et al.*, 2004; Mohamed and Gad, 2008; Klavins *et al.*, 2009; Ozturk *et al.*, 2009; Olowu *et al.*, 2010; Ambedkar and Muniyan, 2011; Wariaghli *et al.*, 2013). There has been an increasing interest in the utilization of fishes as bio-indicators of the integrity of aquatic environmental systems in recent years (Rashed, 2001; Ogbeibu and Ezeunara, 2002; Tawari and Ekaye, 2007).

2.4 Heavy metals in shorebirds

Since the 1960s, the role of shorebirds as monitors of environmental pollution has been recognized, because birds are more sensitive to human-induced environmental changes (Denneman and Douben, 1993). Organisms and populations at different trophic levels are widely used as a biological indicator and/or bio-monitor to provide evidence of contaminant exposure and effects of one or more chemical pollutants (Kojadinovic *et al.*, 2007). Shorebirds are susceptible to bioaccumulation of pollutants mainly through the consumption of contaminated food. They serve as bio-indicators and/or bio-monitors of environmental contamination because they are the topmost predators on the aquatic foodweb, exposed to a wide range of chemicals, susceptible to bioaccumulation, and are geographically widespread (Kojadinovic *et al.*, 2007).

Among the shorebird species, toxicity and heavy metal exposure in shorebirds are relatively well studied (Muralidharan *et al.*, 2004). Long-term exposure to heavy metals can also cause disruptive behaviour and reduction in disease resistance and affect other physiological processes (Dauwe *et al.*, 2005). This is because shorebirds are high at the top of their food pyramid and can yield information over a large area around each sampling site, not only on bioavailability of contaminants but also on how, where, and when they are transferred within the food web (Battaglia *et al.*, 2005). Chronic heavy metals exposure can also produce detrimental effects on behavior, resistance to diseases, and other physiological mechanisms (Dauwe *et al.*, 2005). Morphometric parameters such as the body mass; tarsus length and wing length which correlate with concentration of trace metals had been used as indicators of survival and reproductive success of different species of shorebirds. Heavy metals concentrations can be assessed in shorebirds by using various organs (liver, kidney), tissues (muscle, bone, fat), eggs, feathers and excrements (Burger 1993; Dauwe *et al.*, 2000). However, heavy metal concentrations in the feather are representative of long-term exposure, whereas the liver concentrations reflect short- term exposure (Dauwe *et al.*, 2000).

Feathers are pathways for trace metals excretion (Lewis and Furness, 1991), and are useful for determining trace metal levels in shorebirds without causing harm to the individual (Greenwood, 1993). Feathers are best for monitoring of heavy metal levels since metals have a higher affinity for the sulfhydryl groups of the feather's structural proteins (Metcheva *et al.*, 2006). An undisputable advantage of using feathers in such analyses is that they can be easily collected and, if necessary, repeatedly sampled without

affecting the health and condition of the studied individuals (Adout *et al.*, 2007). In addition, during the period of growth, feathers are connected with blood-vessels and metals supplied with food may be built into feather keratin structures (Adout *et al.*, 2007). Therefore, the endogenous accumulation reflects nestling physiological condition at the moment of feathering (Burger, 1993). By contrast, exogenous contamination results from adsorption of metals on the feather surface. Some authors also pointed out the fact that shorebird species, especially waterfowl, may secrete metals through salt gland and embrocate them on their feathers (Demoski, 1999). This makes it possible to use them for studies in heavy metals (Lucia *et al.*, 2012). Shorebirds can be contaminated through direct contact with heavy metals (Lanctot *et al.*, 2002), or by the consumption of contaminated prey (Kim and Koo, 2008). Breast feather are used more for heavy metal researches, (Gochfeld, 2000; Burger, 1993).

The incorporation of heavy metals in feathers renders them inert and stable (Burger, 1993). Scheifler *et al.*, (2006) reported that lead concentrations in the feather were much higher in unwashed samples than in washed samples. Therefore, unwashed feathers indicate both exogenous contamination from heavy metals and movement from internal tissues. It is reasonable to assume that lead concentrations in the unwashed feather at a given area reflect local heavy metal exposure. Females also excrete some heavy metals in their eggs and egg- shells (Fasola *et al.*, 1998). Movalli (2000) assessed heavy metal and other residues in feathers of *Biarmicus jugger* from six districts of Pakistan and suggested that trace metal burden in adult and juvenile feathers reflected the concentration of contamination in particular districts.

Boncompagni *et al.*, (2003) monitored trace metals contamination in three wetlands of Pakistan using eggs and feathers of colonial shorebirds such as little and cattle egret. Numerous studies have evaluated levels of trace metals in tissues of shorebirds (Kojadinovic *et al.*, 2007; Naccari *et al.*, 2009; Zolfaghari *et al.*, 2009; Mansouri *et al.*, 2011b, 2012). Yet, studies on heavy metals in shorebirds in aquatic systems such as wetlands in Ghana have largely not given the necessary attention. In the other hands, there are only a few reports that document heavy metal contamination in Ghanaian shorebirds. This limitation advanced the need to conduct studies of trace metals contamination in Ghanaian shorebirds, particularly resident shorebirds using feathers since it has been suggested as non-destructive means of assessing the contamination of trace metals.

2.5 Effects of heavy metals loads in the tissues of shorebirds

Mercury is widely bioaccumulated by living organisms and more particularly by marine invertebrates (Neff, 2002). Mercury is transported in the environment by water, as well as by biological organisms through the food chain (IPCS, 2003), and is believed to be an immunosuppressant (Bennett *et al.*, 2001).

Large concentrations of heavy metals in biological systems may result in biochemical, genetic, physiological or morphological effects. These effects at higher trophic levels may delay embryonic development, lead to tissue or organ malformation, and reduced growth. High contamination levels by heavy metals may negatively affect the

reproduction and the general health of some shorebirds (Dauwe *et al.*, 2004), as well as may cause death of individuals (Bull *et al.*, 1983). In this way, anthropogenic factors, such as chemicals and pollutants, can contribute to causing continental level declines of migrant and resident shorebird populations (Zöckler *et al.*, 2003). Non-essential heavy metals like cadmium and mercury are widely dispersed in the environment, since they are released from both natural and anthropogenic sources (Nriagu, 1996). Food is the major pathway of these metals for shorebirds (He´douin *et al.*, 2007).

Heavy metals pollution in wetlands not only reduces the water quality, but also makes a decline in the range of many shorebird species, leading to the loss of biodiversity (Adams *et al.*, 2001). Shorebirds suffer severe health impairment or death when subjected to high concentrations of some heavy metals (Be´ata Farkas, 2006). Trace metals pollution can make shorebird species suffer severe impaired damage and decline in population dramatically or even disappear (Kertész, 2006).

The effects of cadmium were demonstrated on the embryogenesis, hatching success and viability of the mallard and the results proved cadmium to have adverse effects on the embryonic development, hatching and viability of the mallard (Furness, 1996). Effects of cadmium includes; behavioural changes, disturbances in the metabolism of some essential elements, reduced egg production, kidney damage, and testicular damage (Furness, 1996). Other damages that have been detected include development toxicity and immunological effects (Apostoli and Catalani, 2011).

2.6 Heavy metals pollution in wetlands

Investigating the impacts of contaminants in individual shorebirds provides key information as to if specific contaminants pose a threat to endangered species (Adams *et al.*, 2001). Oxidative stress in some shorebirds have been attributed to high levels of heavy metal concentrations (Lucia *et al.*, 2009). Cellular damages in shorebirds due to high metal levels are practically unexplored in Ghana (Adams *et al.*, 2001). Levels of heavy metals in organs and tissues of fish and other aquatic vertebrates are determined by the level of heavy metals concentration of the water and sediment, and so indicative of the level of heavy metals pollution in the aquatic system (Farkas *et al.*, 2000).

Maintaining healthy wetland ecosystems to protect the organisms living within, requires information of how stressors vary in these ecosystems (EcoHealth, 2008). Understanding the impacts of heavy metals in wetlands to provide early diagnosis of changes of any potential adverse effect is very necessary (Kempnaers, 2004). Therefore, regular monitoring of metal pollutants in wetland ecosystems is critical in order to prevent ecological risk (Kempnaers, 2004).

2.6.1 Arsenic

Arsenic is a metalloid found in trace quantities in rocks, soils, water and air (Smedly and Kinniburg, 2002). It is mostly found in realgar (AS_2S_4), Orpiment (AS_2S) and arsenolite (AS_4O_3) (Budavari *et al.*, 2001). Fossil-fuel combustion, mine waste and mill tailing are the most anthropogenic inputs into coastal waters (Mclamed, 2005). Arsenic form insoluble complexes with Iron, Aluminum and Magnesium oxides found in soil surfaces

(McLamed, 2005). However, under reducing conditions, arsenic can be released from the solid phase, resulting in soluble mobile forms of arsenic, which may potentially leach into groundwater or result in runoff into surface waters (Welch *et al.*, 1988). In aquatic systems, inorganic arsenic occurs primarily in two oxidation states, Arsenic (V) and Arsenic (III). (Pongratz, 1998). Both forms generally co-exist, although Arsenic (V) predominates under oxidizing conditions and Arsenic (III) predominates under reducing conditions (Welch *et al.*, 1988, Pongratz, 1998).

Concentration in water are usually less than 10 µg/l although higher levels may occur near natural mineral deposits or anthropogenic sources (Pongratz, 1998). Natural levels of arsenic in soil usually range from 1 – 40 mg/kg with a mean concentration of 5 mg/kg, although much higher levels may occur in mining areas, waste sites, and pesticide application sites (Pongratz, 1998). Arsenics exhibit unique sensitivity to pH values found in ground waters (pH 6.5-8.5) (Nriagu, 1995). Arsenic III and IV are the most stable and hence the main forms present in marine and estuarine environments (Ehrlich, 1996). The concentration of both Arsenic III and IV in free pore water is solely a function of redox potential as Arsenic III may dominate in more anoxic sediments while Arsenic IV may dominate under toxic conditions. The more toxic form Arsenic III, significantly dominates over the less toxic form Arsenic IV, as water depth increases towards the bottom. This trend is attributed to increasing microbial activities that cause greater reduction of Arsenic IV (Rajeeva *et al.*, 2012).

2.6.2 Cadmium

Cadmium is rare, non-essential, toxic element which enter into coastal waters through natural and anthropogenic processes (Pacyna, 2001). Natural release of cadmium from the crust and mantle into aquatic systems occurs by volcanic activities, weathering, burning of vegetation, sea salt spray (Pacyna, 2001). The concentrations of cadmium are of the order 0.02 – 0.12 µg/l of oceanic concentrations (Bruland *et al.*, 1979). Cadmium finds its way into aquatic systems through numerous man-made activities such as the processing of non-ferrous ores, combustion of fossil-fuel, and incineration of refuse and disposal of cadmium containing products (Pacyna, 2001). Environmental factors also affect the uptake of cadmium (Rosenberg, 1979).

Cadmium usage in agricultural activities is increasingly becoming a concern in many aquatic systems (Osei *et al.*, 2010). Shorebirds whose lives are centered in wetlands are at high risk, as their body burdens increases (Kress, 2008). Shorebirds are more sensitive to pollutants than other organisms (Sayadi *et al.*, 2010). Hence, Shorebirds numbers in wetlands are used as sentinel species for biological and anthropogenic toxicological problems in the environment (Sayadi *et al.*, 2010). Chelating agents such as dithiocarbamates and xanthates, and increasing temperature increases uptake and toxicity of cadmium in aquatic environment (WHO, 1992b). The amount of cadmium relies heavily on the concentrations of other metals like zinc and copper (WHO, 1992b).

2.6.3 Mercury

Mercury is a biological element known to be available in every compartment of the earth at low concentrations (Sonke *et al.*, 2013). Naturally mercury is released into the aquatic environment through volcanism and gradual degassing of soil systems (Sonke *et al.*, 2013). Intentional usage includes mercury usage in gold mining and in chemical industrial processes while unintentional usage of mercury emission are through cement production and pyrometallurgical treatment of copper, lead, and zinc sulfide ores (Sonke *et al.*, 2013). The mobility and availability of mercury in aquatic systems is influenced by several processes including the thermodynamic solubility of mercury and mercury compounds (Randall and Chattopadhyay, 2013). Mercury is converted by micro-organisms into methylmercury, a highly toxic chemical that builds up in fish, and animals that eat fish (USEPA, 2007). At high concentrations of methylmercury exposure, harmful effects may include reduced reproduction, slower growth and development, abnormal behavior, and death (USEPA, 2007). Mercury is present in an elemental volatile forms (Hg^0) which is relatively non-reactive, and a number of toxic mercuric species (Hg^{2+}), and organic mercury mainly monomethylmercury (MeHg), dimethylmercury (Me_2Hg) and some ethylmercury (Ulrich *et al.*, 2001).

Wetlands and estuarine sediments have a lower oxidation-reduction potential, one of the key pathways to mercury speciation (Randal, 2013). Some portions of methylmercury formed in an ecosystem are taken up or bioaccumulate in organisms such as algae (USEPA, 2009). Methylmercury in aquatic food webs increases at every trophic level (biomagnifies) reaching highest level at the top of the food web (USEPA, 2009). There

are no biological requirements for mercury and it has been listed as a high priority pollutant due to its persistence in the environment and high toxicity to organisms (Jiang *et al.*, 2006). The conversion of inorganic mercury to methylmercury is an important link in the bioaccumulation of mercury in fish and ultimately its toxicity to wildlife and humans (Randall and Chattopadhyay, 2013). The range of mercury concentration in oceanic and coastal water is 0.001 - 0.004 $\mu\text{g/l}$. It may increase especially near the mouths of industrialized rivers (Olafsson, 1983).

2.6.4 Copper

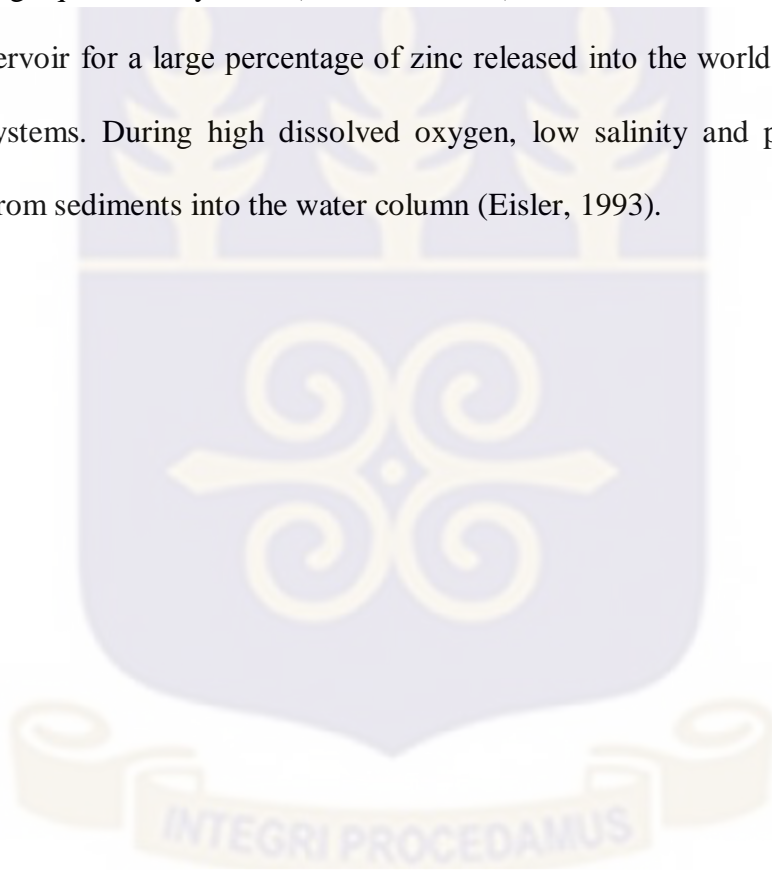
Copper is an essential trace metal that is required in small amounts (5-20 $\mu\text{g/g}$) by fish, shellfish and other invertebrates for metabolism and the function of more than thirty enzymes (Heike Bradl, 2005). However, copper concentrations that exceeds 20 $\mu\text{g/g}$ can be toxic (Heike Bradl, 2005). Copper can be very toxic to aquatic organisms, and can impact populations and ecosystems (Taub, 2004). Copper is toxic to most aquatic lives at relatively low concentrations with the maximum level being 50 mg/l (Anon, 2003).

The most bioavailable and toxic form of copper is the cupric ion (Cu^{+2}). Fish and crustaceans are 10 to 100 times more sensitive to the toxic effects of copper than mammals. (Wright and Welbourn, 2002).

2.6.5 Zinc

Zinc is a naturally occurring element that is released into the coastal environment through the weathering of parent rocks (Liu *et al.*, 2013). Anthropogenic sources include;

drainage from active and inactive mining operations, domestic and industrial sewage, combustion of fossil fuel and solid waste, corrosion of zinc alloys and erosion of agricultural soils (Liu *et al.*, 2013). The application of zinc in several agro processes such as fertilizers, liming materials, fungicides and pesticides usually increases the concentration of zinc in farmlands compared to adjacent lands (Liu *et al.*, 2013). The elevated levels of zinc in farmlands results in increased zinc concentration in the surrounding aquatic ecosystems (Liu *et al.*, 2013). Marine and estuarine sediments act as major reservoir for a large percentage of zinc released into the world's oceans and other aquatic systems. During high dissolved oxygen, low salinity and pH periods, zinc is released from sediments into the water column (Eisler, 1993).



CHAPTER THREE

MATERIALS AND METHODS

3.1 The study site

The Densu Delta Ramsar Site (Figure 1) was selected due to its importance in providing a habitat for many species of resident shorebirds and also receives large number migratory shorebirds (Teley, 2001). The Densu Delta is located in the river valley formed by the Aplaku-Tukuse and Weija-McCarthy Hills west of Accra, Latitude 5° 31' N and Longitude 0° 20' W (Figure 1). The wetland takes its source from the Densu River which originates from the Atewa Mountains in the East Akim Abuakwa District of Eastern Region. The main lagoons and wetland are bounded on the south by the Atlantic Ocean coastline between Bortianor and Gbegbeyise. The Aplaku-Bortianor road and the Sakumo stream define the western and eastern boundaries respectively. The Densu Delta, a Ramsar Site, covers an area of 46.2 km², of which about 18 km² has been developed into saltpans, and 28 km² covered by saltmarsh, lagoons, marsh and scrub (Gbogbo, 2007).

Some communities along the wetland are Aplaku, Oblogo, Bortianor, Panbrons, and Weija. Its proximity to the rapidly developing Accra metropolis have resulted in massive encroachment on the wetland environment for farming and residential accommodation (Teley, 2001).

On the eastern slope of Aplaku-Bortianor hill, three other streams also drain into the Densu Delta Ramsar Site while the eastern section of the wetland consists of a lagoon and marshes serving as a drain into the Densu River (Teley, 2001). The average annual temperature of the area is about 26 °C and the relative humidity is between 75% - 85%, 65% from December to February (Teley, 2001).

The geology of the area forms part of the Akwapim Range dominated by the formation of the Akwapim – Togo Range. The range are formed mostly by the formation of the pre-Cambrian quartzite schist with smaller amount of phyllite, sericite schist, sandstone and shale (Ametakpo, 1998). The sediments of the Densu Delta Ramsar Site are composed of sand and silt with different incorporations of clay (Biney, 1995). Most of the sediments into the area are trapped by the Weija Dam upstream.

The Site falls within the Coastal Savanna zone of Ghana where rainfall is seasonal with two peaks in June and October (Teley, 2001). Mean annual rainfall for the area is 800 mm (Teley, 2001). The rainfall pattern is bimodal with the main wet season occurring from mid-March to end-July, followed by the minor wet season from early September to end of November (Teley, 2001). About 75% of the annual rainfall is in the major wet season. Maximum rainfall is in June and October for the two seasons respectively (Teley, 2001).

The vegetation in the saltmarsh, lagoons, saltpans, marsh and scrub are scattered mangrove stands dominated by *Avicennia germinans*, *Sesuvium portulacastrum*, *Paspalum vaginatum*, *Sporobolus virginicus*, *Cyperus articulatus* and *Imperata cylindrical* (Gbogbo, 2007). A total of 15 fin fishes belonging to 14 genera and 9 families

occur in the area, with *Sarotherodon melanotheron* and *Tilapia zillii* being the dominant. Annual temperatures range between 25 °C and 30 °C. The water is shallow with depth ranging between 0 and 2 m (Tigme, 2005). The main economic activities of inhabitants along the delta is stone quarrying, fishing, peasant farming, urban and industrial developments and recreation (Tigme, 2005).

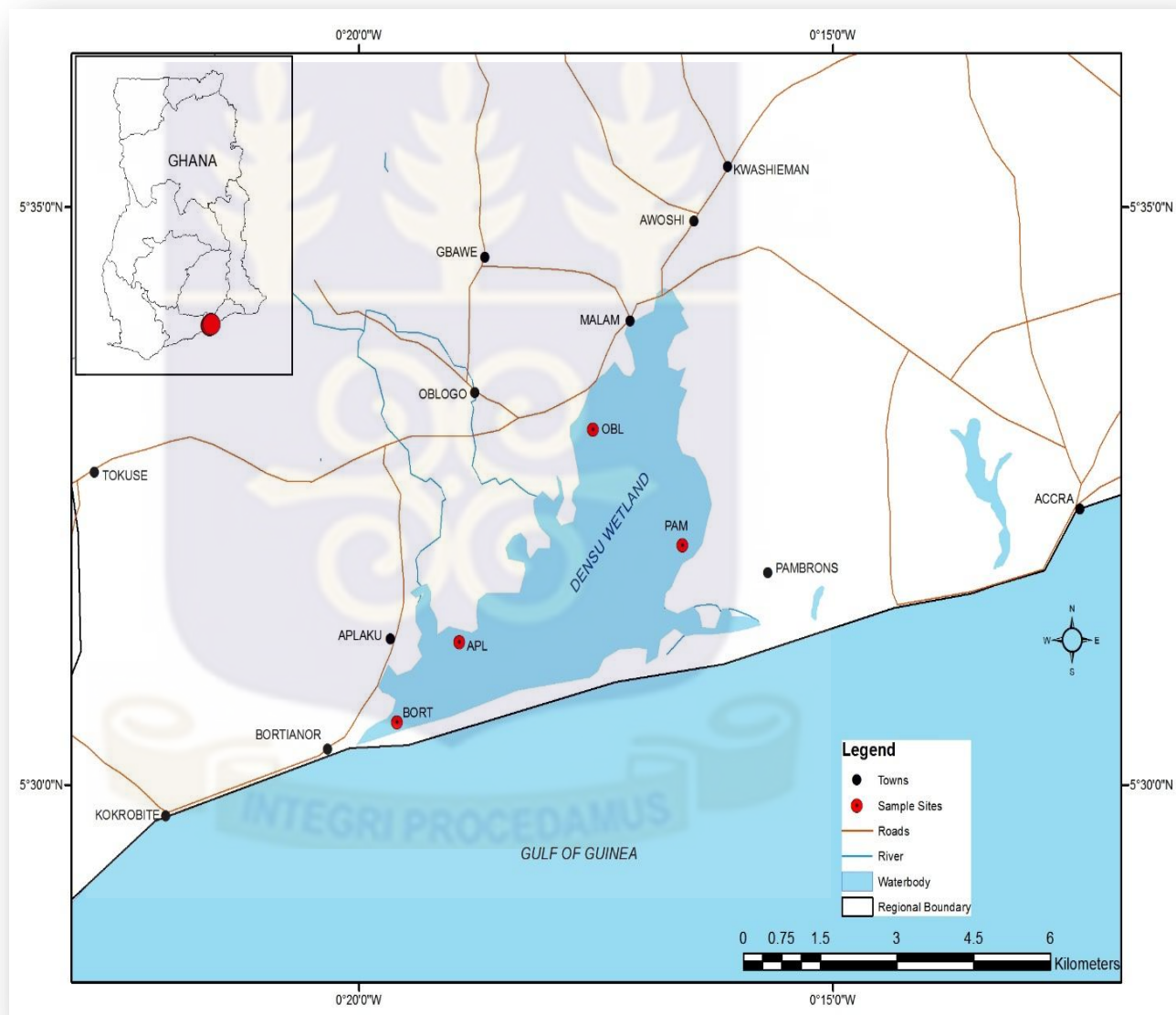


Figure 1: Map of Ghana showing the study area.

3.2 Field methods

3.2.1 Water samples

Three hundred milliliters (300 ml) acid washed plastic bottles were used to collect 72 samples of water across the wet and dry seasons from the periods August 2016 to February 2017 in four sampling stations. Samples were put in ice chest at 4 °C for preservation and transported to the laboratory.

3.2.2 Sediments samples

Zip lock bags were used to collect 56 sediment samples August, November and December (4 samples at each station in the wet season: 5 samples at each station in the dry season (September, January and February): 3 replicates for each station in the wet and dry seasons) using the Ekman grab (Appendix 6).

3.2.3 Shorebirds

Birds in the Densu Delta Ramsar Site were counted from September 2016 to January 2017 with the aid of 'Yitsu 50×50 High Definition optic zoom binoculars 357 ft 1000 yards high powered telescope for bird watching' and Canon EOS 350D' digital camera.

Species of birds were identified using 'Helm Field Guide-Birds of Ghana' (Barrow and Demey, 2010). Out of the list of birds counted, resident species of birds with the highest counts for the months were selected and targeted for trapping. They include; *Ceryle rudis*

(Piedkingfisher), *Phalacrocorax africanus* (Longtailed cormorant), and *Egretta ardesiaca* (Black heron).

Permits was sought from the Forestry Commission of Ghana, and birds were trapped by mist netting (Plate 1), and feathers from 12 *Ceryle rudis* (Plate 2), 9 *Phalacrocorax africanus*, and 7 *Egretta ardesiaca* were collected. A total of 15 to 20 breast feathers were extracted from each bird, put in zip lock bag and marked with bird type and location, and the bird marked and released. Breast feathers were collected because they are considered a better indicator of body burden (Burger, 1993).



Plate 1: *Ceryle rudis* (Piedkingfisher) trapped in a mist net



Plate 2: Extraction of feathers of *Ceryle rudis* (Piedkingfisher) into zip lock bag

3.2.4 Fish

A fisherman was contracted to do experimental fishing for two hours per day using multifilament 1 inch by 1 inch cast net. Out of a total 11 species of fish caught, *Sarotherodon melanotheron* (Blackchin tilapia) and *Coptodon zillii* (Formerly known as *Tilapia zillii*) were the dominant species from the four subsampling stations from August 2016 – January, 2017. A total of one hundred and five (105) pieces of *Sarotherodon melanotheron* (Appendix 5a) forming 80% and *Coptodon zillii* (Appendix 5b) forming 20% were selected. The assessment of the dominant fish species were done through the use of relative abundance of fish species obtained from the sampling area during the study. Obtained fish species were identified to the species level using freshwater fish

species identification keys by Dankwa *et al.*, (1999). The fish samples were stored in a container containing water and ice block.

3.2.5 Physical parameters

At the various sampling locations, the following physico-chemical parameters were measured in situ; pH, Salinity, Dissolved Oxygen (DO), and water temperature using the WQC-24 Multi-Parameter Water Quality Meter within the period monthly.

3.3 Laboratory method

3.3.1 Water

Each 300 ml of the water sample was diluted with 1.5 ml of concentrated nitric acid. This was done to preserve the samples by preventing flocculation, suppress bacterial and microbial activity, as well as lower the pH to less than two (2). The sample were then ready for digestion.

3.3.2 Digestion of water

In each 300 ml, 30 ml of water sample was taken and put in a 100 ml borosilicate beaker, 5 ml of aqua regia in the ratio of 4.5 ml concentrated hydrochloric acid to 0.5 ml concentrated HNO₃ was added to the sample in the fume chamber. The samples in the beaker were then covered with a cling film and placed on the hot plate and digested for 3 hours at a temperature of 45°C. The samples were then filtered and the content

transferred into acid washed cleaned mini plastic bottles (Plate 3) ready for analysis by the Atomic Absorption Spectrometer AAS-240 FS analysis (Atomic Absorption Spectrometer (AAS) Standard methods for water, waste water, and biota, 1995)

The concentration of each metal was calculated using the formula below:

$$\text{Final concentration (mg/l)} = \frac{\text{concentration of metal} \times \text{dilution factor} \times \text{nominal Volume}}{\text{Sample volume (ml)}}$$

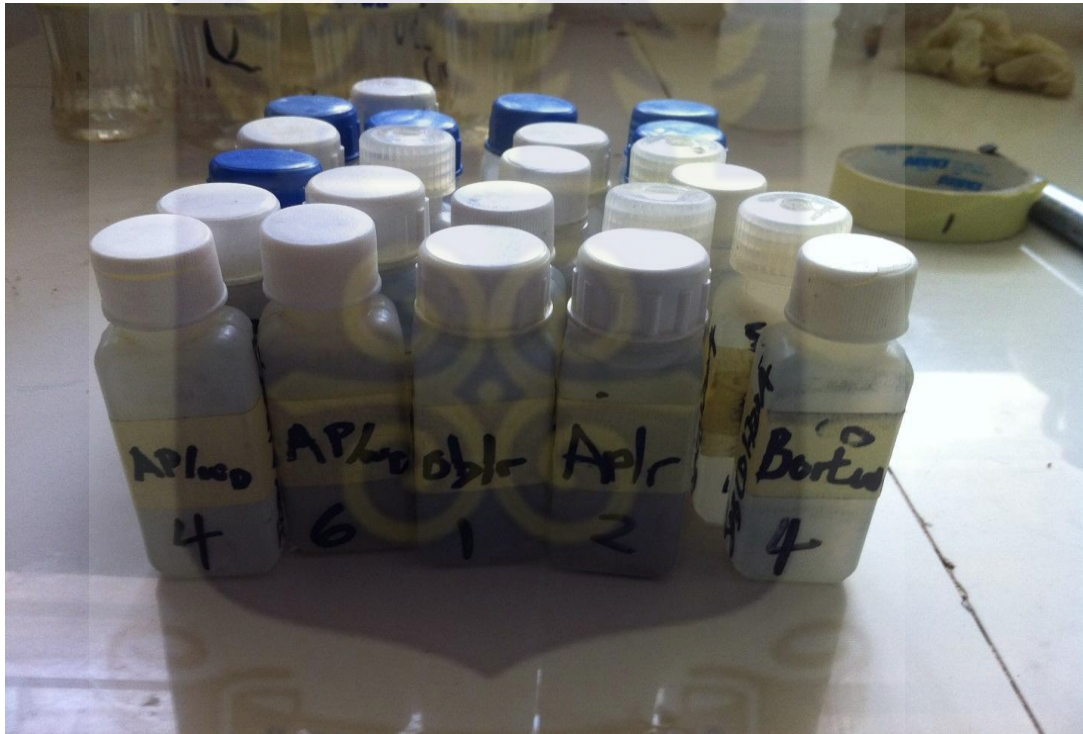


Plate 3: Digested water samples ready for analysis

3.3.3 Sediments

Sediment samples were oven-dried at 60 °C for 24 hours. They were ground and sieved through a 250 micron, 125 micron, and 60 micron mesh. This was done to obtain fine-grained sediment due to the fact that heavy metals are absorbed onto fine-grained sediments more readily than coarse-grained sediment (Blanton, 1995). Samples weighing above 0.1 g of sediment of the silt component were stored in zip lock bags for digestion.

3.3.4 Digestion of sediments

Sample bottles were shake for about 2 minutes for homogenization. Weighed 0.2 g of dry sample were put in labeled Teflon tubes (FEP, 50 ml, Nalgene). Slowly 1 ml of aqua regia (HNO_3 : HCl , 1:3 v/v) and 6 ml of concentrated hydrofluoric acid (HF) were added to the samples and was left at room temperature for at least 1 hour. After that the tubes were closed and placed in an aluminum block on a hot plate at 120 °C for 2 hours and 30 minutes.

Weighed 2.70 g of boric acid was put into labeled 50 ml polypropylene graduated tubes and 20 ml of Milli-Q water was added and shook. The samples were then allowed to cool to room temperature and the tubes opened. The samples were then transferred into 50 ml polypropylene graduated tubes (containing boric acid), after which the Teflon tubes were rinse with Milli-Q water 3 times and put in ultrasonic bath at 60 °C for at least 30 minutes until all boric acid is dissolved. The samples were allowed to cool at room temperature and then dilute to the mark 50 ml with Milli-Q water. Particles were allowed

to settle before analysis by AAS-240FS (International Atomic Energy Agency (IAEA) Monaco Digestion protocol (MC-98000 Monaco)

The concentration of each metal was calculated using the formula below:

$$\text{Final concentration (mg/kg)} = \frac{\text{concentration of metal} \times \text{dilution factor} \times \text{nominal Volume}}{\text{Sample weight (g)}}$$

3.3.5 Fish

The samples of fish were measured both in total lengths (cm), and weight (g). The scales were removed and was washed with distilled water three times to get rid of any external contaminations. The samples were then cut into pieces (Plate 4) and oven dried at 60 °C for 48 hours. The samples were then blended and a dry weight greater than 0.1 g was obtained (Boyden 1977).



Plate 4: Processing of fish samples at the department of marine and fisheries graduate laboratory of the University of Ghana

3.3.6 Digestion of fish

The samples were placed in bottles and shook for about 2 minutes for homogenization and opened a few minutes after. Dry weight of 0.2 g of the sample was weighed and put in labeled Teflon tubes (FEP, 50 ml, Nalgene). 5 ml of Nitric acid was added and the samples were left at room temperature for at least 1 hour. The tubes were closed and placed in an aluminum block on a hot plate at 90 °C for 3 hours. After that the samples were allowed to cool to room temperature after which the tubes were carefully opened. The samples were then transferred into labeled 50 ml polypropylene graduated tubes and diluted to 50 ml mark with milli-Q water and shaken. Then the samples analyzed by Atomic Absorption Spectrometer AAS-240FS analysis (International Atomic Energy Agency (IAEA) Monaco protocol (MC-98000 Monaco))

3.3.7 Digestion of feathers

Feathers taken for analysis were washed in double distilled water three times to remove any external contamination. They were dried in the oven at 60°C until reaching constant dry mass of 0.001 g (Dauwe *et al.*, 2000). Subsequently, the feathers were digested in a 4:1 mixture of 65 % nitrogenous acid and 70 % perchloric acid (Nyholm *et al.*, 1995). Afterwards, all samples were diluted by adding deionized water up to 10 ml and stored in polypropylene metal-free vials at -18°C until the time of analysis by Atomic Absorption Spectrometer AA-240FS analysis (Atomic Absorption Spectrometer (AAS) Standard methods for water, waste water, and biota, 1995)

3.3.8 Metals analysis by Atomic Absorption Spectrometer (AAS – 240FS) and Direct Mercury Analyzer (DMA-80)

The AAS determines metals from only liquid solutions. Determination or measurement of metals using the AAS is done by first optimizing the AAS. The AAS is then calibrated using three standards for each element of interest.

For the determination of Arsenic, the hydride generation method was used. The Vapour Generation Accessory (VGA) is hooked to the AAS. The sample, 6M of Hydrochloric acid (HCl) and 0.6 % Sodium borohydride (NaBH₄) in 0.5 % Sodium hydroxide (NaOH) is mixed in the reaction chamber. The reaction results in liquid and gaseous states and is separated by the separation device. The vapour flows through a fluorinated tube connected to the sample holder on the burner head whilst the flame (Acetylene flame) is on which causes the excitation of the electrons. The beam from the lamp (Hollow Cathode Lamp) then absorbs all the excited electrons travelling at the selected wavelength through the eye piece past the monochromater to the detector which then converts the measurement into absorbance and concentration which is the displayed on the monitor.

The limit of detection was taken as the concentration of an analyte in a sample that gives rise to a peak with a signal-to-noise ratio (S/N) of 3.

Table 1: Elements wavelengths and detection limit by the Varian AAS- 240FS

Elements	Wavelength (nm)	Lamp Current	Slit Moth	Support	Fuel	Detection Limit
Copper	324.7	4	0.5	Air	Acetylene	<0.003
Zinc	213.9	5	1	Air	Acetylene	<0.001
Cadmium	228.8	4	0.5	Air	Acetylene	<0.002
Arsenic	193.7	10	1	Argon	Acetylene	<0.001

Table 2: Sensitivity check for AA- Standards

	ELEMENT	CONC(mg/l)	MEAN ABS
1	Cu	2''	0.266
		5	0.665
		7	0.932
2	Zn	0.25	0.166
		0.5	0.333
		1	0.666
3	Cd	0.5	0.166
		2	0.666
		3	1
4	As	0.2	0.001
		0.4	0.002
		0.8	0.004
		1	0.005
5	Hg	0.2	0.0006
		0.4	0.0012
		0.8	0.0024
		1	0.0029

DMA-80 Principle of operation: Solid or liquid samples are weighed and introduced in the DMA-80. The sample is initially dried and then thermally decomposed in an oxygen or air flow. Combustion products are carried off and further decomposed in a hot catalyst bed. Mercury vapors are trapped on a gold amalgamator and subsequently desorbed for quantitation. The mercury content is determined using atomic absorption spectrophotometry at 254 nm.

Direct mercury determination of trace level on solid, liquid and gas samples has advantages which includes; No sample digestion step, no wet chemistry pre-treatment step, it is faster five minutes per sample, and eliminates waste disposal.

3.3.9 Quality control/Quality assurance

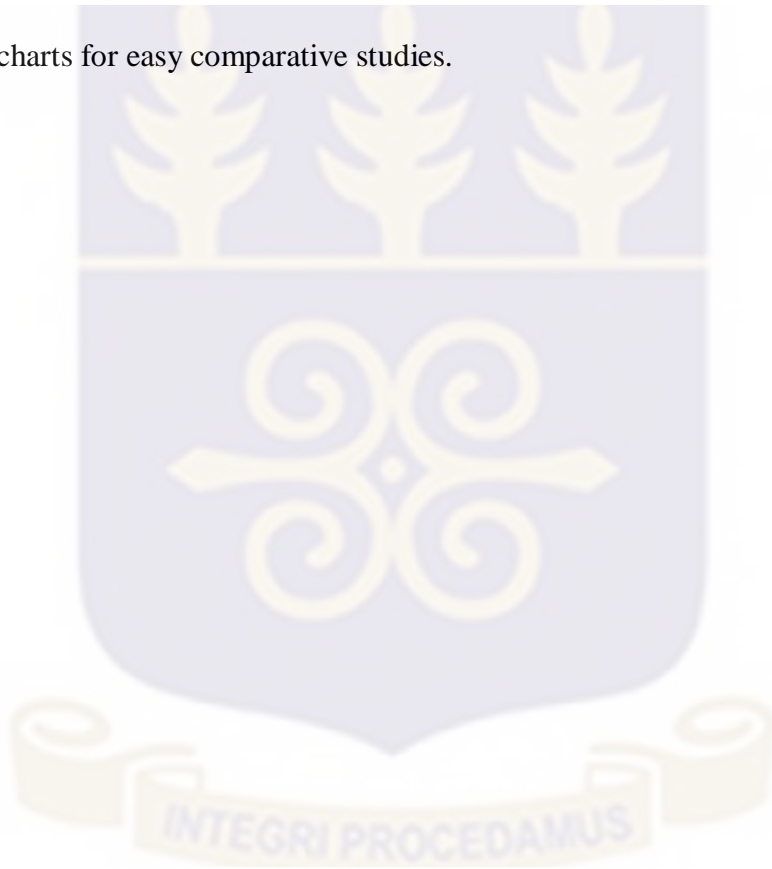
Procedural blanks to check contamination during sample preparation and to ensure that readings are within the acceptable limits. The AA-Standards were used to calibrate the equipment. Repeats (of the second sample) were also done to check the reproducibility of the methods. For every ten readings; 2 standard reading, 1 blank, 1 quality control standards, and 1 repeat. Below is a sensitivity check for AA-Standards used for the five metals analyzed.

3.4: Statistical analysis

Data obtained for sediment and water were subjected to normality test using Anderson Darling Test. Data followed a normal distribution when the Anderson Darling test was

greater than 0.05 and, when lower than 0.05, data was known to non-normal (Amponsah, 2015). Non-normal data were subjected to non-parametric test including Mann Whitney Test or Kruskal Wallis test while parametric test such as ANOVA and t-test were applied when normal data were realized.

Significant difference regarding inferential statistics was obtained at p-value < 0.05 or 95 % confidence level. Minitab and Microsoft Statistical Tool Pac were used to generate table and charts for easy comparative studies.



CHAPTER FOUR

RESULTS

4.1 Sediment samples

4.1.1 Heavy metals in sediments

Figure 2 shows the levels of heavy metals analyzed from Densu Delta Ramsar Site sediment samples. In all, five (5) different trace metals were assessed. Concentration of Copper ranged from 5.050 mg/kg – 9.010 mg/kg at an average of 6.676 ± 0.238 mg/kg during the wet season while during the dry season, its content ranged from 4.120 mg/kg – 8.010 mg/kg with an average 6.013 ± 0.210 mg/kg. Using one sample t-test, difference in copper concentration between the two seasons was significant ($p < 0.05$) (Appendix 6a). Concentration of zinc during the wet season ranged from 21.200 mg/kg to 36.100 mg/kg at an average of 28.988 ± 0.954 mg/kg while during the dry season, its content ranged from 20.600 mg/kg to 38.400 mg/kg with an average 30.024 ± 0.990 mg/kg (Figure 2). Using one sample t-test, difference in zinc concentration between the two seasons was not significant ($p > 0.05$) (Appendix 6a).

Concentration of cadmium during the wet season ranged from 0.050 mg/kg to 0.140 mg/kg at an average of 0.104 ± 0.005 mg/kg while during the dry season, its content ranged from 0.050 mg/kg to 0.150 mg/kg with an average 0.103 ± 0.006 mg/kg (Figure 2). Using one sample t-test, difference in cadmium concentration between the two seasons was not significant ($p > 0.05$). Concentration of arsenic during the wet season ranged from 0.030 mg/kg to 0.090 mg/kg at an average of 0.056 ± 0.003 mg/kg while

during the dry season, its content ranged from 0.030 mg/kg to 0.071 mg/kg with an average 0.055 ± 0.002 mg/kg (Figure 2). Using one sample t-test, difference in arsenic concentration between the two seasons was not significant ($p > 0.05$). Concentration of mercury during the wet season ranged from 0.003 mg/kg to 0.013 mg/kg at an average of 0.078 ± 0.001 mg/kg while during the dry season, it content ranged from 0.000 mg/kg to 0.009 mg/kg with an average 0.005 ± 0.001 mg/kg (Figure 2). Using Mann-Whitney test, difference in mercury concentration between the two seasons was significant ($p > 0.05$) (Appendix 6a). Overall, zinc was the most dominant metal in sediment followed by copper.

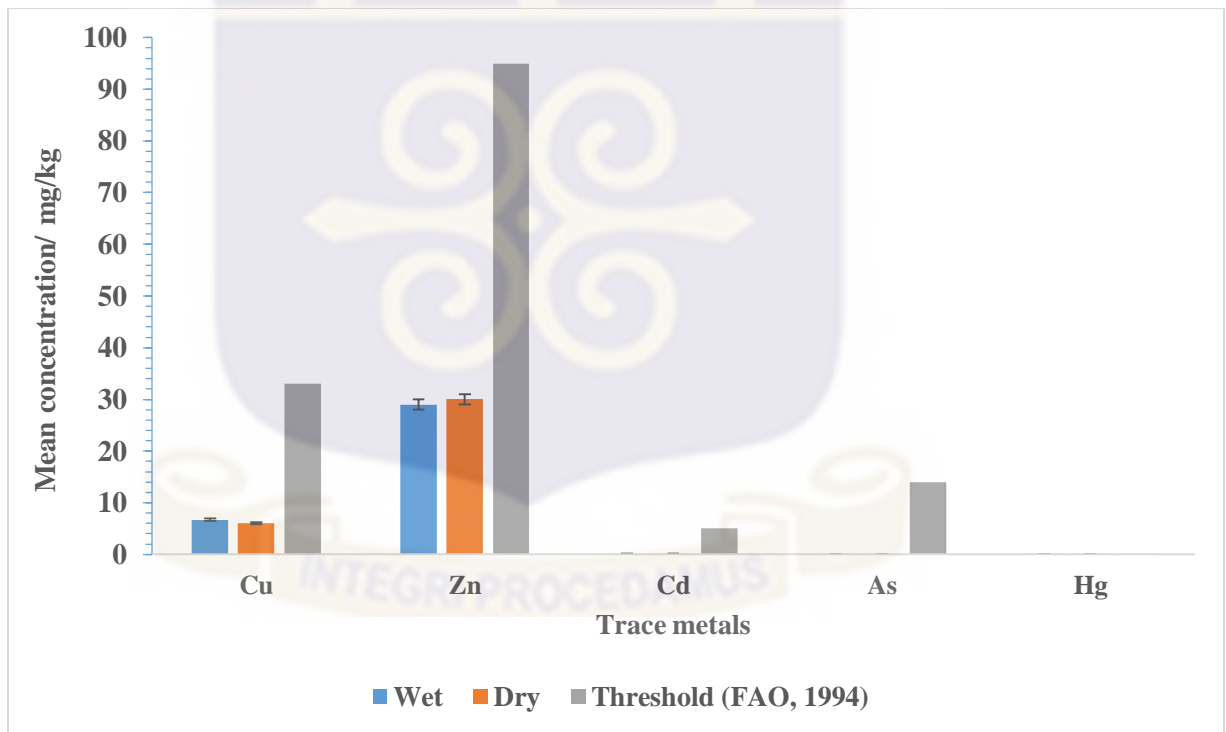


Figure 2: Heavy metal content in sediments obtained from Densu Delta Ramsar Site, Ghana.

4.1.2 Correlation matrix for heavy metals in sediments

Table 3 shows the correlation matrix for heavy metals obtained from sediments during wet and dry seasons from the Densu Delta Ramsar Site, Ghana. Cadmium and copper during the dry season exhibited a relatively strong negative correlation (-0.33). Mercury and copper as well as arsenic and copper showed a relatively strong negative correlation of -0.20 and -0.42 in the dry season respectively. Arsenic and cadmium as well as mercury and arsenic exhibited a positive correlation of 0.20 and 0.39 in the dry season respectively. However, cadmium and copper also exhibited a strong positive correlation of 0.27 in the wet season. Furthermore, the positive correlation between zinc and copper 0.20 during the dry season was relatively strong. This may suggest that the relationship among the concentrations of the zinc & copper, and cadmium & copper are almost equal to each other.

Table 3: Correlation matrix for heavy metals in sediments from Densu Delta Ramsar Site, Ghana

	Cu_W	Zn_W	Cd_W	As_W	Hg_W	Cu_D	Zn_D	Cd_D	As_D	Hg_D
Cu_W	1.00									
Zn_W	-0.03	1.00								
Cd_W	0.27	-0.20	1.00							
As_W	-0.31	-0.11	0.04	1.00						
Hg_W	0.17	-0.15	0.16	-0.10	1.00					
Cu_D	-0.22	-0.29	-0.13	0.11	0.12	1.00				
Zn_D	-0.13	-0.06	0.23	0.30	0.10	0.20	1.00			
Cd_D	0.16	0.13	-0.06	0.00	0.10	-0.33	0.08	1.00		
As_D	0.06	-0.10	-0.02	-0.14	-0.22	-0.42	0.02	0.20	1.00	
Hg_D	0.06	0.18	-0.22	-0.04	0.14	-0.20	-0.19	0.15	0.39	1.00

4.2 Water samples

4.2.1 Physical parameters of water

Table 10 shows the physical parameters of water measured in the Densu Delta Ramsar Site for both rainy and dry seasons during the study period. They include: Salinity, pH, Dissolved Oxygen (DO), Total Solids (TS), and Temperature (T). The average salinity was 14 ‰ during low tide and 20 ‰ during high tide in the rainy season, and 25 ‰ during low and 28 ‰ during high tide in the dry season. The lowest salinity recorded in the rainy season was as a result of the influx of freshwater through rains and the opening of the Weija dam.

Table 4: Mean Physical parameters of water in the rainy and dry seasons.

Parameter	Mean			
	<i>Rainy</i>		<i>Dry</i>	
S‰	17	±0.769	26.5	±1.122
DO(mg/L)	7.12	±2.070	6.09	±2.886
pH	8.91	±1.812	8.06	±2.439
T(° C)	24	±0.272	31	±0.078
TS(ppt)	0.64	±0.151	0.72	±0.167

4.2.2 Heavy metals in water

Figure 3 shows the levels of heavy metals analyzed from Densu Delta Ramsar Site water samples. In all, five (5) different trace metals were assessed. Concentration of Copper ranged from 0.72 mg/l – 3.11 mg/l at an average of 1.537 ± 0.111 mg/l during the wet season while during the dry season, its content ranged from 0.590 mg/l to 1.731 mg/l with

an average 1.107 ± 0.065 mg/l (Figure 3). Using one sample t-test, difference in copper concentration between the two seasons was significant ($p < 0.05$) (Appendix 6 b). Concentration of zinc during the wet season ranged from 7.060 mg/l to 10.600 mg/l at an average of 2.980 ± 0.3810 mg/l while during the dry season, its content ranged from 10.100 mg/l to 16.000 mg/l with an average 13.040 ± 0.401 mg/l (Figure 3). Using Mann-Whitney test, difference in zinc concentration between the two seasons was significant ($p < 0.05$) (Appendix 6b).

Concentration of cadmium during the wet season ranged from 0.000 mg/l to 0.072 mg/l at an average of 0.036 ± 0.005 mg/l while during the dry season, it ranged from 0.00 mg/l to 0.06 mg/l with an average 0.025 ± 0.004 mg/l (Figure 3). Using Mann-Whitney test, difference in cadmium concentration between the two seasons was not significant ($p < 0.05$). Concentration of arsenic during the wet season ranged from 0.010 mg/l to 0.08 mg/l at an average of 0.052 ± 0.004 mg/l while during the dry season, its content ranged from 0.00 mg/l to 0.06 mg/l with an average 0.022 ± 0.004 mg/l (Figure 3). Using Mann-Whitney test, difference in arsenic concentration between the two seasons was significant ($p < 0.05$). Concentration of mercury during the wet season ranged from 0.000 mg/l to 0.016 mg/l at an average of 0.008 ± 0.001 mg/l while during the dry season, its content ranged from 0.00 mg/l to 0.011 mg/l with an average 0.002 ± 0.001 mg/l (Figure 3). Using Mann-Whitney test, difference in mercury concentration between the two seasons was significant ($p < 0.05$) (Appendix 6b).

Overall, the dominant heavy metals in the water for both seasons were copper and zinc, with zinc been the most dominant.

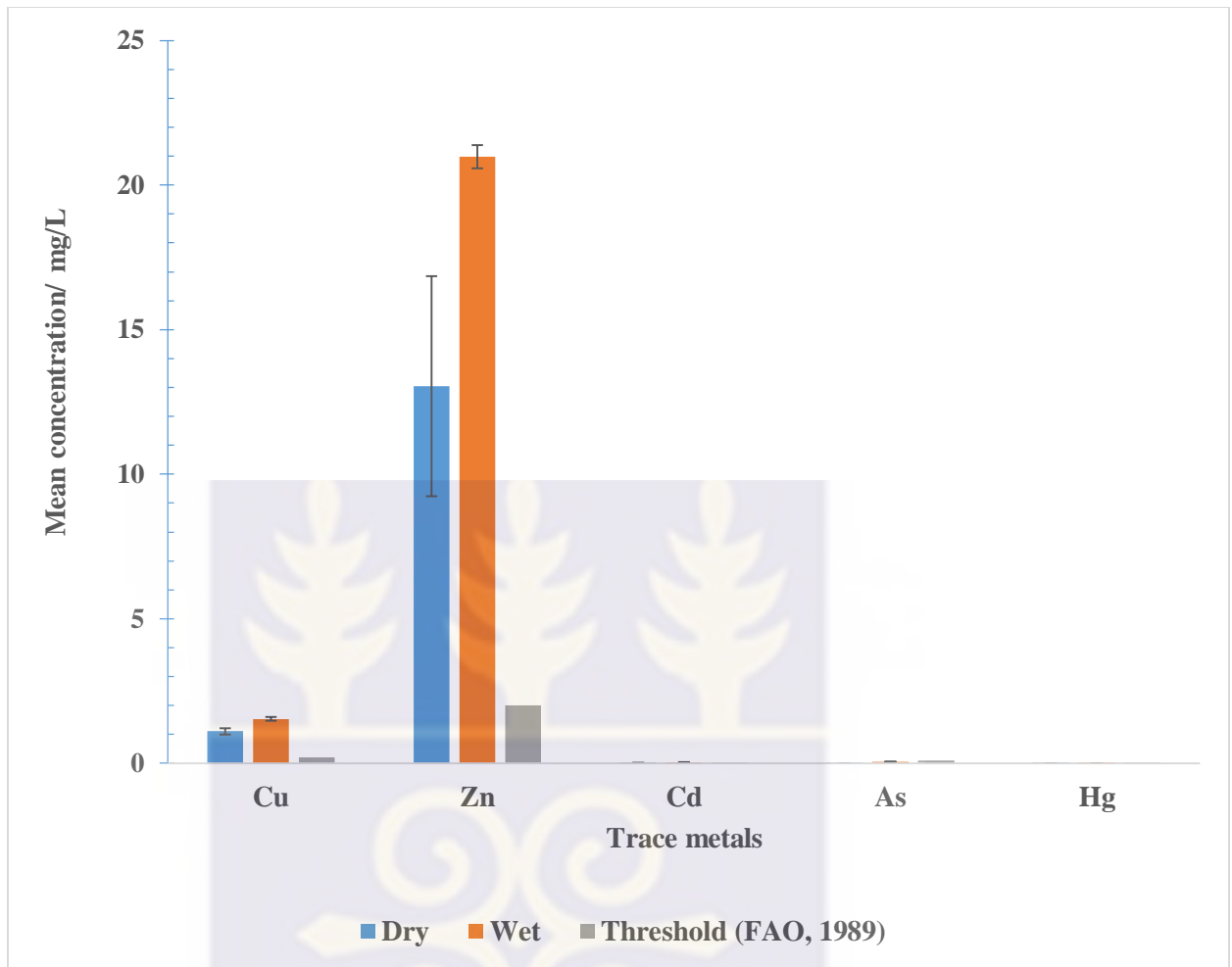


Figure 3: Heavy metal content in water samples obtained from Densu Delta Ramsar Site, Ghana

4.2.3 Correlation matrix of heavy metals in water samples

Table 4 shows the correlation matrix for heavy metals obtained during wet and dry season from the Densu Delta Ramsar Site, Ghana. Cadmium and copper during the wet season exhibited a relatively strong positive correlation (0.32). Mercury and cadmium as well as zinc and copper showed a relatively strong negative correlation of -0.46 and -0.21 respectively. Similarly, arsenic and cadmium showed a relatively strong negative correlation of -0.25. During the dry season, arsenic and cadmium exhibited a positive

correlation of 0.23 while mercury and arsenic showed a relatively strong negative correlation of -0.30 (Table 4). The negative correlation exhibited by mercury & cadmium, zinc & copper as well as mercury & arsenic may be due to other factors such as pH in water that affects these metal uptake (Sauve *et al.*, 2000).

Table 5: Correlation matrix for heavy metals in water samples from Densu delta Ramsar Site, Ghana

	Cu_W	Zn_W	Cd_W	As_W	Hg_W	Cu_D	Zn_D	Cd_D	As_D	Hg_D
Cu_W	1.00									
Zn_W	-0.21	1.00								
Cd_W	0.32	-0.03	1.00							
As_W	0.08	0.18	-0.25	1.00						
Hg_W	0.18	-0.05	-0.46	0.16	1.00					
Cu_D	0.15	-0.11	0.18	0.16	0.04	1.00				
Zn_D	0.13	0.19	-0.03	0.06	0.09	-0.10	1.00			
Cd_D	-0.27	-0.27	-0.12	0.11	-0.08	-0.07	-0.05	1.00		
As_D	0.13	-0.21	0.51	-0.29	-0.43	0.02	0.08	0.23	1.00	
Hg_D	-0.10	0.16	-0.29	0.36	0.54	0.08	-0.06	0.01	-0.30	1.00

4.3 Fish samples

4.3.1: Heavy metals in fish species.

Figure 4 shows the levels of heavy metals analyzed from Densu Delta Ramsar Site fish samples. In all, five (5) different trace metals were assessed. Concentration of copper in *Sarotherodon melanotheron* (Blackchin tilapia) ranged from 0.050 mg/kg – 0.190 mg/kg

at an average of 0.140 ± 0.101 mg/kg while in *Coptodon zillii* (Red belly tilapia), copper content ranged from 0.090 mg/kg – 0.140 mg/kg with an average 0.112 ± 0.008 mg/kg (Figure 4). Using one sample t-test, difference in copper concentration between the two-fish species was not significant ($p > 0.05$) (Appendix 6 c). Concentration of zinc in *Sarotherodon melanotheron* (Blackchin tilapia) ranged from 3.160 mg/kg – 8.150 mg/kg at an average of 5.350 ± 0.813 mg/kg while in *Coptodon zillii* (Red belly tilapia) zinc content ranged from 2.110 mg/kg – 6.010 mg/kg with an average 4.198 ± 0.556 mg/kg (Figure 4). Using one sample t-test, difference in zinc concentration between the two-fish species was not significant ($p > 0.05$) (Appendix 6c).

Concentration of cadmium in *Sarotherodon melanotheron* (Blackchin tilapia)) ranged from 0.004 mg/kg – 0.017 mg/kg at an average of 0.008 ± 0.002 mg/kg while in *Coptodon zillii* (Red belly tilapia) cadmium content ranged from 0.000 mg/kg – 0.013 mg/kg with an average 0.004 ± 0.002 mg/kg (Figure 4). Using one sample t-test, difference in cadmium concentration between the two (2) fish species was not significant ($p > 0.05$). Concentration of arsenic in *Sarotherodon melanotheron* (Blackchin tilapia) ranged from 0.000 mg/kg – 0.013 mg/kg at an average of 0.005 ± 0.002 mg/kg while in *Coptodon zillii* (Red belly tilapia) arsenic content ranged from 0.000 mg/kg – 0.004 mg/kg with an average 0.010 ± 0.001 mg/kg (Figure 4). Using Mann Whitney test, difference in arsenic concentration between the two fish species was not significant ($p > 0.05$). Concentration of mercury in *Sarotherodon melanotheron* (Blackchin tilapia)) and *Coptodon zillii* (Red belly tilapia) ranged from 0.000 mg/kg – 0.005 mg/kg at an average of 0.002 ± 0.001 mg/kg (Figure 4). Using Mann Whitney test, difference in mercury

concentration between the two (2) fish species was not significant ($p > 0.05$) (Appendix 6 c).

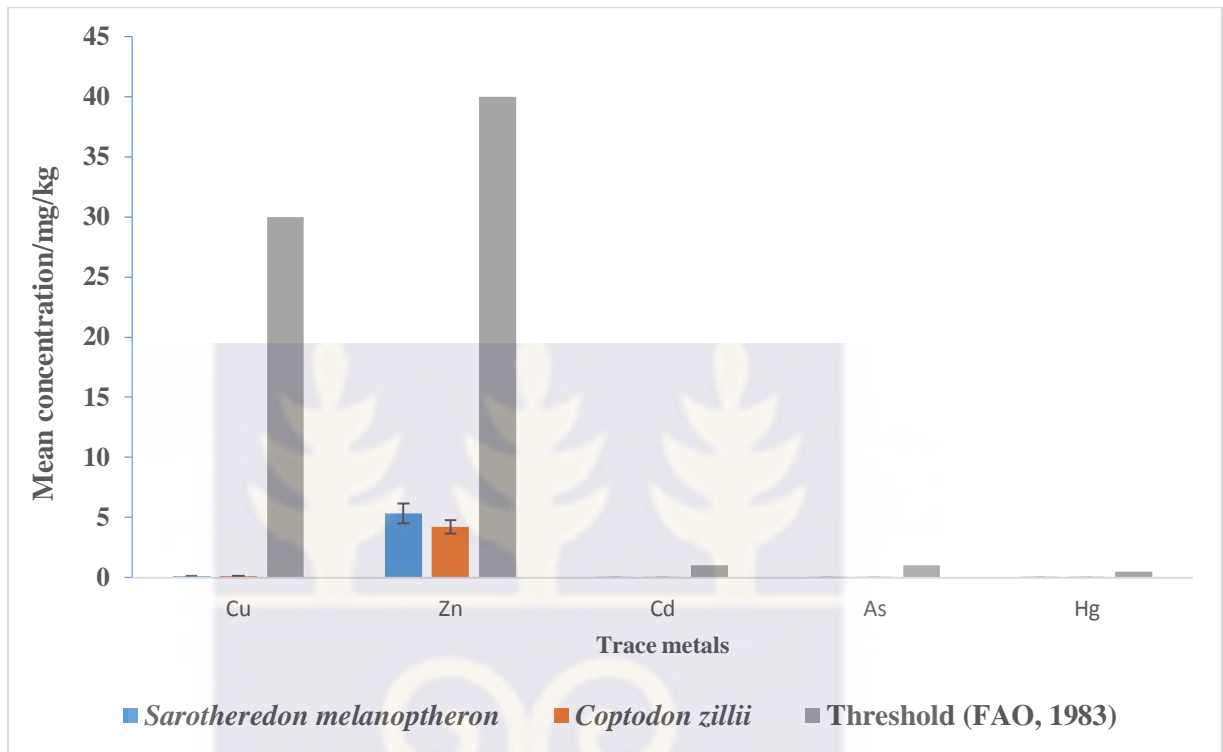


Figure 4: Mean concentration of heavy metals in fish species found in Densu Delta Ramsar Site, Ghana

4.3.2: Correlation matrix of heavy metals in fish species

Table 5 shows the correlation matrix for heavy metals obtained during wet and dry season from the Densu Delta Ramsar Site, Ghana. Regarding *Sarotherodon melanotheron* (Blackchin tilapia), zinc & copper, cadmium & zinc, arsenic & copper and arsenic & cadmium exhibited negative correlation (-0.60, -0.46, -0.41 and -0.41 respectively) as revealed in Table 5. However, observed correlation between cadmium and copper in *Sarotherodon melanotheron* (Blackchin tilapia) was positive (0.45).

In *Coptodon zillii* (Red belly tilapia) cadmium & copper, mercury & cadmium as well as mercury & arsenic exhibited negative correlation at -0.64, -0.55 and -0.20 respectively which is an indication that the metals concentration in tissues has differing metabolic action. Nonetheless, cadmium & zinc as well as arsenic & cadmium showed positive correlation at 0.46 and 0.47 respectively.

Table 6: Correlation matrix of heavy metals in fish from Densu Ramsar Site, Ghana.

	Cu_S	Zn_S	Cd_S	As_S	Hg_S	Cu_T	Zn_T	Cd_T	As_T	Hg_T
	M	M	M	M	M	Z	Z	Z	Z	Z
Cu_S										
M	1.00									
Zn_SM	-0.60	1.00								
Cd_S										
M	0.45	-0.46	1.00							
As_SM	-0.41	-0.05	-0.41	1.00						
Hg_S										
M	0.51	0.19	0.51	-0.66	1.00					
Cu_TZ	0.58	0.06	-0.30	-0.03	0.27	1.00				
Zn_TZ	-0.33	0.48	-0.75	-0.26	-0.20	0.12	1.00			
Cd_TZ	-0.43	-0.04	-0.25	-0.03	-0.28	-0.64	0.46	1.00		
As_TZ	0.18	-0.65	-0.26	0.45	-0.49	-0.01	0.02	0.47	1.00	
Hg_TZ	-0.22	0.53	-0.60	0.55	-0.18	0.60	0.11	-0.55	-0.20	1.00

4.4 Shorebirds

4.4.1. Percentage abundance and composition of shorebirds

From Figure 5, out of the thirteen shorebirds, three dominant species were observed. These species were *Phalacrocorax africanus* (Longtail cormorant) 39 %, *Egretta ardesiaca* (Black heron) 14 % and *Ceryle rudis* (Piedkingfisher) 9 %. However, the least dominant shorebird species were *Sterna maxima* and *Bulbulcus ibis* (Cattle egret) 3 %, *Actitis hypoleucos* (Common sandpiper) 1 %, *Milvus migrans* (Yellow billed kite) and *Streptopelia senegalensis* (Laughing dove) 1 %.

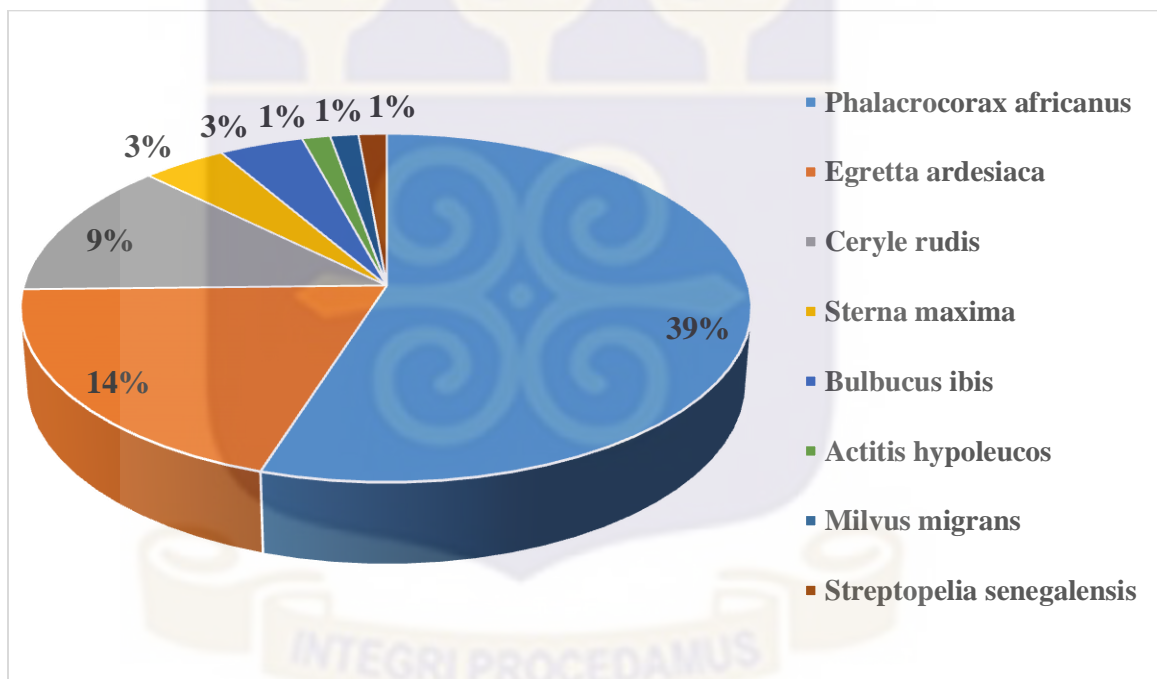


Figure 5: Percentage composition of shorebirds in the Densu Delta Ramsar Site

Table 6 shows the various species and family of birds observed at the Densu Delta Ramsar Site, Ghana. The number of species observed in August, September and November was ten, twelve and thirteen respectively. Overall, seventeen (17) species of

shorebirds were observed during the study period. Furthermore, four shorebird species were not common to all the three study months, these species include *Streptopalia senegalensis*, *Motacilia flava*, *Tringa totanus* and *Calidris alba*. Nine family of shorebird species were observed, including Ardeidae, Sterridae, Scolopacidae, Accipitidae, Alcedimidae, Carvidae, Columbidae, Phalacrocoracidae and Motacillidae. Dominant families of species recorded were Ardeidae (4 species), Scolopacidae (4 species) and Sterridae (3 species) as shown in Table 6.



Table 7: Checklist of shorebirds in Densu Delta Ramsar Site from August- October, 2016

No.	Family	Scientific Name	English Name	August	September	November
			Long-tailed			
1	Phalacrocoracidae	<i>Phalacrocorax africanus</i>	Cormorant	√	√	√
2	Alcedimidae	<i>Ceryle rudis</i>	Piedkingfisher	√	√	√
3	Ardeidae	<i>Egretta garzetta</i>	Little Egret	√	√	√
4	Ardeidae	<i>Bulbucus ibis</i>	Cattle Egret	√	√	√
5	Ardeidae	<i>Egretta gularis</i>	Western Reef Egret	√	√	√
6	Ardeidae	<i>Egretta ardesiaca</i>	Black Heron	√	√	√
7	Sternidae	<i>Sterna maxima</i>	Royal Tern	√	√	√
8	Sternidae	<i>Sterna hirundo</i>	Common Tern	√	√	√
9	Sternidae	<i>Sterna sandvicensis</i>	Sandwich Tern	√	√	√
10	Carvidae	<i>Cornus albus</i>	Pied Crow	√	√	√
11	Motacillidae	<i>Motacilia flava</i>	Yellow Wagtail	-	√	√
12	Scolopacidae	<i>Tringa tetanus</i>	Common Redshank	-	√	√
13	Scolopacidae	<i>Actitis hypoleucos</i>	Common Sandpiper	√	√	√
14	Scolopacidae	<i>Calidris minuta</i>	Little Stint	√	√	√
15	Scolopacidae	<i>Calidris alba</i>	Sanderling	√	-	√
16	Accipitidae	<i>Milvus migrans</i>	Yellow-billed Kite	√	√	√
17	Columbidae	<i>Streptopelia senegalensis</i>	Laughing Dove	-	√	√

Legend: √ (Present during bird count) - (Absent during bird count)

4.4.2 Heavy metals in shorebirds

Figure 6 shows the levels of heavy metals analyzed from shorebirds sampled at Densu Delta Ramsar Site. In all, five (5) different heavy metals were assessed. Copper concentration in *Ceryle rudis* (Piedkingfisher) ranged from 0.0190 mg/kg to 2.418 mg/kg at an average of 1.567 ± 0.238 mg/kg. In *Phalacrocorax africanus* (Longtail cormorant) copper content ranged from 4.670 mg/kg to 8.340 mg/kg with an average 6.157 ± 0.546 mg/kg. Copper concentration in *Egretta ardesiaca* (Black heron) ranged from 7.04 mg/kg to 16.50 mg/kg with an average 11.890 ± 0.149 mg/kg. Using one-way ANOVA, difference in copper concentration between the two three (3) shorebird species was significant ($p < 0.05$) (Appendix 6d).

The concentration of zinc in *Ceryle rudis* (Piedkingfisher) ranged from 2.020 mg/kg to 6.440 mg/kg at an average of 4.355 ± 0.751 mg/kg. In *Phalacrocorax africanus* (Longtail cormorant), zinc content ranged from 9.450 mg/kg to 15.500 mg/kg with an average 12.410 ± 1.010 mg/kg. Zinc concentration in *Egretta ardesiaca* (Black heron) ranged from 11.500 mg/kg to 22.800 mg/kg with an average 17.580 ± 0.159 mg/kg. Using one-way ANOVA, difference in zinc concentration between the three (3) shorebird species was significant ($p < 0.05$).

The concentration of cadmium in *Ceryle rudis* (Piedkingfisher) ranged from 0.030 mg/kg to 0.060 mg/kg at an average of 0.045 ± 0.006 mg/kg. In *Phalacrocorax africanus* (Longtail cormorant), cadmium content ranged from 0.050 mg/kg to 0.120 mg/kg with an average 0.075 ± 0.011 mg/kg. Cadmium concentration in *Egretta ardesiaca* (Black heron), ranged

from 0.007 mg/kg to 0.019 mg/kg with an average 0.014 ± 0.002 mg/kg. Using one-way ANOVA, difference in cadmium concentration between the three (3) shorebird species was significant ($p < 0.05$) (Appendix 6 d).

From Figure 6, amount of mercury in *Ceryle rudis* (Piedkingfisher) ranged from 0.000 mg/kg to 0.004 mg/kg at an average of 0.001 ± 0.001 mg/kg. In *Phalacrocorax africanus* (Longtail cormorant) mercury content ranged from 0.000 mg/kg to 0.004 mg/kg with an average 0.001 ± 0.001 mg/kg. Mercury concentration in *Egretta ardesiaca* (Black heron) ranged from 0.000 mg/kg to 0.004 mg/kg with an average 0.002 ± 0.001 mg/kg.

The concentration of arsenic in *Ceryle rudis* (Pied kingfisher) ranged from 0.000 mg/kg to 0.011 mg/kg at an average of 0.004 ± 0.002 mg/kg. In *Phalacrocorax africanus* (Longtail cormorant) arsenic content ranged from 0.000 mg/kg to 0.016 mg/kg with an average 0.009 ± 0.003 mg/kg. Arsenic concentration in *Egretta ardesiaca* (Black heron) ranged from 0.008 mg/kg to 0.105 mg/kg with an average $0.030 \text{ mg/kg} \pm 0.015 \text{ mg/kg}$.

Overall, *Egretta ardesiaca* (Black heron) recorded the maximum concentration in copper (11.890 mg/kg), mercury (0.002 mg/kg) and zinc (17.580 mg/kg) while *Phalacrocorax africanus* (Longtail cormorant) exhibited the highest concentration in cadmium (0.075 mg/kg) and arsenic (0.009 mg/kg).

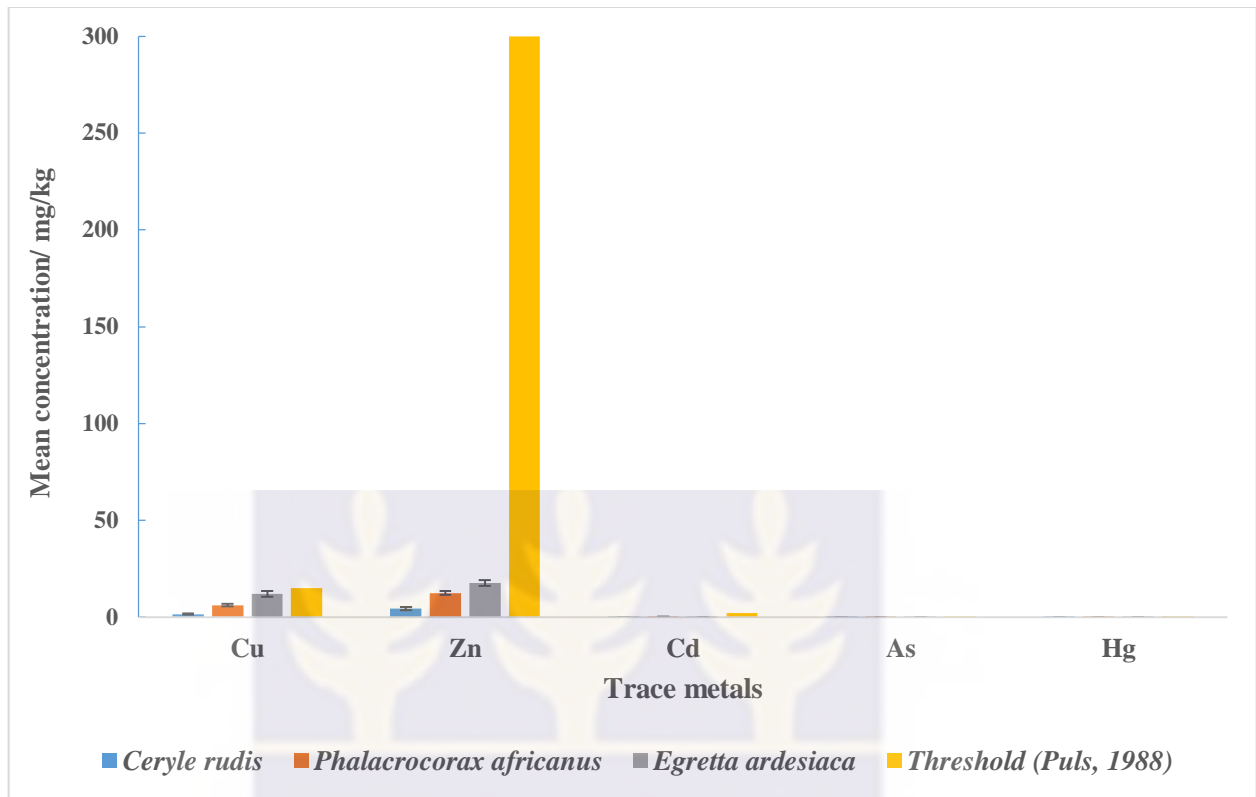


Figure 6: Mean concentration of heavy metals in shorebird species found in Densu Delta Ramsar Site, Ghana

4.4.3: Correlation matrix of heavy metals in dominant shorebird species

Table 7 shows the correlation matrix for heavy metals observed in *Ceryle rudis* (Piedkingfisher) during the study period. Zinc & copper, cadmium & copper, arsenic & zinc, mercury & copper, and arsenic & mercury exhibited negative correlation (-0.85, -0.21, -0.39 and 0.63 respectively). However, observed correlation between cadmium & arsenic, and mercury & zinc was positive (0.49 and 0.67 respectively).

Table 8: Correlation matrix of heavy metals in *Ceryle rudis* (Piedkingfisher), Densu Delta Ramsar Site, Ghana

	Cu	Zn	Cd	As	Hg
Cu	1.00				
Zn	-0.85	1.00			
Cd	-0.21	0.11	1.00		
As	-0.05	-0.39	0.49	1.00	
Hg	-0.20	0.67	0.12	-0.63	1.00

Table 8 shows the correlation matrix for heavy metals observed in *Phalacrocorax africanus* (Longtail cormorant) during the study period. Zinc & copper, cadmium & copper, mercury & copper, zinc & cadmium arsenic & zinc, mercury & zinc, arsenic & cadmium, mercury & cadmium, and mercury & arsenic exhibited positive correlation (0.31, 0.67, 0.20, 0.69, 0.30, 0.24, 0.72, 0.45 and 0.63 respectively).

Table 9: Correlation matrix of heavy metals in *Phalacrocorax africanus* (Longtail Cormorant), Densu Delta Ramsar Site, Ghana

	Cu	Zn	Cd	As	Hg
Cu	1.00				
Zn	0.31	1.00			
Cd	0.67	0.69	1.00		
As	0.17	0.30	0.72	1.00	
Hg	0.20	0.29	0.45	0.63	1.00

Table 9 shows the correlation matrix for heavy metals observed in *Egretta ardesiaca* (Black heron) during the study period. Zinc & mercury, cadmium & zinc, mercury & copper, and arsenic & copper exhibited negative correlation (-0.40, -0.60, -0.22 and -0.41 respectively). However, observed correlation between cadmium and mercury was positive (0.74).

Table 10: Correlation matrix of trace metals in *Egretta ardesiaca* (Black Heron), Densu Delta Ramsar Site, Ghana

	Cu	Zn	Cd	As	Hg
Cu	1.00				
Zn	0.19	1.00			
Cd	-0.01	-0.60	1.00		
As	-0.41	-0.02	0.02	1.00	
Hg	-0.22	-0.40	0.74	-0.11	1.00

4.5 Relationship between heavy metals in fish and shorebirds.

Figure 6 shows the association of trace metals between assessed fish samples and resident shorebirds. Zinc was relatively the highest trace metal in both fish and the investigated shorebirds, followed by copper. However, the remaining trace metals were minute in both fish and the resident shorebirds.

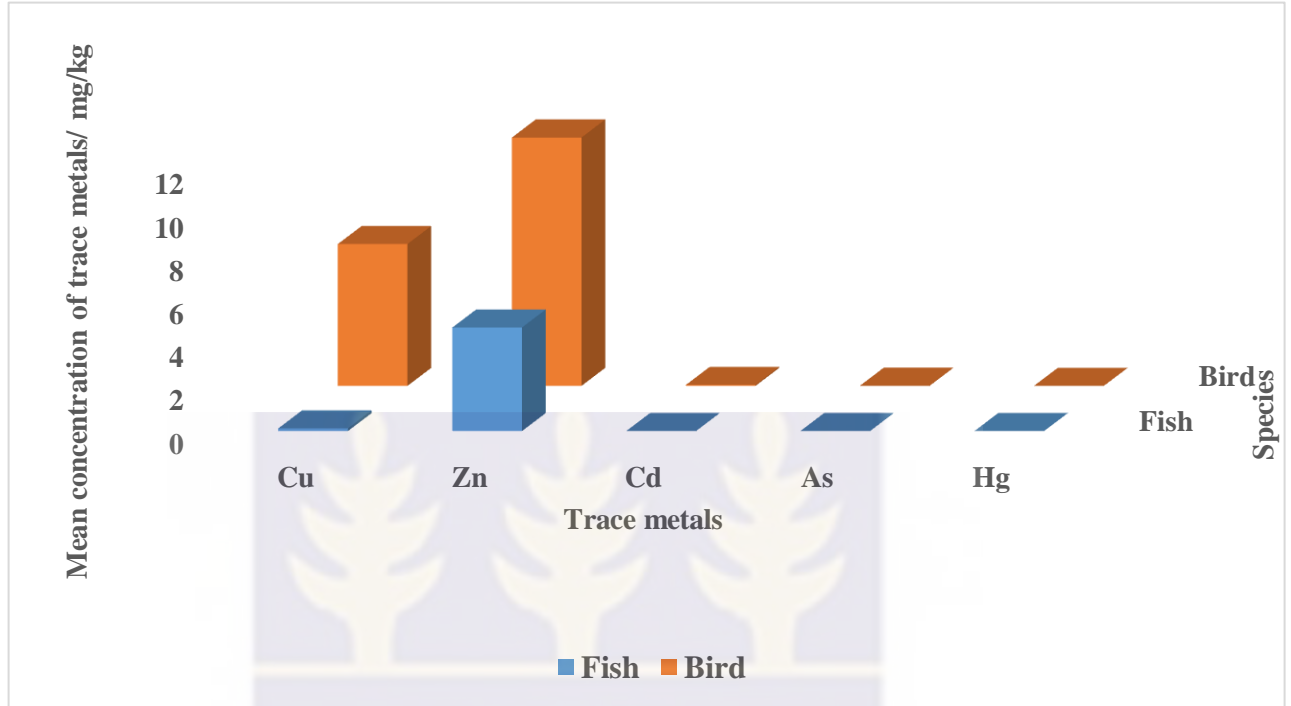


Figure 7: Heavy metals concentrations in fish and shorebirds from Densu Delta Ramsar Site, Ghana.

4.6 Length-frequency distribution of fish species

Figures 8 and 9 shows the length-frequency distribution of the fish species. From Figure 8, majority (48 %) of *Sarotherodon melanotheron* (Blackchin tilapia) were within the length range of 3 cm – 4 cm while 36 % and 16 % were within the 4.1 cm – 5.0 cm and 5.1 cm – 6 cm range respectively. In all, twenty-five (25) specimen of *Sarotherodon melanotheron* (Red belly tilapia) were assessed for length distribution and frequency.

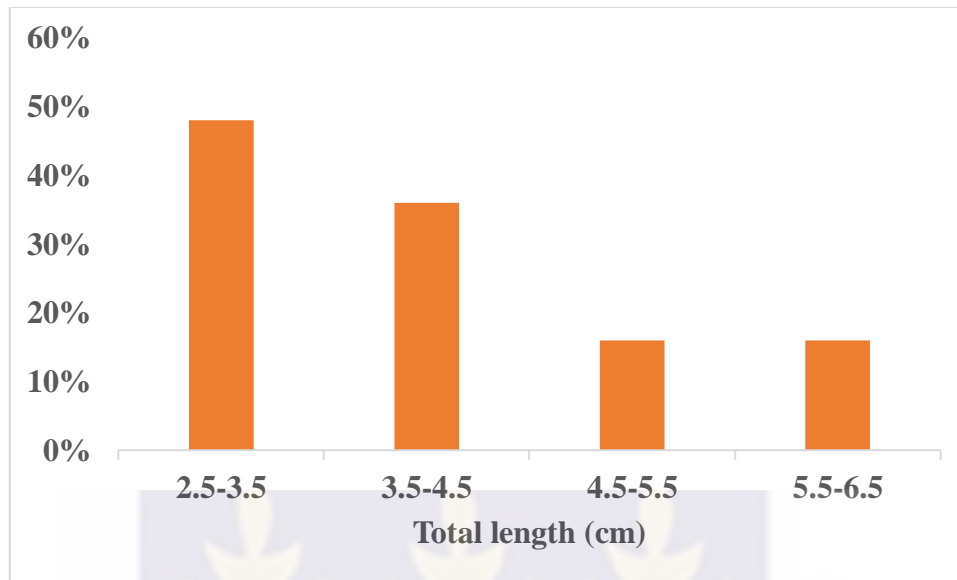


Figure 8: Total length frequency and distribution of *Sarotherodon melanotheron* (Blackchin tilapia)

Figure 9, majority (52 %) of the assessed fish of *Tilapia zilli* (Red belly tilapia) were within the length range of 3.1 cm – 4.0 cm while 8 % and 4 % were within the 7.1 cm – 8.0 cm and 5.1 cm – 6.0 cm range respectively. However, length ranges of 2.1 cm – 3.0 cm, 9.1 cm – 10.0 cm and 10.1 cm – 11.0 cm collectively accounted to 36 % of the assessed fish species (12 % by each length range) as shown in Figure 11. In all, twenty-five (25) specimen of *Tilapia zilli* (Red belly tilapia) were assessed for length distribution and frequency.

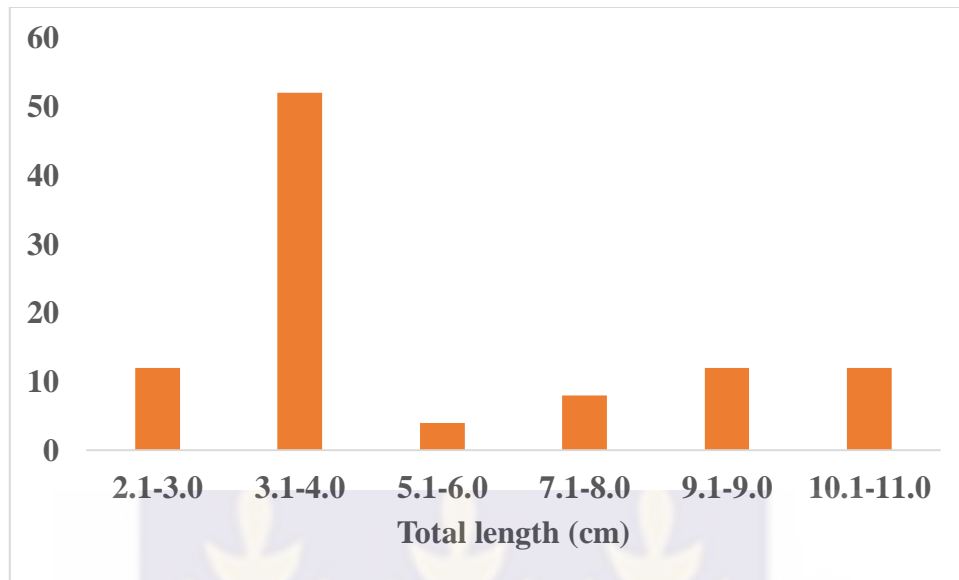
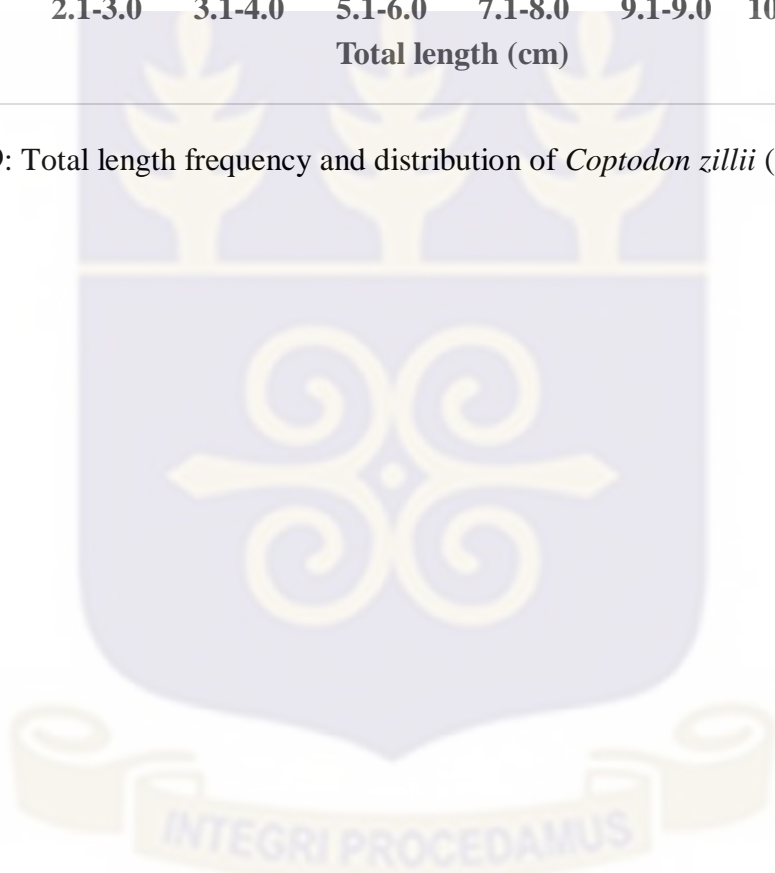


Figure 9: Total length frequency and distribution of *Coptodon zillii* (Red belly tilapia)



CHAPTER FIVE

DISCUSSION

5.1 Heavy metal in water samples

The high concentration of Copper and Zinc in water samples maybe due to lithological processes taking place at the study area which include weathering of rocks such as sandstone and shale, the presence of landfill and domestic sewage from the settlements around the delta. This may also affirms studies by Yoshihaya *et al.* (2010) and Kehrer, (2000) who documented that copper and zinc are transported together and their concentration in aquatic systems and organisms may be co-operative. Besides, there is a resort center in Bortianor which is frequented by many tourists especially on weekends, the activities such as cleaning of waste with various chemicals, application of fertilizer to the grasses and flowers in the resort center as well as the discharge of solid and liquid waste into the wetland as well as recreational boat hull (for copper) which could likely impact on the water quality.

In terms of seasons (dry and wet seasons), the insignificant values ($p > 0.05$) of heavy metals observed could be attributed to evenly distribution of heavy metals within the catchment area. Furthermore, the relatively high amount of heavy metals during wet season compared to dry season could be attributed to run-offs from cultivated lands and storm water from households, surrounding industries, and the influx of water into the Densu Delta Ramsar Site when the Weija Dam is opened. This disagreed with findings by many researchers. For instance, Yahaya *et al.*, (2009) in their study on seasonal variations of heavy metals concentration in Abattoir Dumping Site/wetland in Nigeria experienced

relatively high values of heavy metals during the dry season than in the wet season. Potential reasons for this observation could include geographical location, the climate pattern and sources of water existing within the catchment areas.

Comparatively, heavy metals in water samples were relatively lower than recorded in sediment. This observation could also be due to the fact that sediment serves as a sink for element load in water. This observation lends credence to the findings by Denutsui *et al.* (2011) who recorded higher trace metal values in sediment than in water samples at Densu delta, Ghana. Similarly, Garbarino *et al.* (1995) wrote that heavy metals in water mostly get removed from the water column and subsequently adsorbed to sediment particles. Besides, Zaranyika *et al.* (1994) documented that, heavy metals concentration in water is smaller than the concentration in sediments indicating that sediments are very effective in binding heavy metals and uptake by organisms decreases with increasing input concentrations.

It has also been observed that the concentrations of mercury recorded in this study in both seasons were higher compared to similar studies by Armah *et al.* (1998) in the same catchment area who recorded mercury concentration as 0.005mg/l. This is an indication that though these concentrations are within permissible limits, there is a gradual buildup of mercury in the Densu Delta ecosystem.

5.2 Heavy metal in sediment samples

Heavy metals levels accumulated in sediments were relatively more than observed in water which confirms findings by researchers such as Chindah and Braide (2003), DeGregor *et al.*

(1996) and Eja *et al.* (2003). Generally, the potential reasons for higher concentration of trace metals (particularly zinc and copper) in sediment maybe as a result of leaching of metals from the watershed into water unto the underlying sediments (Ahmed *et al.*, 2013). Regarding the concentrations of dominant heavy metals including zinc and copper, their relatively high concentration in the sediments has been subscribed to by other researchers.

For example, studies undertaken by Ahmed *et al.*, (2013) on seasonal variation of heavy metals accumulation in muscles of the African catfish (*Clarias gariepinus*; ICUN) and in River Nile water and sediments at Assiut Governorate, Egypt reported relatively high amount of copper and zinc in sediments than other assessed heavy metals. The concentration of heavy metals recorded varied between seasons (dry and wet) with wet season accounting for relatively higher levels. The high amount of heavy metals in sediments during the wet season could be attributed to storm run offs coming from land drainages from different sources such as mining sites, industries and farmlands.

Furthermore, this observation was in contrast to findings by other researchers like Nwabueze and Oghenevwairhe (2012) and Bahnsawy *et al.* (2011) who observed higher levels of heavy metals during the summer (dry season). These researchers attributed the high level of heavy metals during the dry season to the release of heavy metals from the water to the overlying sediments under the effect of both high temperature and a fermentation process resulting from the decomposition of organic matter (Ali and Abdel-Satar, 2005).

Osei (2008), recorded the concentration of copper in the study area in the range of 0.43 mg/kg to 7.98 mg/kg which is lower to the levels recorded in this study indicating that, there is gradual appreciation of copper concentration in the delta which need to be monitored before threshold levels.

5.3 Heavy metals in fish species

Levels of zinc in *Coptodon zillii* (Red belly tilapia) was lower than observed in other researches done elsewhere. For instance, Eneji *et al.* (2011) in their study on bioaccumulation of heavy metals in fish (*Coptodon zillii* and *Clarias gariepinus*) organs from River Benue, North Central Nigeria recorded zinc concentration of 7.15 mg/kg and 5.66 mg/kg respectively. In addition, Anim *et al.* (2010) in their study on accumulation profile of heavy metals in fish samples from Nsawam, along the Densu River Ghana, also reported concentration of zinc in *Coptodon zillii* (Red belly tilapia) as 28.24 ± 0.84 mg/kg. Considering the concentration of copper in fish samples, Eneji *et al.* (2011) in their study on bioaccumulation of heavy metals in fish (*Coptodon Zillii*) organs from River Benue, North Central Nigeria recorded copper concentration to be 2.98 mg/kg and 5.36 mg/kg while Anim *et al.* (2010) from their study on accumulation profile of heavy metals in fish samples from Nsawam, along the Densu River Ghana, also reported copper concentration as 91.08 ± 0.84 mg/kg.

For *Sarotherodon melanotheron* (Blackchin tilapia) concentration of zinc from the study was lower than reported by other researchers elsewhere. For instance, Studies by Arthur *et al.* (2015) on contamination of *Sarotherodon melanotheron* (Blackchin tilapia) by Lead,

Zinc and Copper: Case of Porto-Novo lagoon, south of the Republic of Benin indicated concentration of zinc to be 35.82 mg/kg – 247.19 mg/kg. Studies undertaken by Essumang *et al.*, (2007) on comparative studies of heavy metals in lagoon snail, black chin tilapia and water in Brenu lagoon of Ghana recorded lower zinc concentration (0.96 mg/kg) in *Sarotherodon melanotheron*. Similarly, concentrations of copper in *Sarotherodon melanotheron* from other study locations were higher than observed from the present study. For example, concentration of copper recorded by Laar *et al.* (2011) whose studies focused on determination of heavy metals in the *Sarotherodon melanotheron* from the Sakumo Lagoon, Ghana, fell within the range (0.000 mg/kg – 73.47 mg/kg). Besides, studies carried out by Essumang *et al.* (2007) on comparative studies of heavy metals in lagoon snail, blackchin tilapia and water in Brenu lagoon of Ghana recorded higher copper concentration (1.50 mg/kg) in *Sarotherodon melanotheron* (Black chin tilapia). Arthur *et al.* (2015) on contamination of *Sarotherodon Melanotheron* by lead, zinc and copper: Case of Porto-Novo lagoon, south of the Republic of Benin indicated concentration of copper to be 0.79 mg/kg – 1.76 mg/kg. Again, values of copper concentration obtained from the study was lower than values (4.24 mg/kg to 77.79 mg/kg) reported by Tyokumbur and Okorie (2014) who studied heavy metals concentration (Copper, Manganese and Nickel) in the *Sarotherodon melanotheron* from Alaro wetland in Ibadan, Nigeria.

The observed variation in concentration of the dominant heavy metals (zinc and copper) in the tissues of both species could be attributed to a string of factors such as use of chemical fertilizers, sewage sludge, wastes from the catchment, the portion of the organism sampled as well as the size of the organism. In support of this assertion, Nzeve *et al.* (2014) wrote

that heavy metal concentrations in the tissue of fresh water fish varies due to differences in metal concentrations and chemical characteristics of water from which fish are sampled, their ecological needs; metabolism and feeding habits. Nageeb (2001) supported this claim by indicating that increase in the concentration of studied elements in fish can be the result of high levels of pollutants in the lake originating largely from agricultural sewage discharges containing fertilizers.

Similarly, Ahmed *et al.* (2013) in their study on seasonal variation of heavy metals accumulation in muscles of the *Clarias gariepinus* (African Catfish) and in River Nile water and sediments at Assiut Governorate, Egypt attributed the elevation of zinc accumulation in the assessed fish samples to industrial and sewage wastes and elevated metal-binding protein synthesis. Again, WHO (1989) reported that copper toxicity in fish is taken up directly from the water via gills and stored in the liver. The copper concentration recorded from the two selected fish species were below the WHO recommended limit of 30 mg/kg in fish and fish products (WHO 2004, FAO 1983). Zinc levels recorded during this study in the two food fish species were below the 75 mg/kg recommended limit for Zinc in fish and fish products (FAO, 2003). The concentrations recorded for cadmium (Cd) were below the WHO's recommended limit of 1.0 mg/kg for fish and fish products (FAO/WHO, 1983). This observation indicates the quality and safety of fish species to consumers including shorebirds. However, the consumption of fish should be cautious as cumulative effects might constitute health hazards to aquatic life and man who feeds on fish (Oronsaye *et al.*, 2010).

The remaining heavy metals namely arsenic, mercury and cadmium were relatively absent possibly due to the fact that rocks within the assessed Densu Delta do not deposit such minerals. Furthermore, allochthonous materials within the delta mostly do not contain these heavy metals in substantial quantities hence their minute amount within the tissue of the assessed species. Specifically, the presence of cadmium in the assessed fish from all sampling stations could be attributed to discharge of industrial effluents and municipal wastes, geology of river bed and catchment area (Obasohan, 2008; Kar *et al.*, 2008). Again, the low concentration of cadmium, mercury and arsenic in muscles of assessed fish species may be associated with the life style of the species spending more time at the bottom and or muds (Nziku, 2013). Following the toxicity of these heavy metals, their relatively absence in the tissue of the assessed fish species indicates that the Densu Delta Ramsar Site is far from toxicological threat and subsequent consequences to fish, fish products and consumers (Mahu, 2014).

5.4 Shorebirds

5.4.1 Variation in heavy metals among shorebird species

The assessed shorebirds exhibited significant variation in the level of heavy metals during the study period. The significant difference in heavy metal levels among the assessed shorebirds could be due to differences in foraging locations and the nature of the shorebirds (resident or migratory). In furtherance to this assertion, Burger *et al.*, (2015) wrote that shorebirds feed on different prey and in different locations some of the time. For instance, sanderlings spend time foraging on the ocean beaches, semi-palmated sandpipers (*Calidris*

pusilla) sometimes forage on the salt marshes, and red knots (*Calidris canutus*) mainly forage on mudflats and beaches.

Kober (2004) in his studies on foraging ecology and habitat use of wading birds and shorebirds in the mangrove ecosystem of the Caete Bay, Northeast Para in Brazil also submitted that some locations contain more prey items (fish) or prey items are better available or detectable. The varied amount of heavy metals observed from the assessed shorebirds could be assigned to the size of these shorebirds. Zwarts *et al.*, (1990) wrote that large sized shorebirds increase their feeding time day and night while small size shorebirds increase feeding rates mostly during the day. Though size related heavy metals content in shorebirds was not covered in this study, it is recommended for further studies.

Furthermore, sex of shorebirds could play significant role in the amount of heavy metals within their body systems. For instance, (Burger, 1993; Furness, 1996; Lacoue-Labarthe *et al.*, 2008; Bond and Diamond, 2009; Burger, and Gochfeld, 2009), indicated that female shorebirds can eliminate heavy metals by sequestering them in the eggshell or transferred via vitellus or the albumen, thus leading to relatively lower amount of heavy metals. In view of this, additional research is needed to address the relative contribution of sex to heavy metals in shorebirds. Again, the significant differences in heavy metal levels among species may indicate slightly different trophic levels and trophic plasticity. For instance, Lucia *et al.* (2014; 2012) attributed differences in heavy metals among shorebirds found using mudflats along coastal France to trophic levels and plasticity. Thus, the variation in heavy metals

among different shorebird species on the same trophic level can accumulate different heavy metal levels by consuming different prey items (Shin 2009).

On the other hand, the relatively low amount of copper within the assessed species of shorebirds could be due to the fact that shorebirds mostly retain a small portion of copper and other metals ingested (Norouzi *et al.*, 2012). Furthermore, the rationale behind birds retaining a small portion of copper after ingestion could be due to the impacts of its toxicity to bird growth, egg production and behavioral changes (Schmitt-Jansen *et al.*, 2008).

5.4.2 Heavy metals in fish and shorebirds

It is assumed by many studies that heavy metal levels in shorebirds reflect local food levels (Monteiro and Furness, 1995). This may have led to higher accumulation of heavy metals, particularly Zinc and Copper in the assessed shorebirds. Burger *et al.* (2017) whose studies on heavy metal levels in three species of shorebirds during stopover on Delaware Bay reflects levels in their food, he observed higher level of heavy metals in both shorebirds and their prey (horseshoe crab). In furtherance, findings from studies by Kim and Ko (2013) on Lead and cadmium contaminations in feathers of Heron and Egret chicks reported that, variation of heavy metals in shorebirds may reflect diet as well as habitat contamination. Overall, Hoshyari *et al* (2012) wrote that heavy metals in predators (shorebirds) are examined because it concentrates in the prey consumed.

Levels of heavy metals in the assessed shorebirds in this study exhibited the above assertion whereby metals concentrations in individual shorebirds were higher than their prey items

(fish). This may also be attributed to the fact that, the shorebirds pick the metal contaminants from other sources other than their prey items such as directly from the water, sediments, plants or prey items other than fish.

5.4.3 Effects of heavy metals on shorebirds

Cadmium can cause adverse behavioural effects at lower concentrations (Eisler, 1985; 1987) including slow growth rates (Spahn and Sherry, 1999). Feather levels known to cause adverse effects in the shorebirds range from 0.1 mg/kg to 2 mg/kg (Burger *et al.*, 2015). In this study, the mean cadmium levels in feathers of shorebirds averaged 0.01- 0.05 mg/kg, well below any effects levels. Thus, shorebirds found at the Densu Delta are not vulnerable to adverse impacts from cadmium contamination. Mercury levels in feathers of shorebirds are linked to adverse reproductive effects, particularly at levels greater than 5 mg/kg (Burger and Gochfeld, 2000; Eisler, 1987), although Jackson *et al.* (2000) demonstrated effects at feather levels below 5 mg/kg (2.4 mg/kg) in *Thryothorus ludovicianus* (Wrens)

The mean levels of mercury in the feathers of shorebirds in this study were 0.001 mg/kg to 0.002 mg/kg, which submits that mercury is not posing a problem for these shorebird species. The low cadmium concentrations in the assessed samples including shorebirds could be due to the absence of cadmium in batteries seeping into the delta (Agency for Toxic Substances and Disease Registry, 1997). Supporting the above-mentioned claim, Burger (1993) in his studies on heavy metals in avian feathers: Bioindicators of environmental pollution wrote that, cadmium from batteries and gasoline exit into aquatic

environments, where they get accumulated by invertebrates and fish, which were then consumed by shorebirds.



CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusion

In conclusion, the research reveals that the distribution of heavy metals in the waters of Densu Delta was significantly higher during the wet season than in dry season which is an indication that the wetland receives lots of detritus through run-offs, from domestic sewage, agricultural activities, industries and recreational activities in the wetland coupled with the opening of the Weija Dam in the wet season. Seasonal distribution of the heavy metals in sediment of Densu Delta Ramsar Site were not significantly different from the concentrations in water apart from copper. Zinc and copper concentrations were the dominant heavy metals found in both shorebirds and fish species assessed from the study which primarily may be due to industrial sewage, agricultural erosion, weathering of parent rocks material and drainage from mining activities upstream into the Densu Delta.

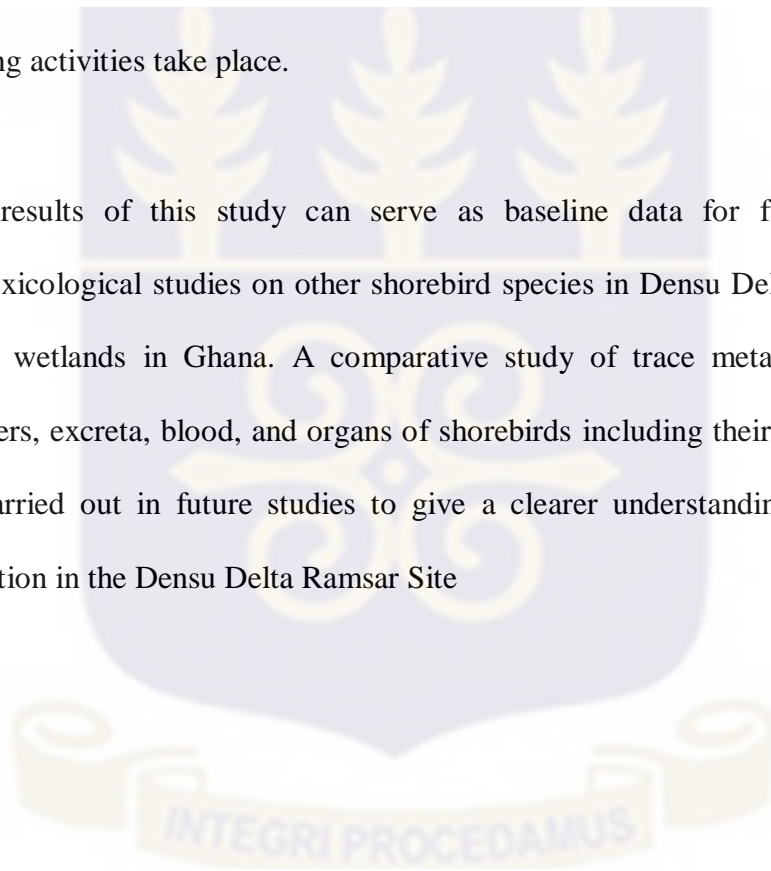
Similarly, the concentration of heavy metals in the assessed fish and shorebirds were consistently below threshold by FAO (2011). This is an indication that the assessed shorebirds and their prey (fish) are far from toxicological threats.

Overall, resident shorebirds assessed within the Densu Delta Ramsar Site are not polluted to level that can affect their physiological behaviour. Nonetheless, there is therefore the need for preventive measures to sustain the Densu Delta Ramsar Site since many heavy metals reach toxic levels as their concentrations become magnified along the food chain.

6.2 Recommendations

Based on the findings of this research the following are recommended;

- Consumption of fish from the Densu Delta Ramsar Site should be monitored due to presence of small concentrations of toxic heavy metals like mercury and cadmium levels in the tissues of the two fish species. This is because the Densu Delta Ramsar Site continuous to receive water from the city of Accra, agricultural fields and from the Densu River which has its source from the Atiwa Mountains where illegal mining activities take place.
- The results of this study can serve as baseline data for further research on ecotoxicological studies on other shorebird species in Densu Delta Ramsar Site and other wetlands in Ghana. A comparative study of trace metals concentration in feathers, excreta, blood, and organs of shorebirds including their morphometric data be carried out in future studies to give a clearer understanding of heavy metals pollution in the Densu Delta Ramsar Site



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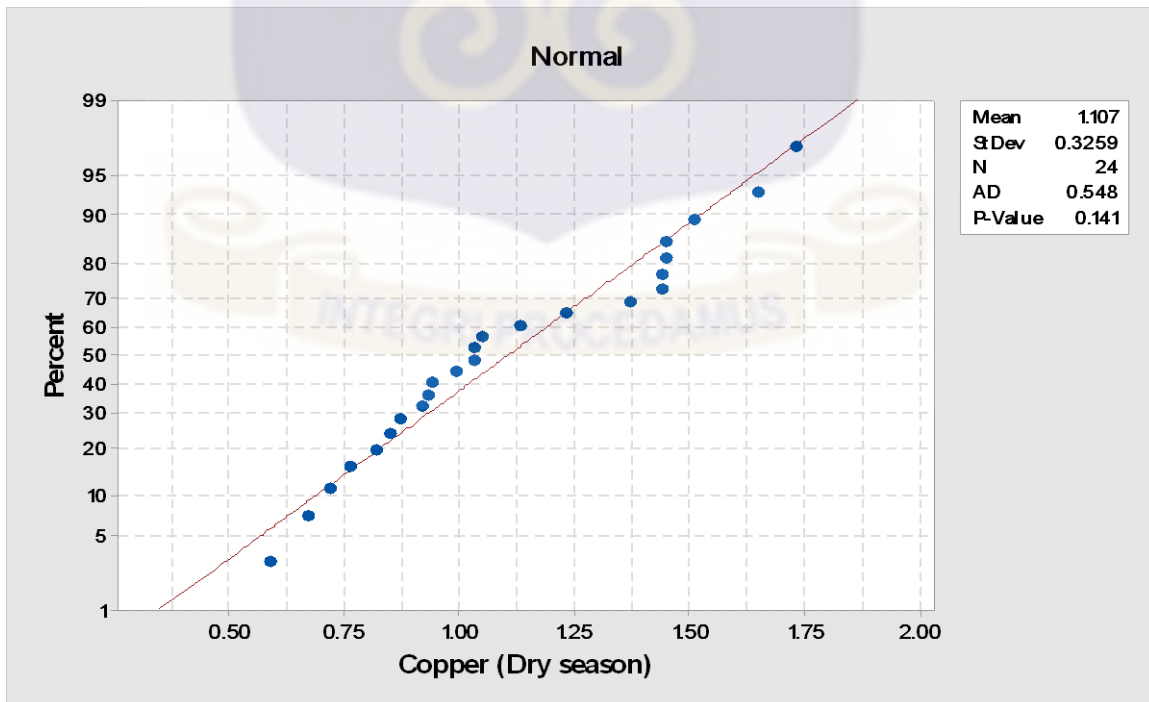
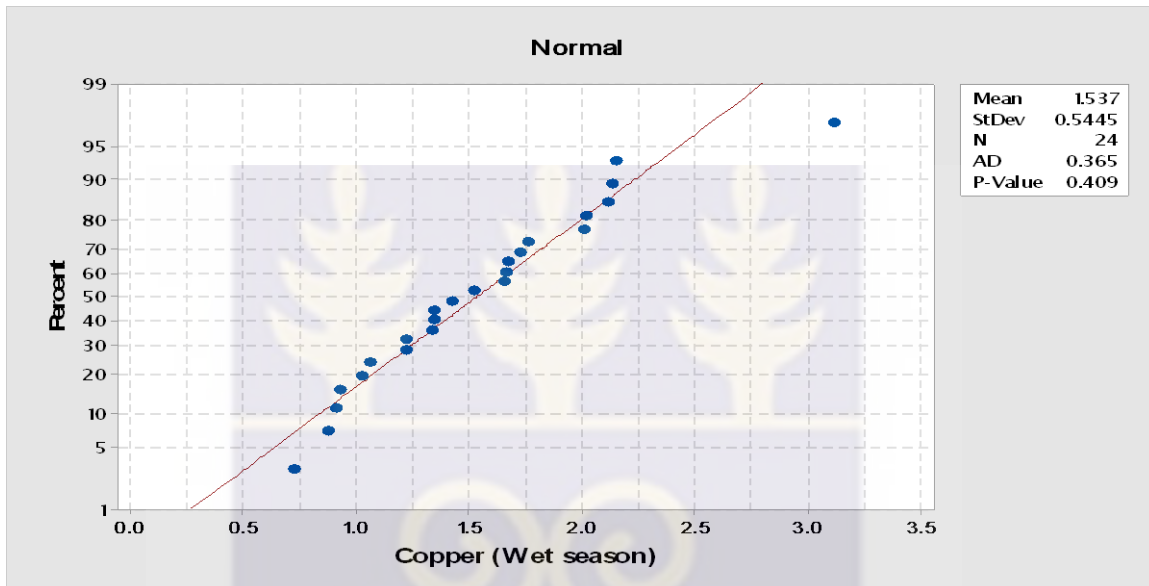
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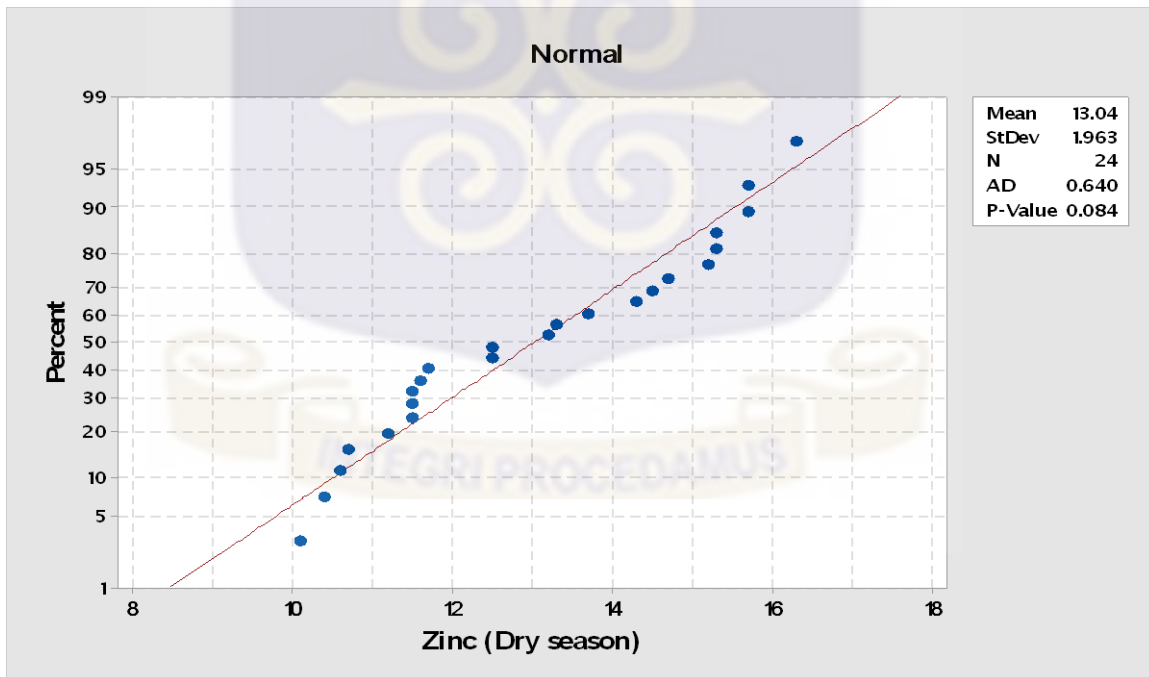
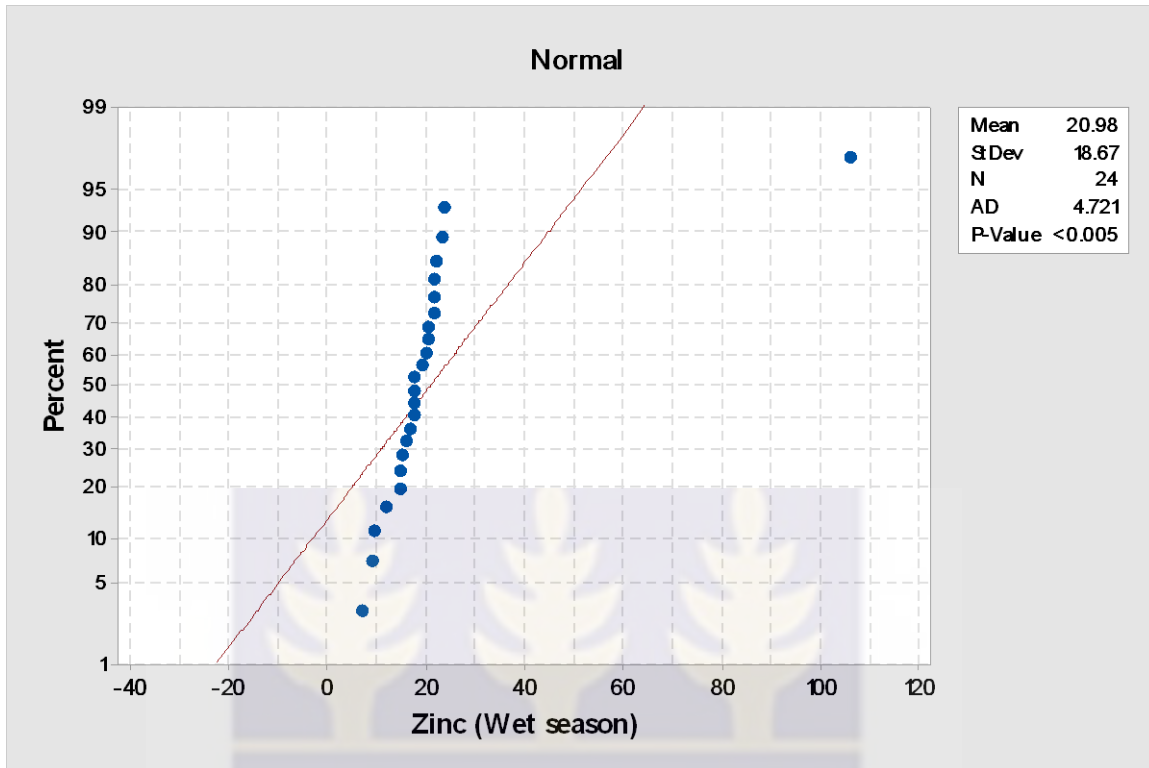
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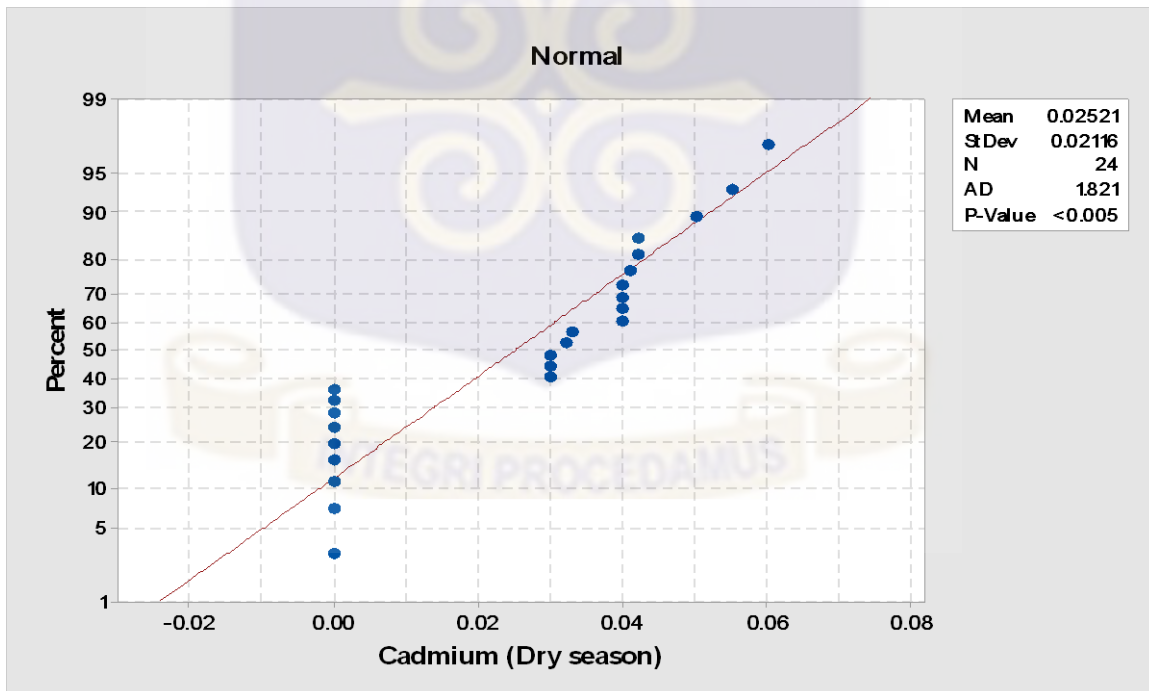
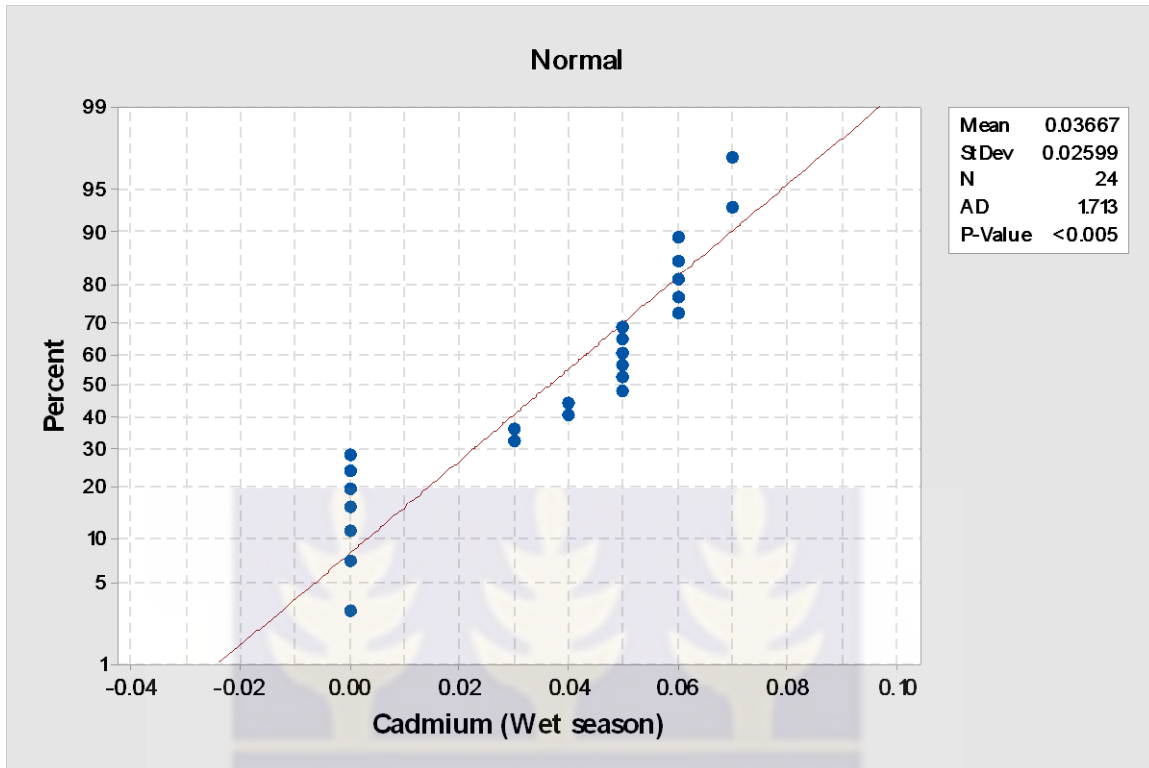


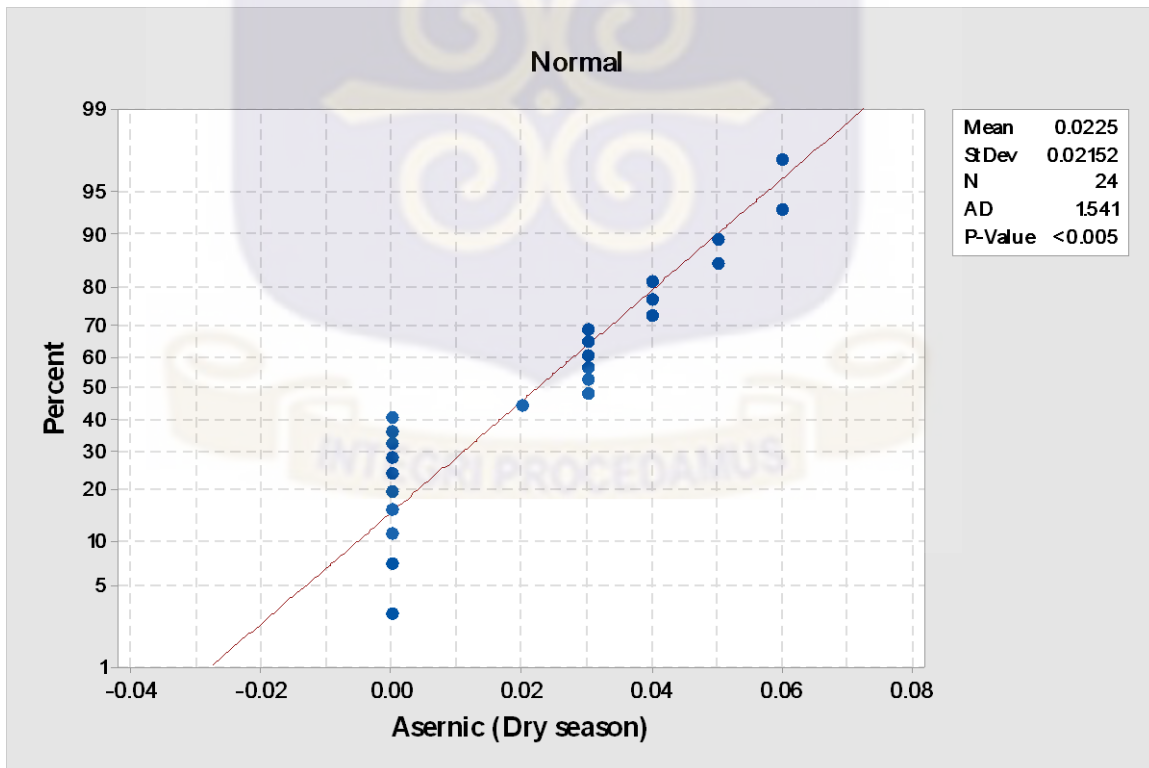
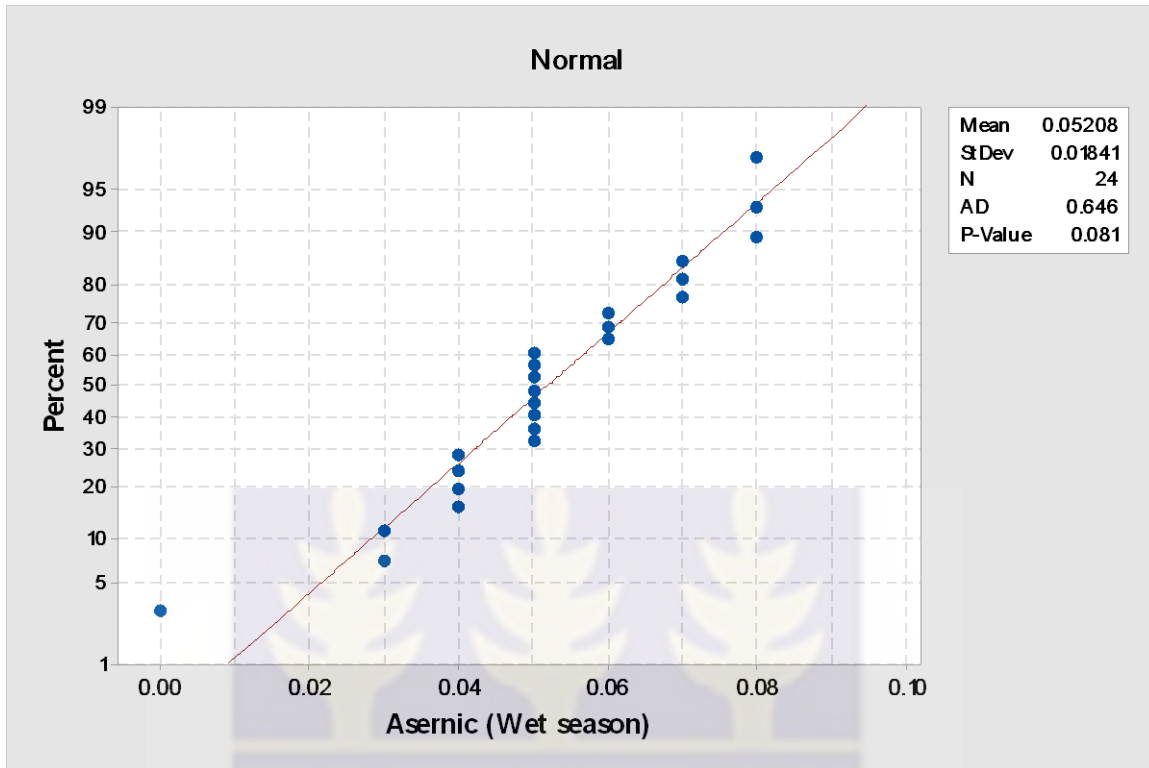
APPENDICES

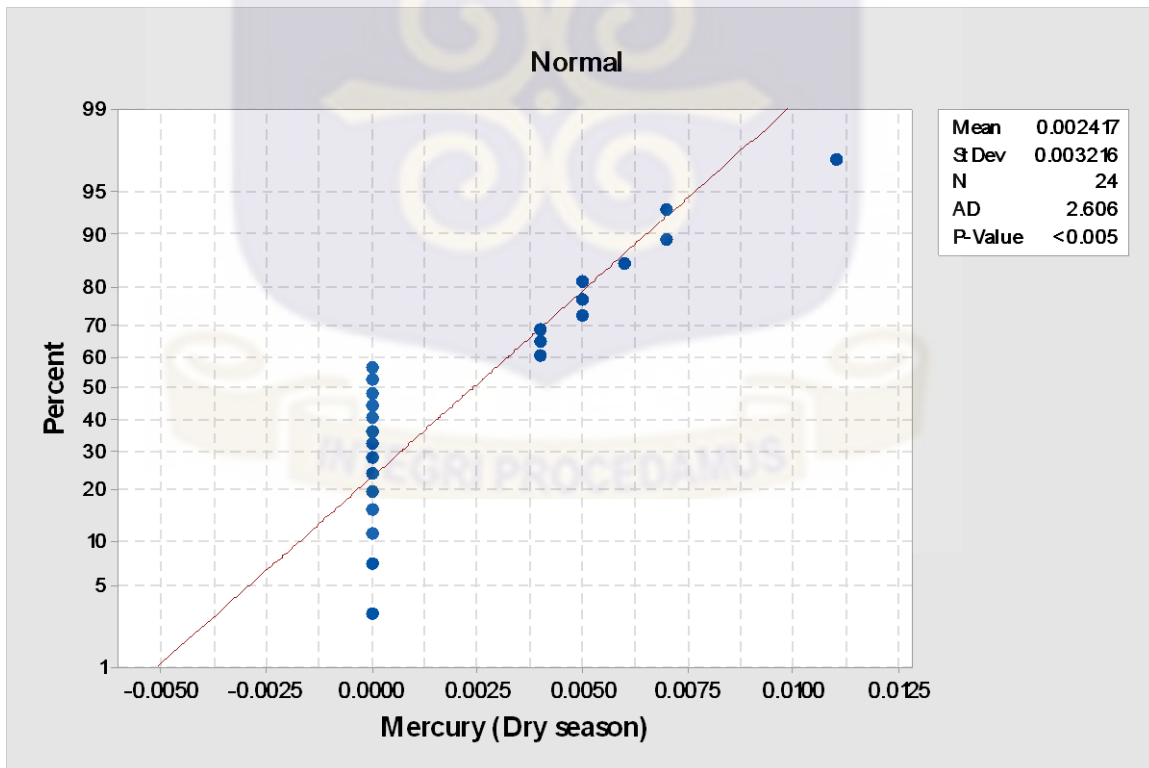
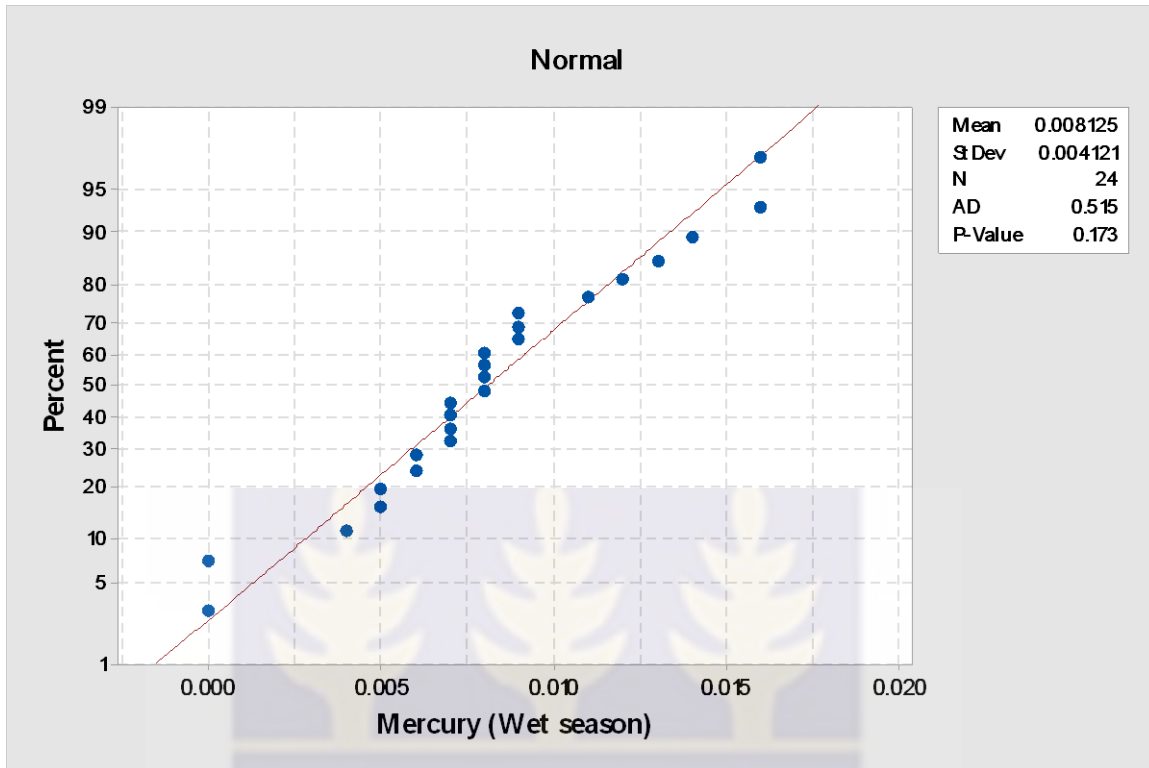
Appendix 1: Normality test for heavy metal concentrations in water samples according to seasons (wet and dry seasons)



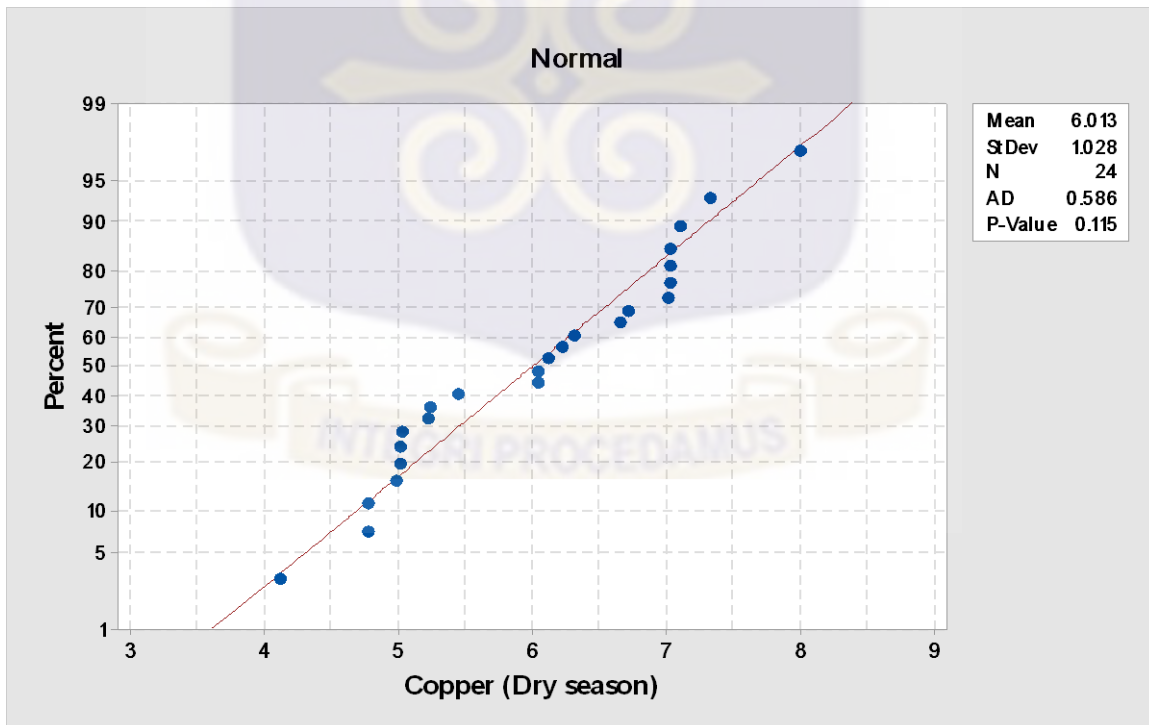
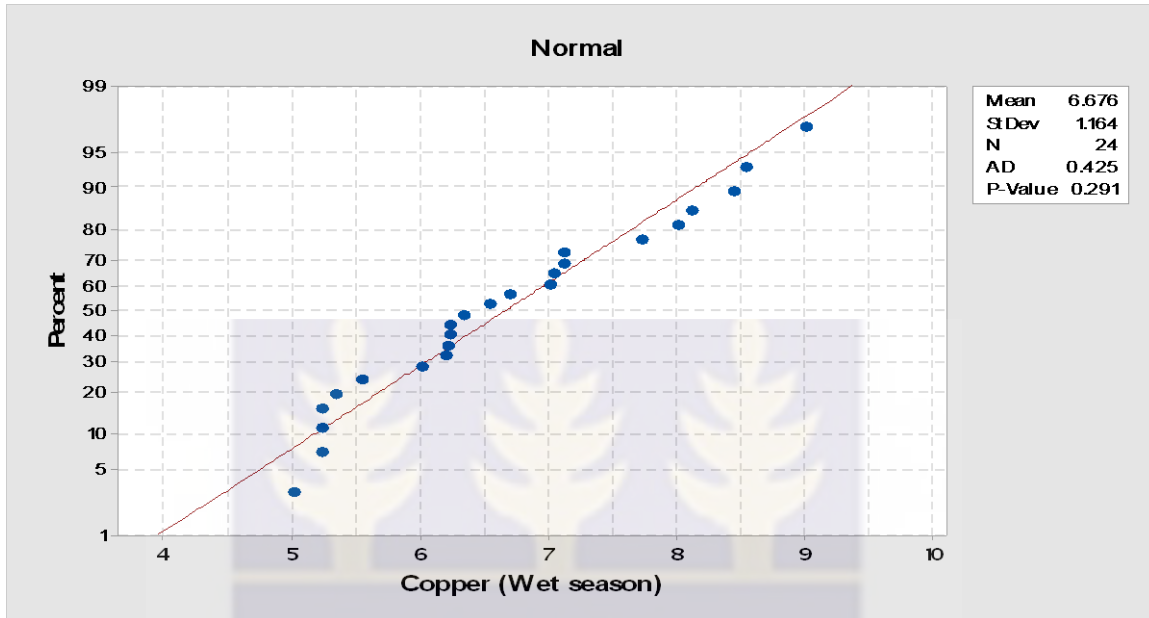


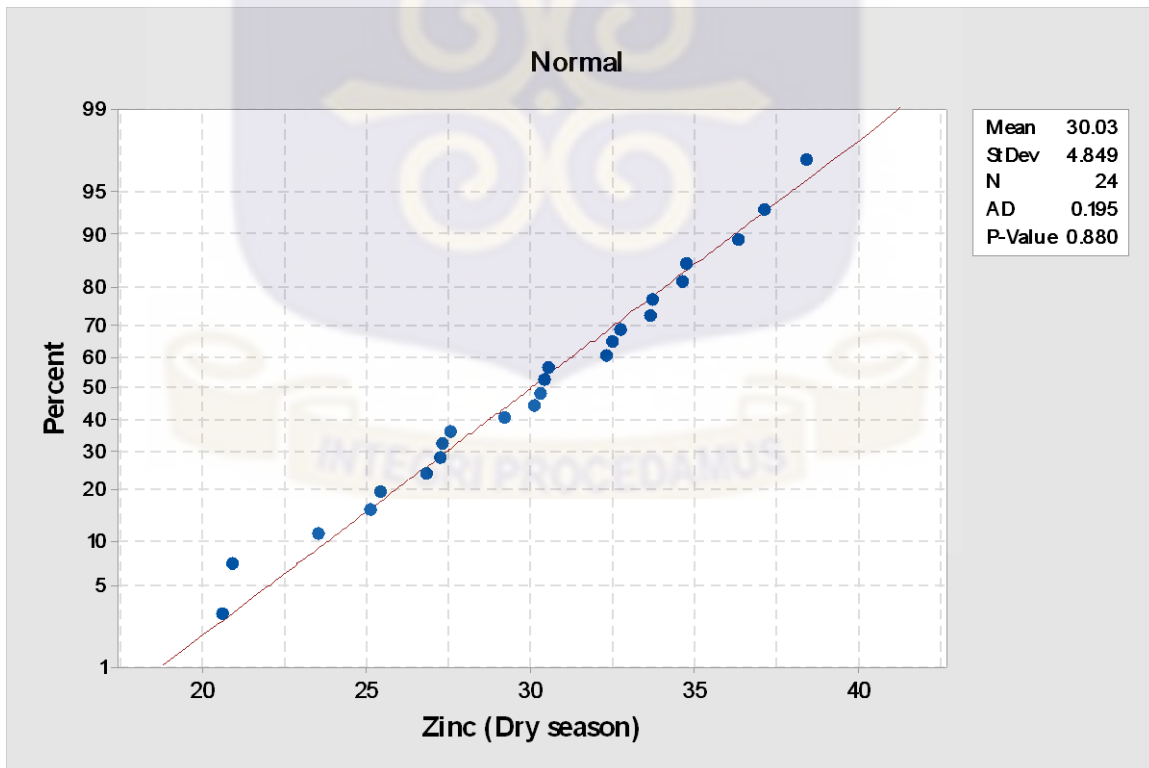
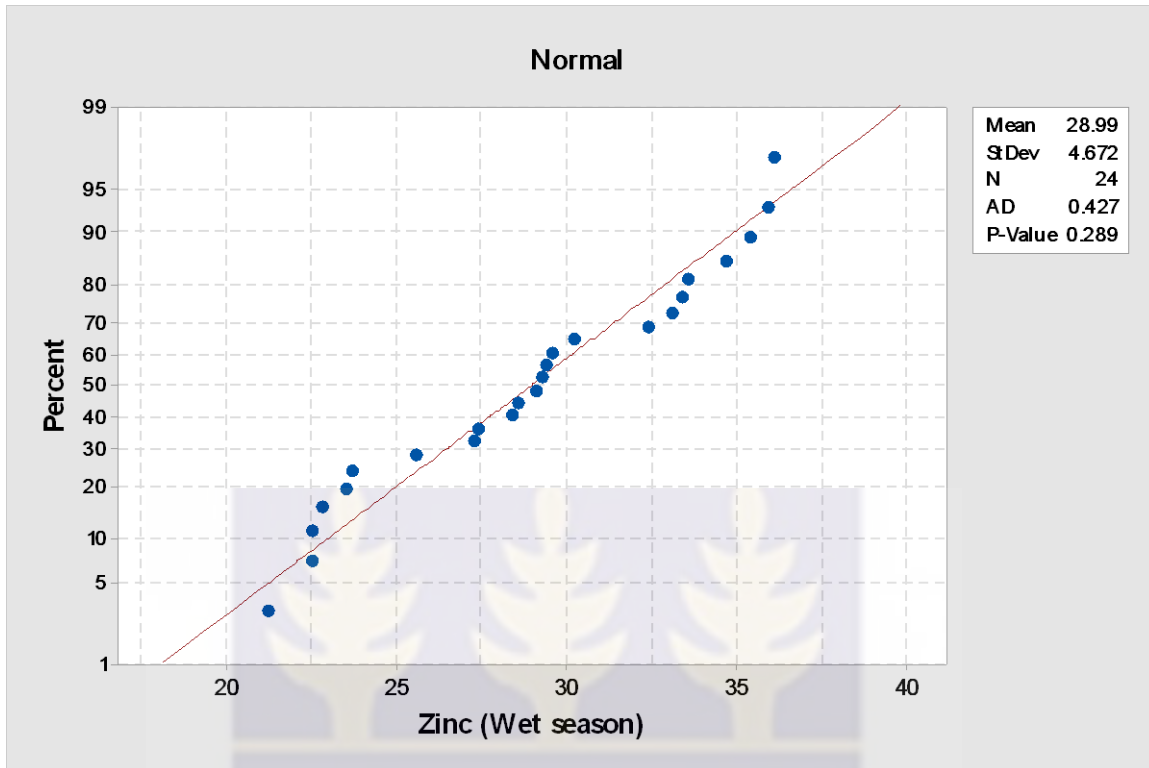


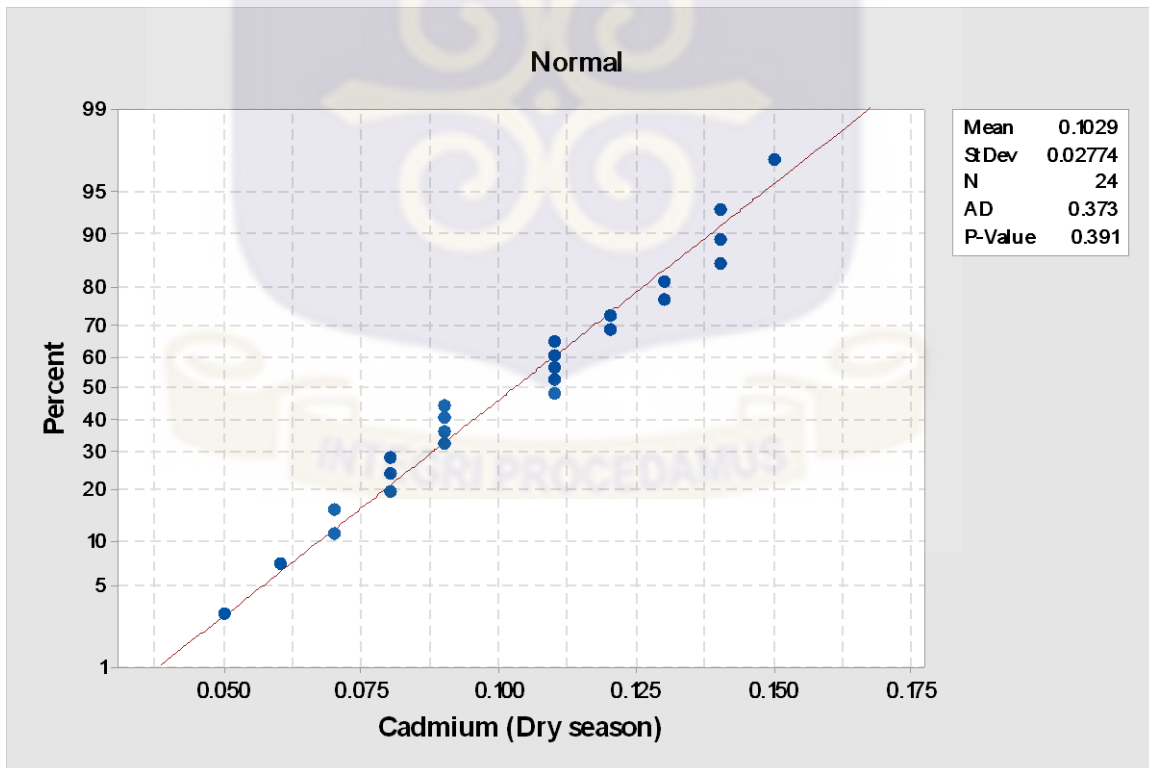
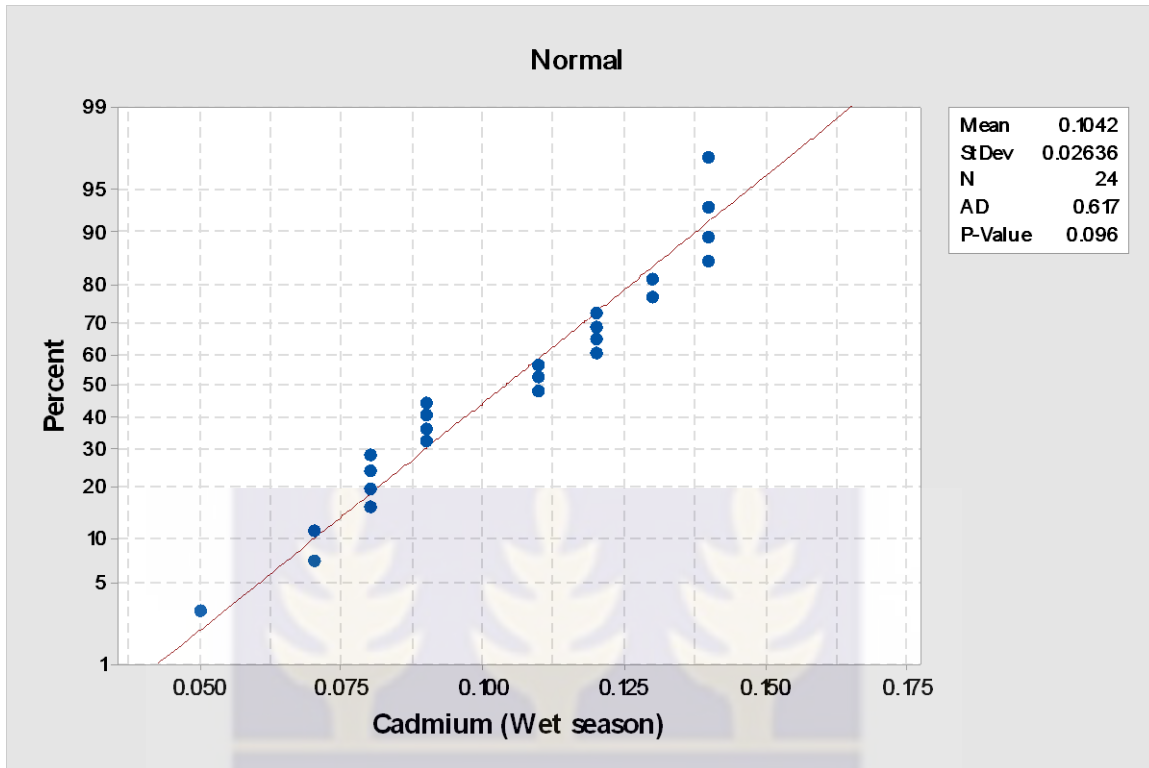


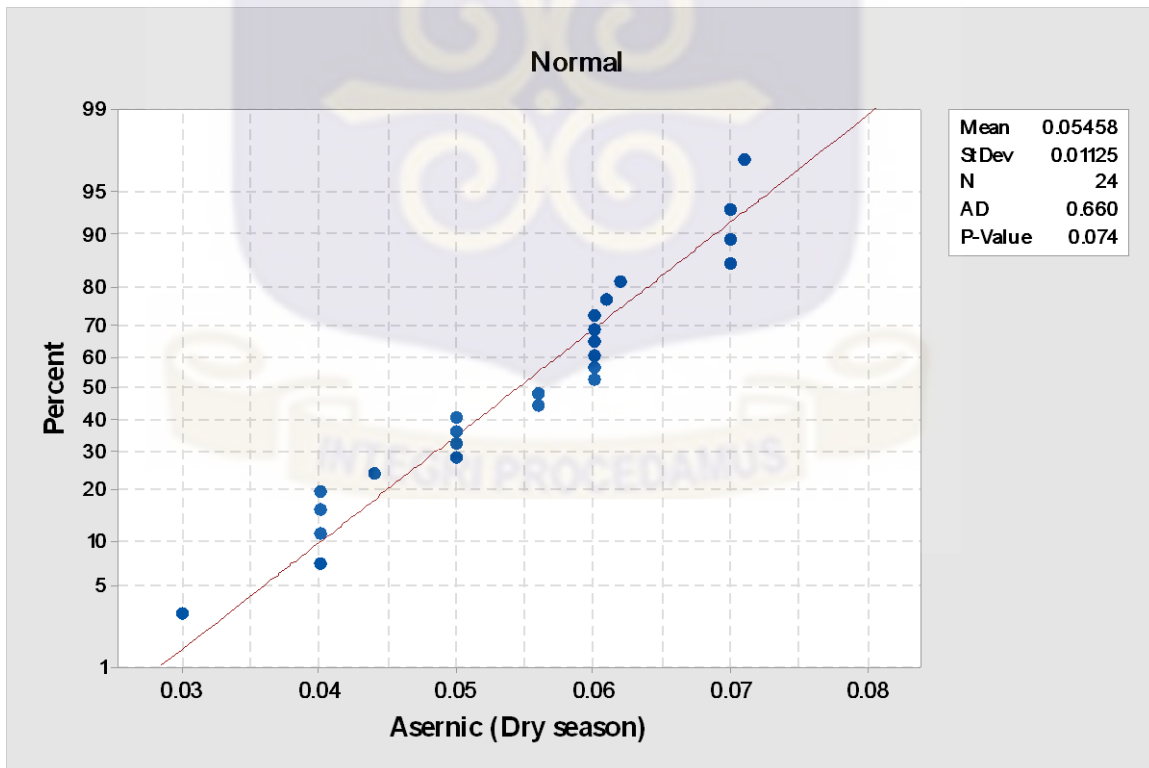
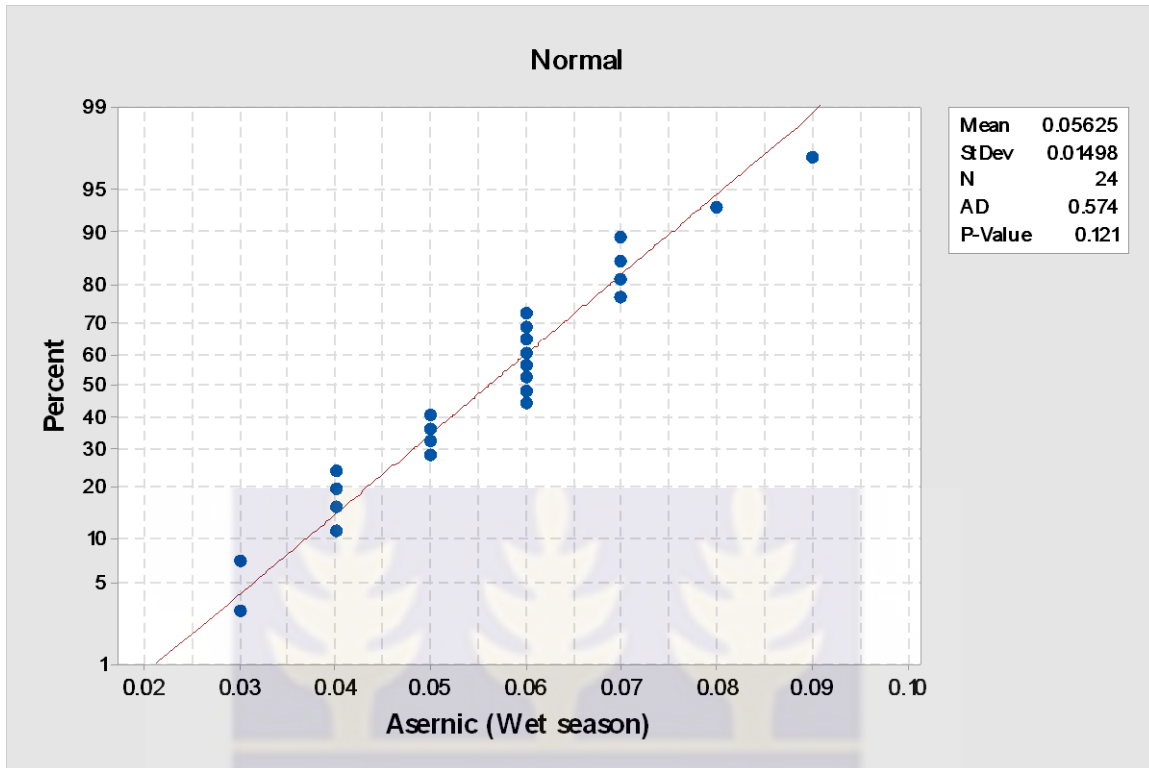


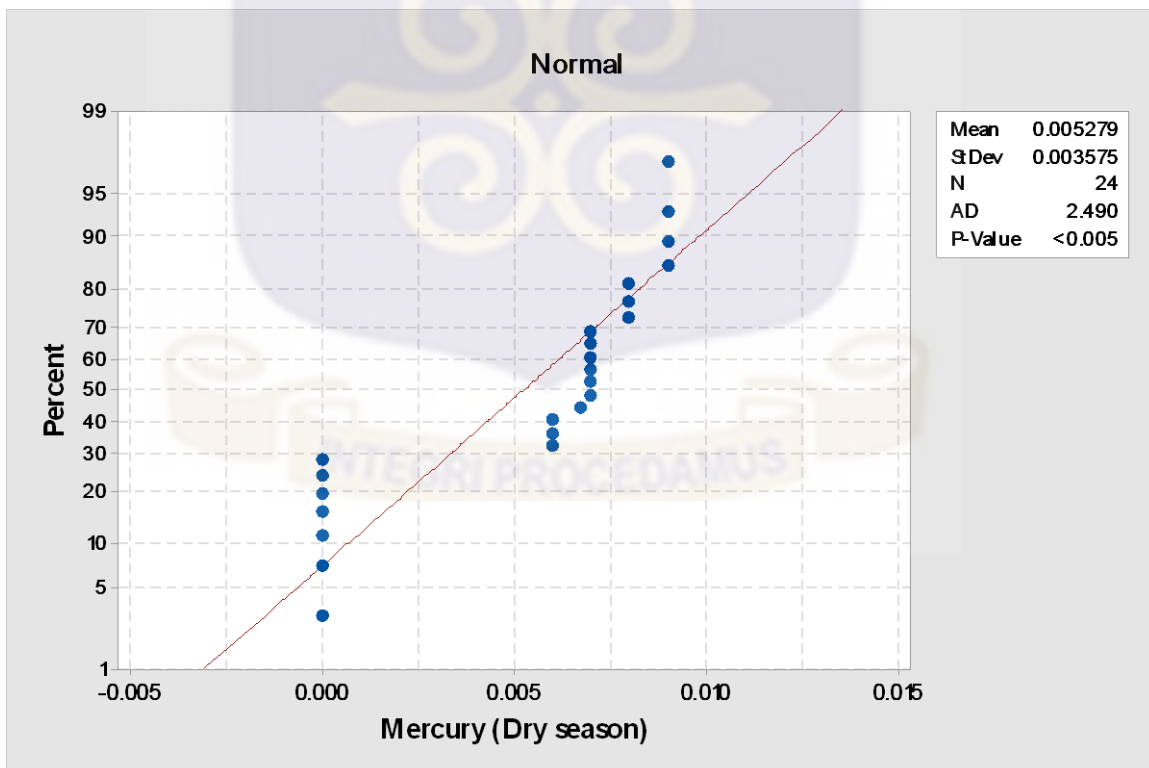
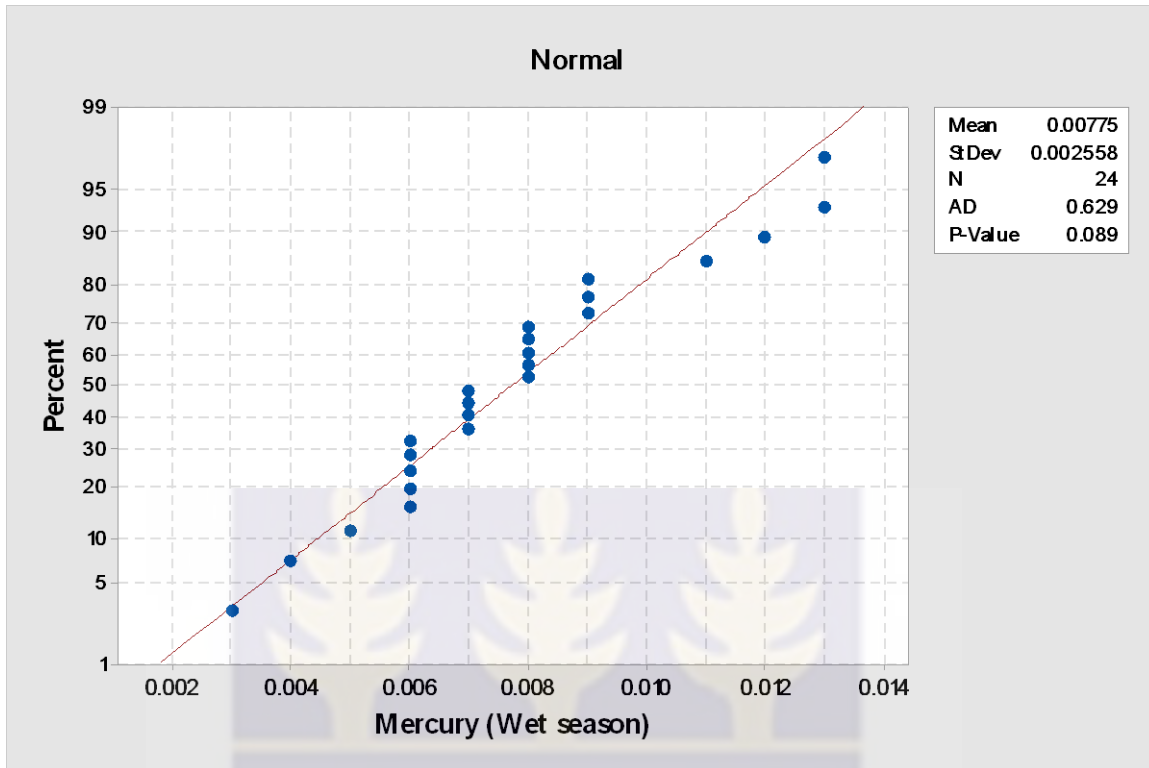
Appendix 2: Normality test for heavy metal concentrations in sediment samples according to seasons (wet and dry seasons).



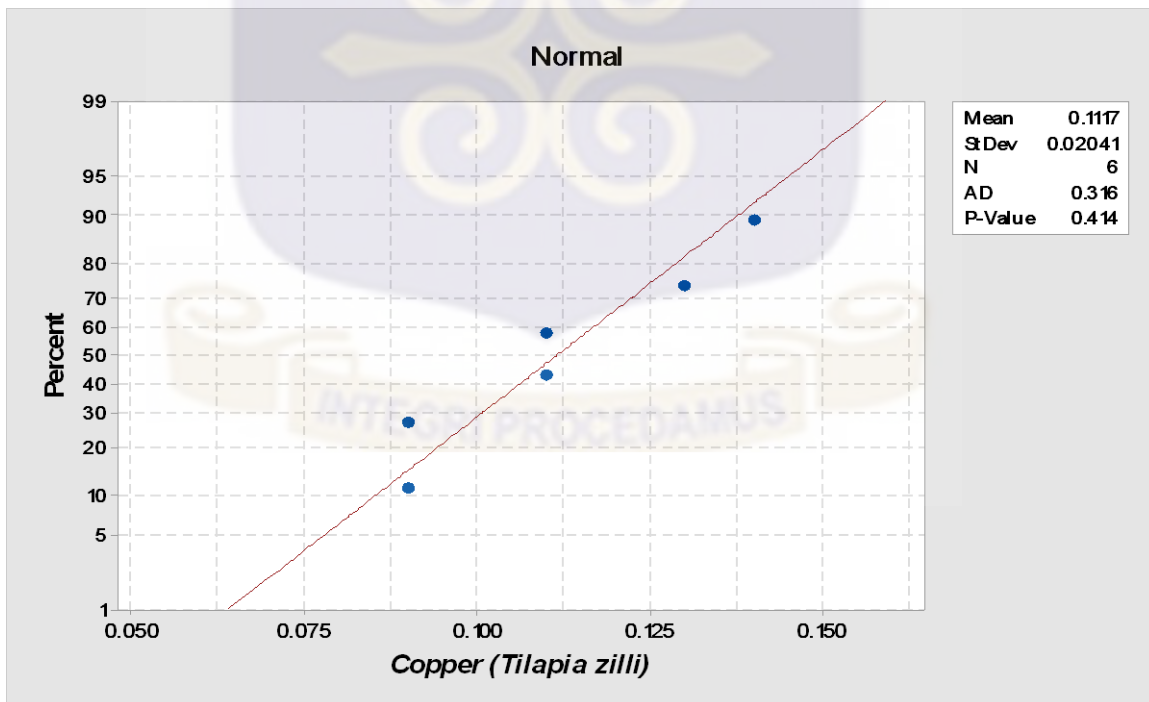
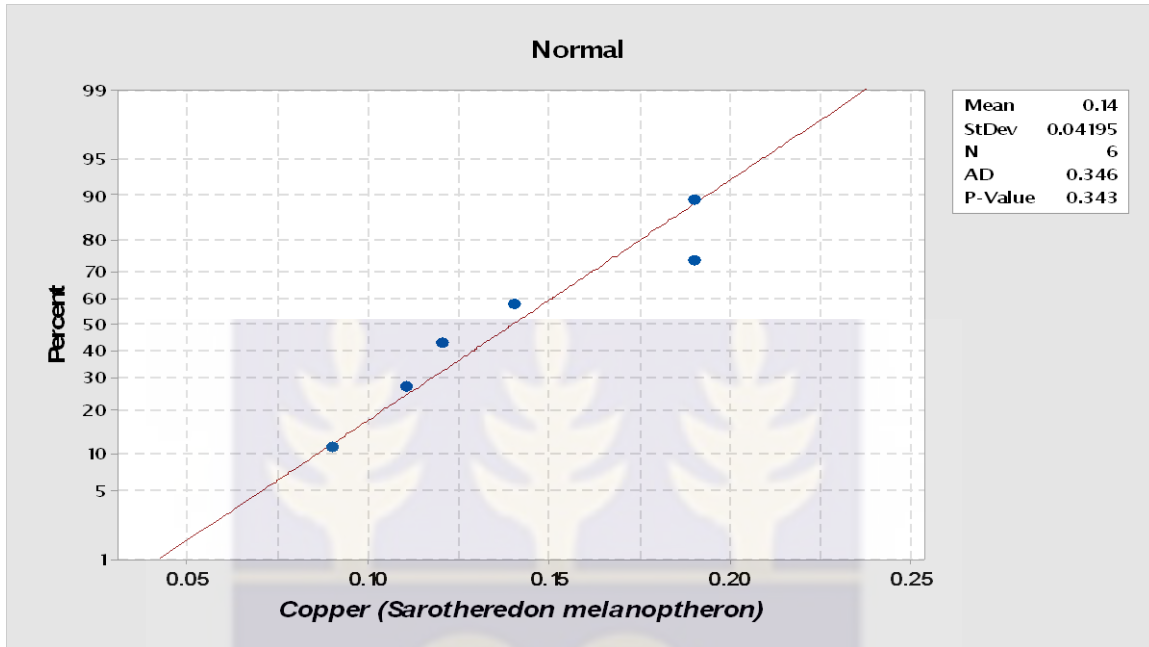


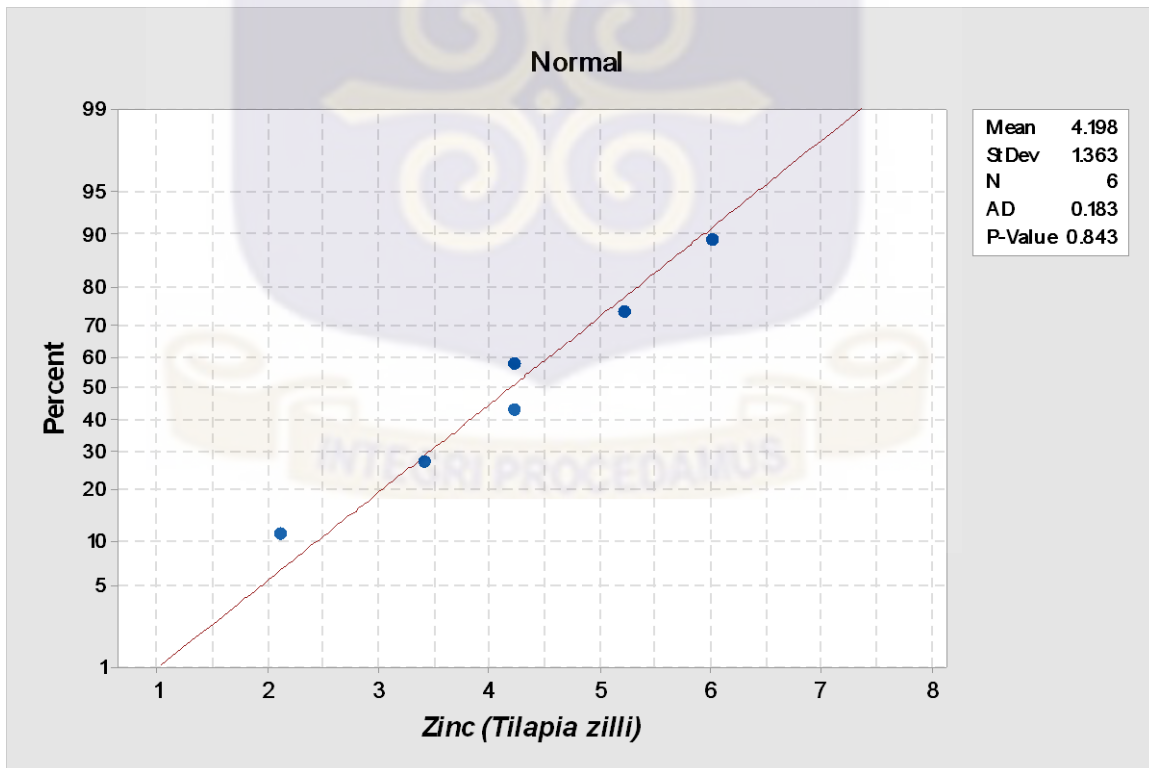
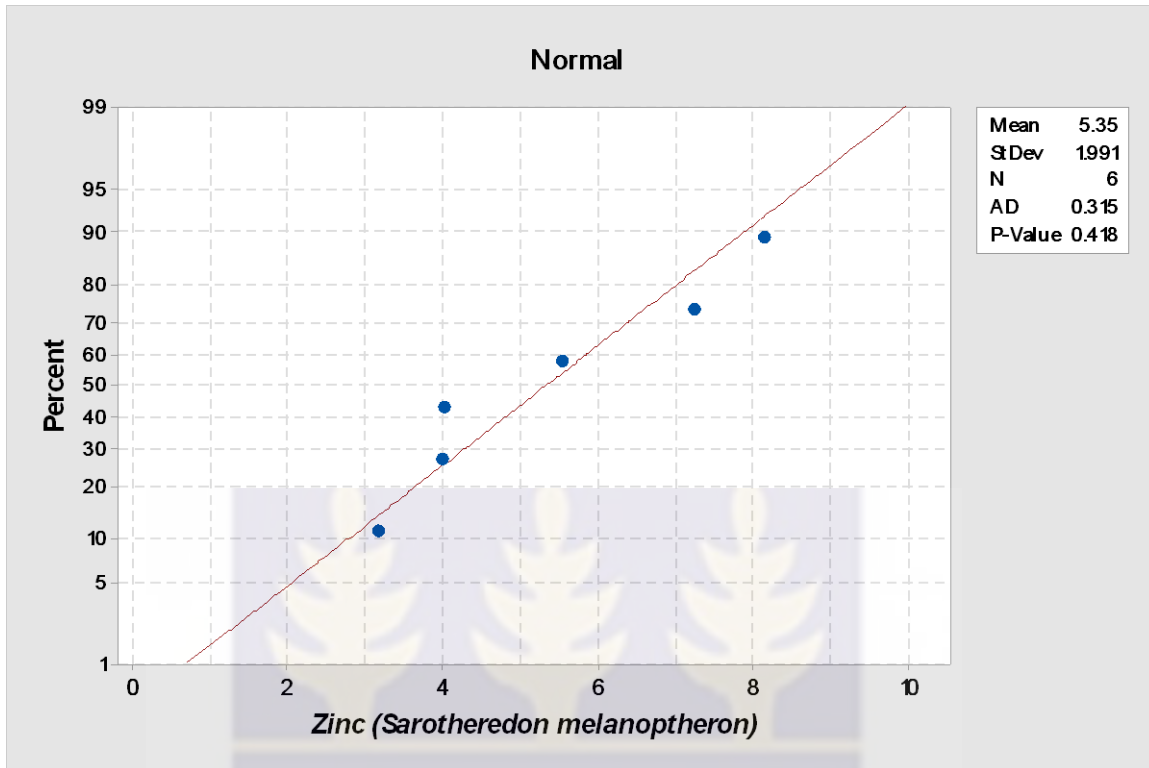


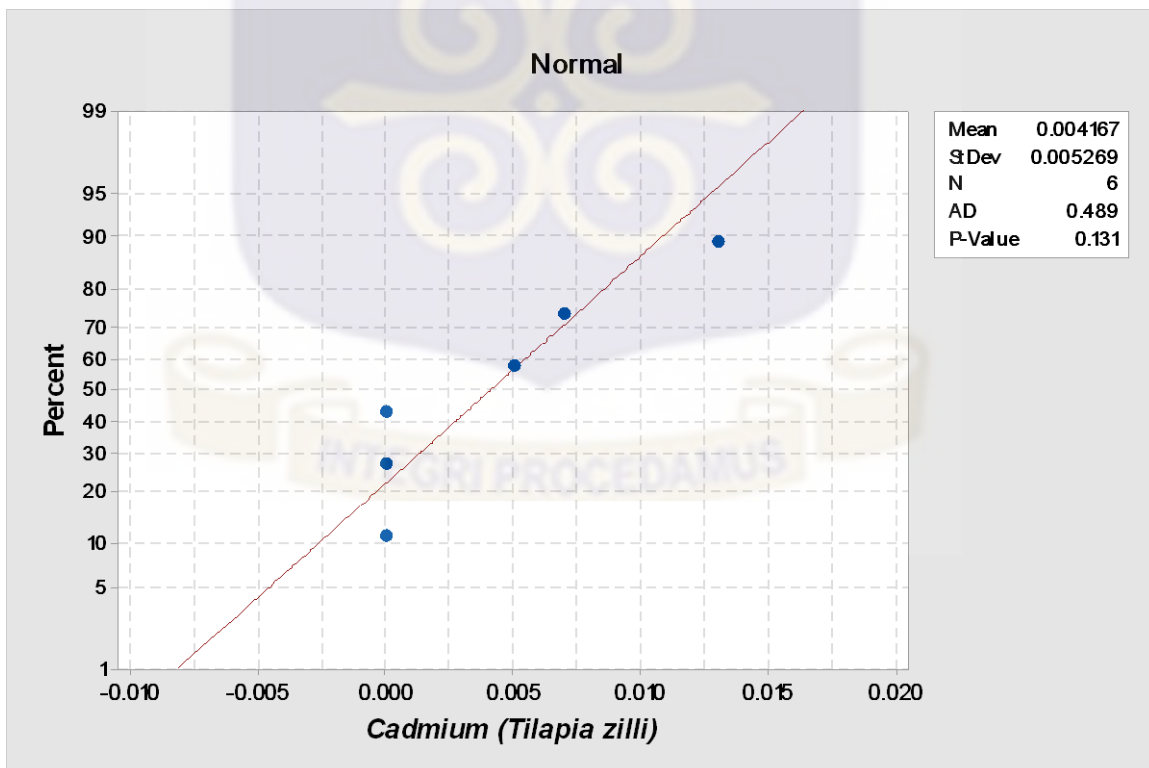
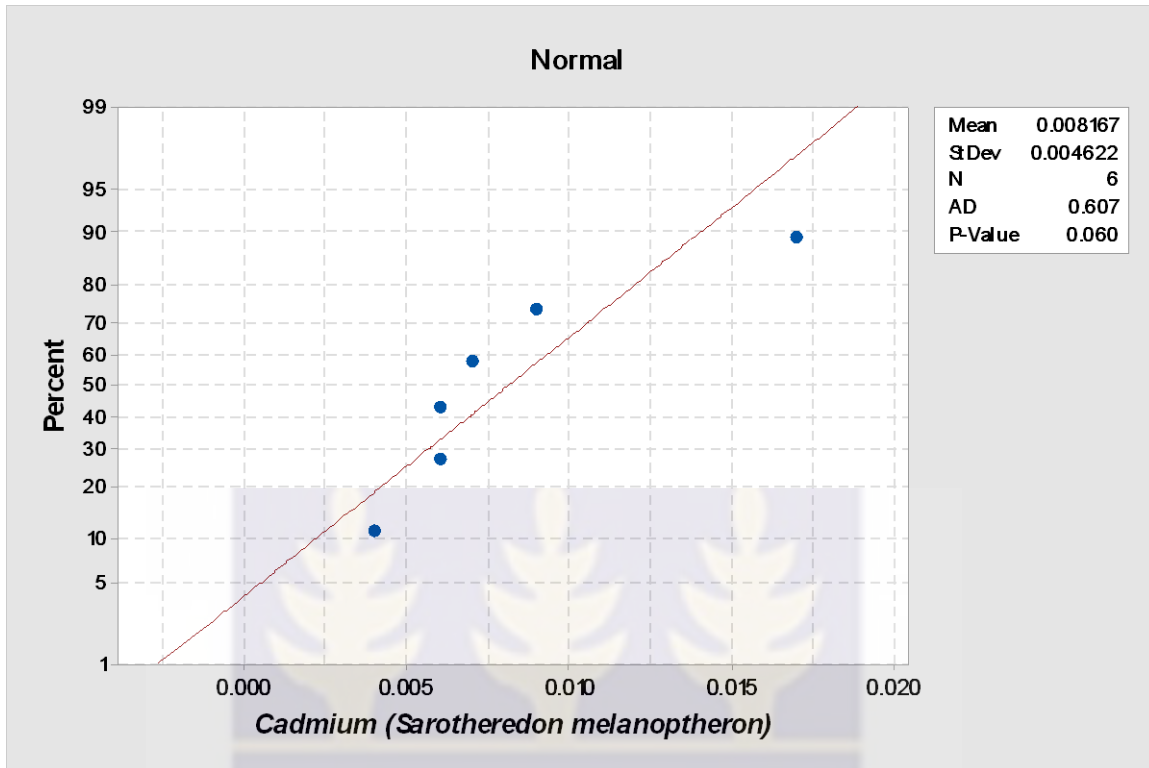


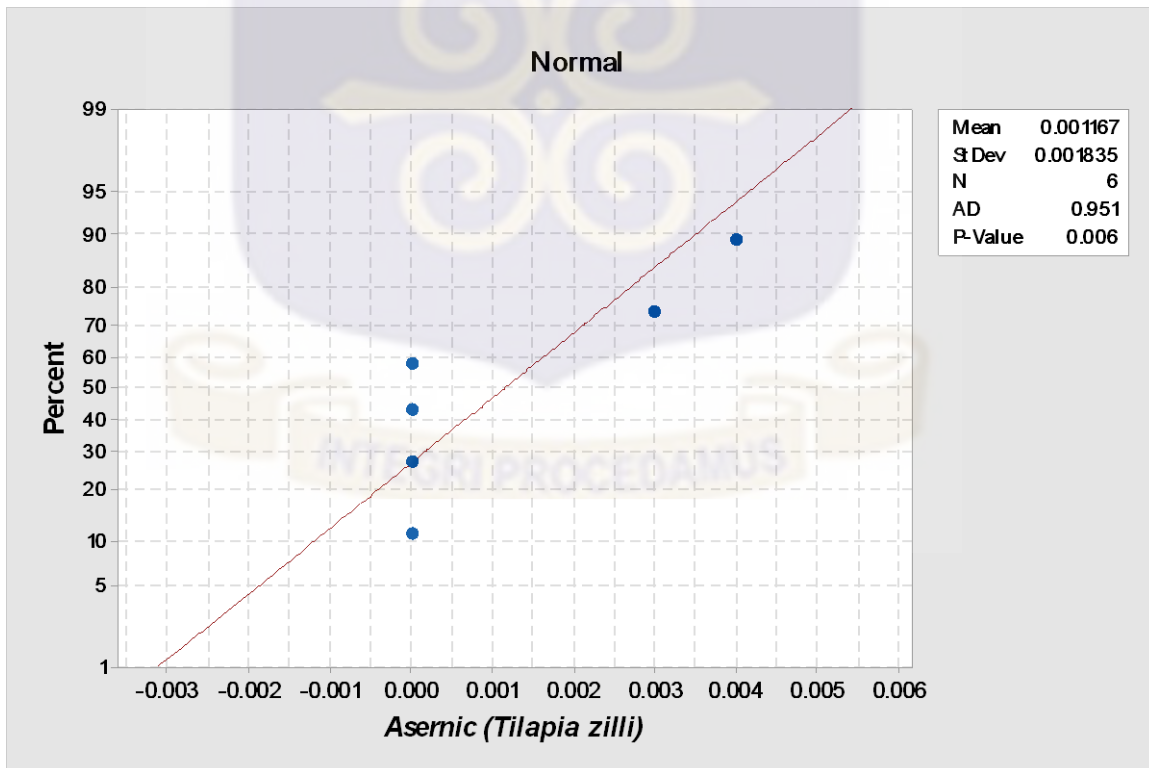
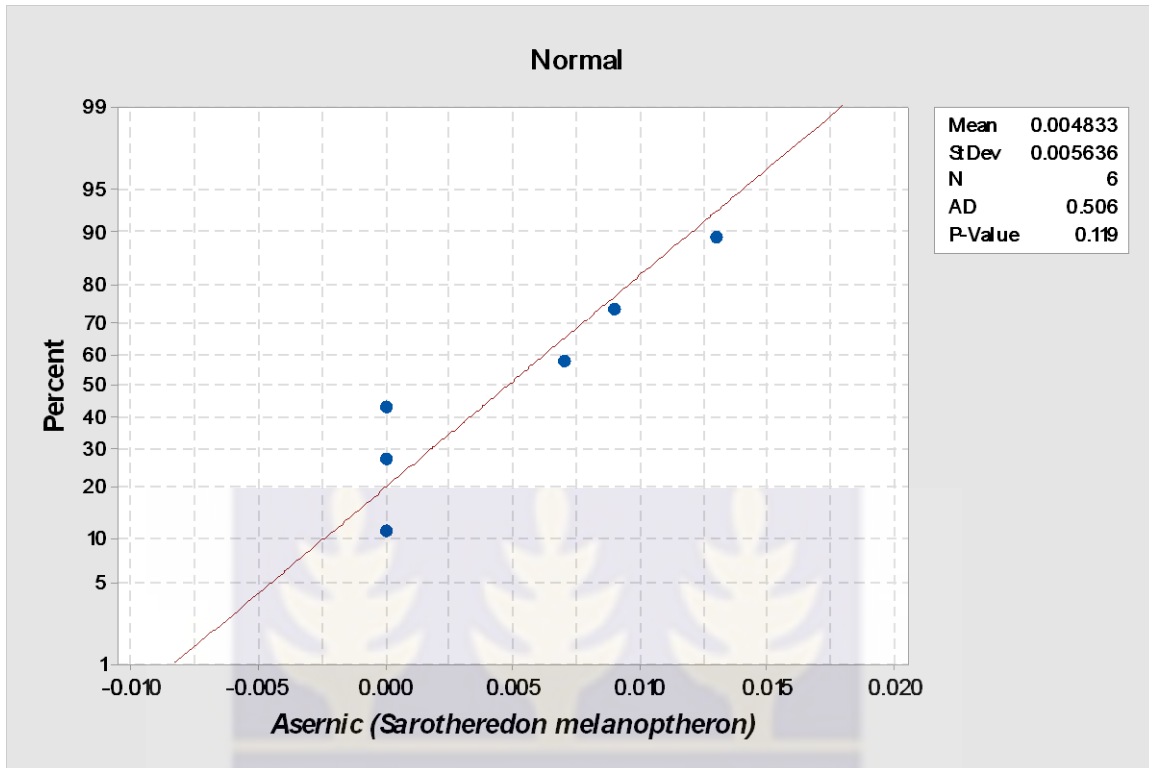


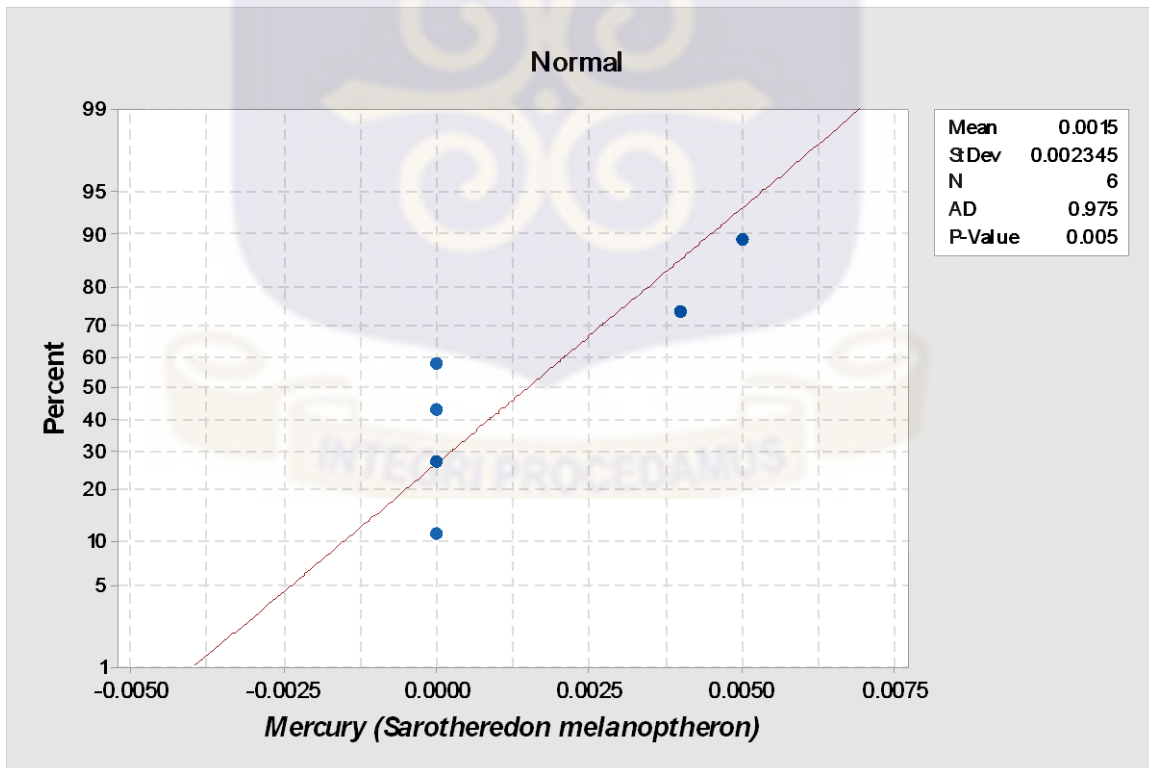
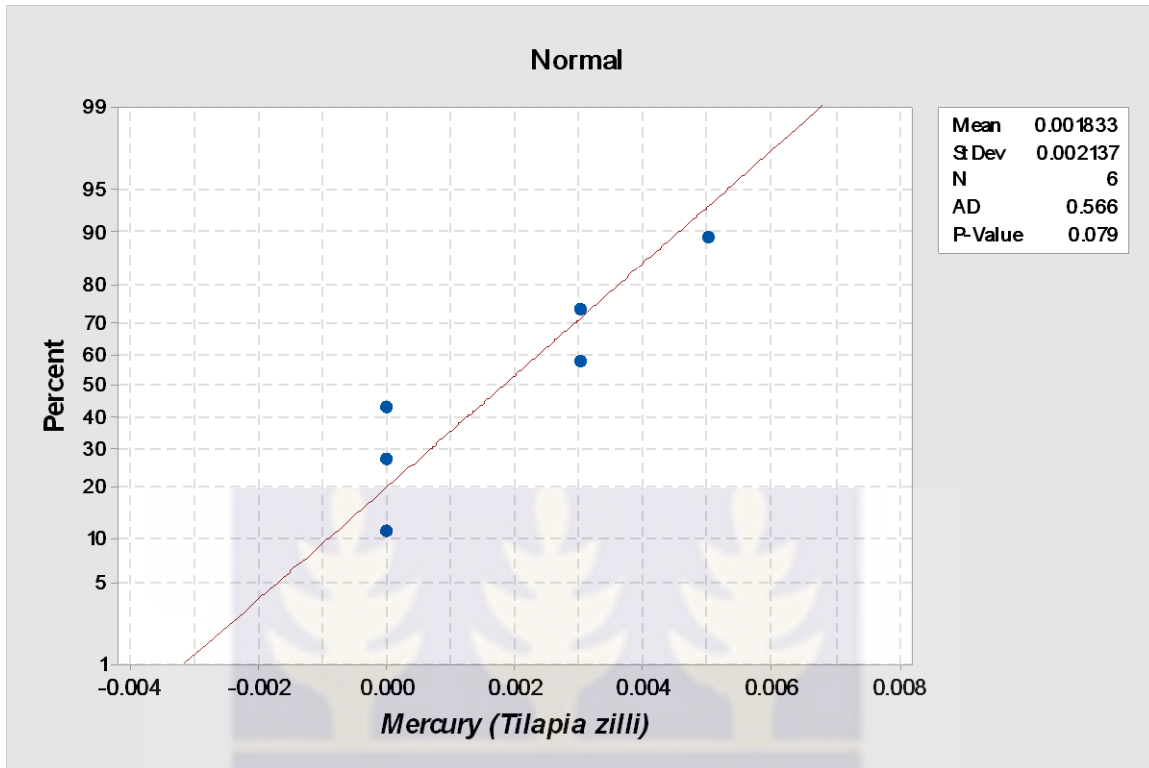
Appendix 3: Normality test for heavy metal concentrations in fish samples according to species



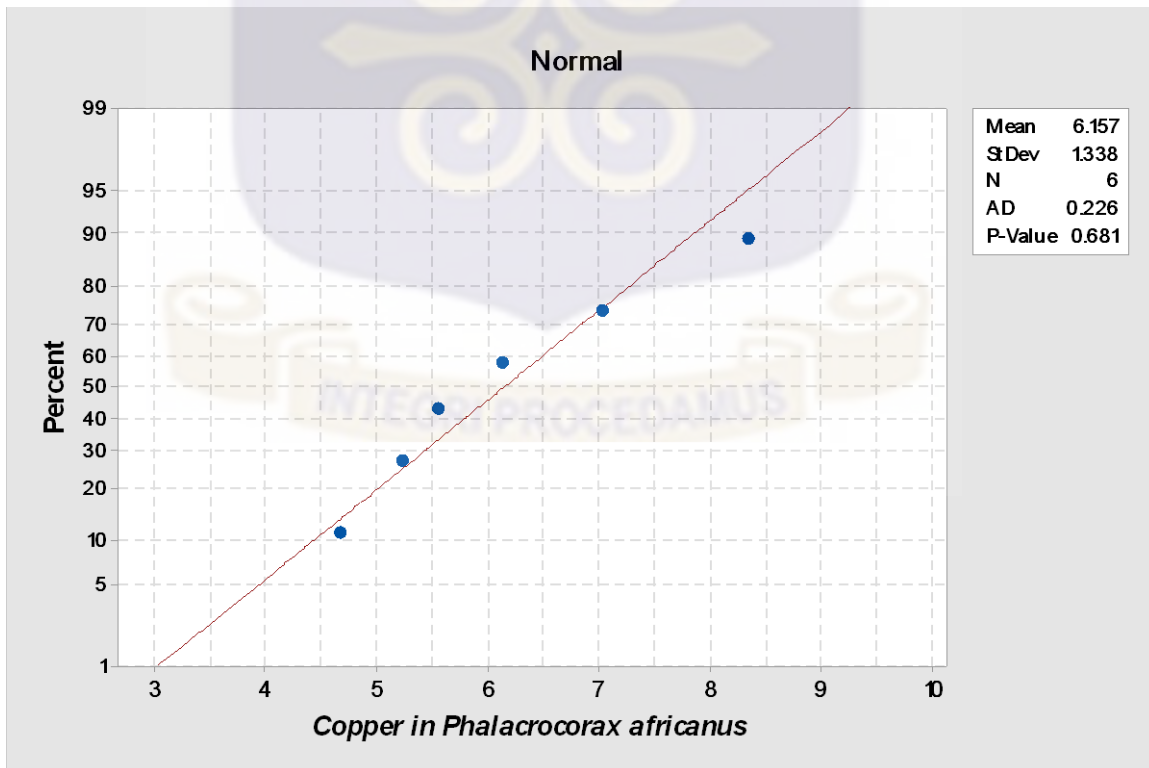
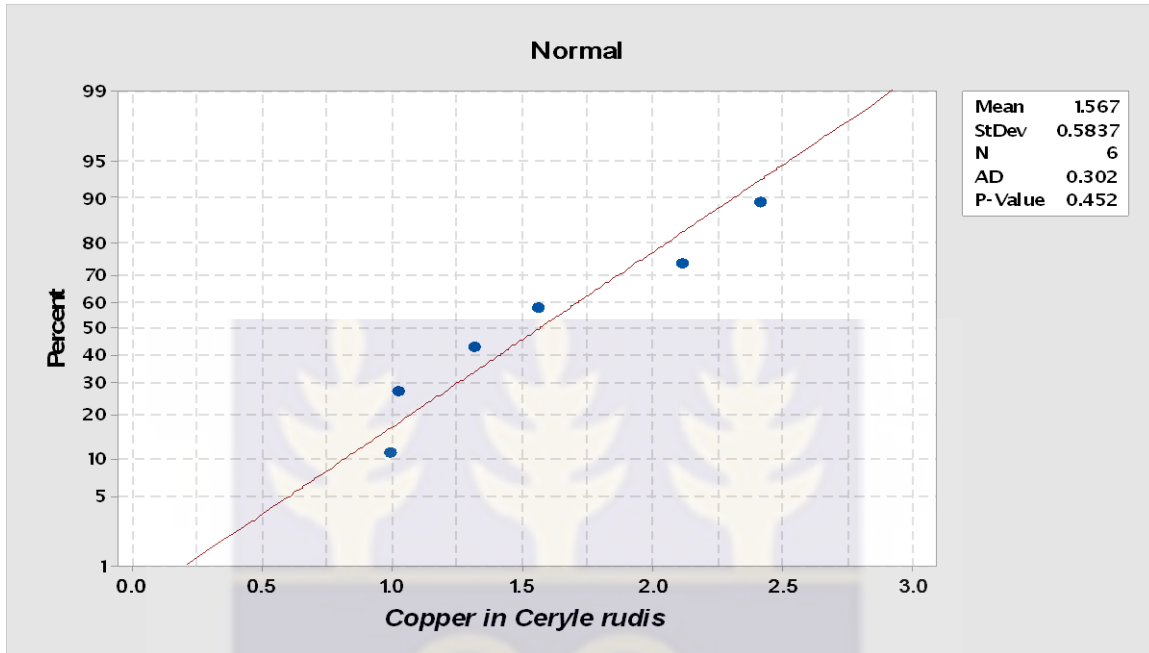


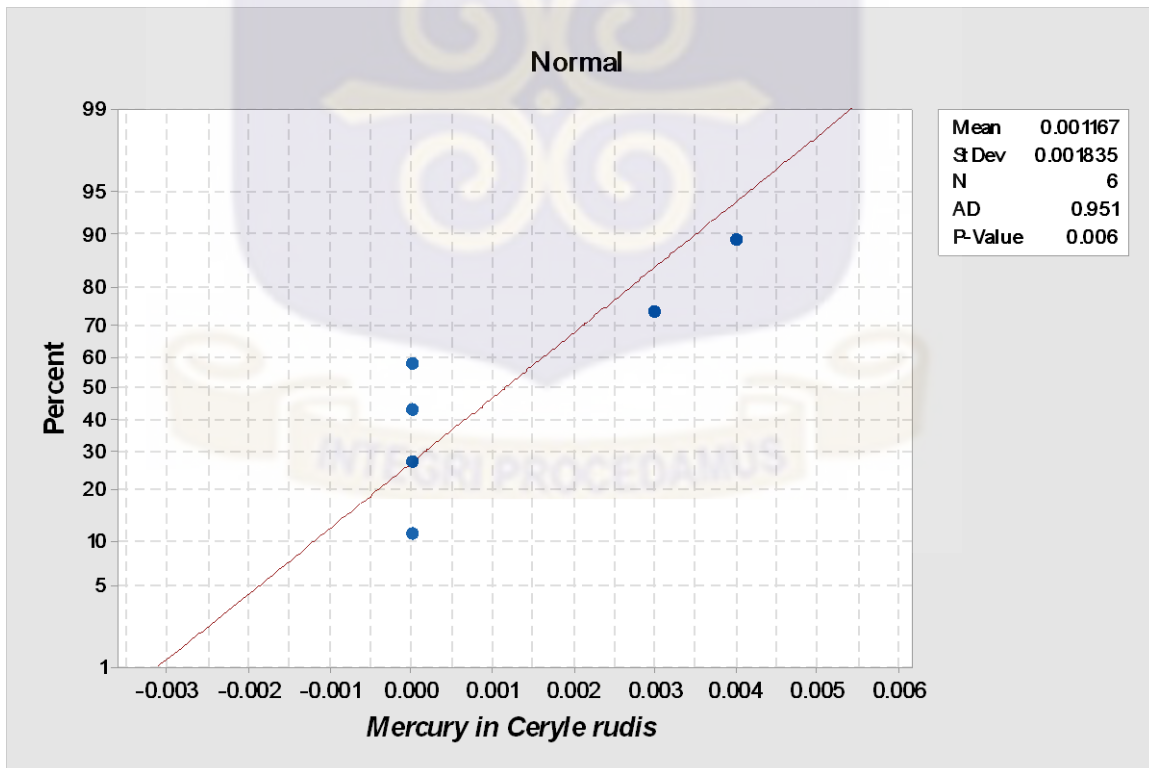
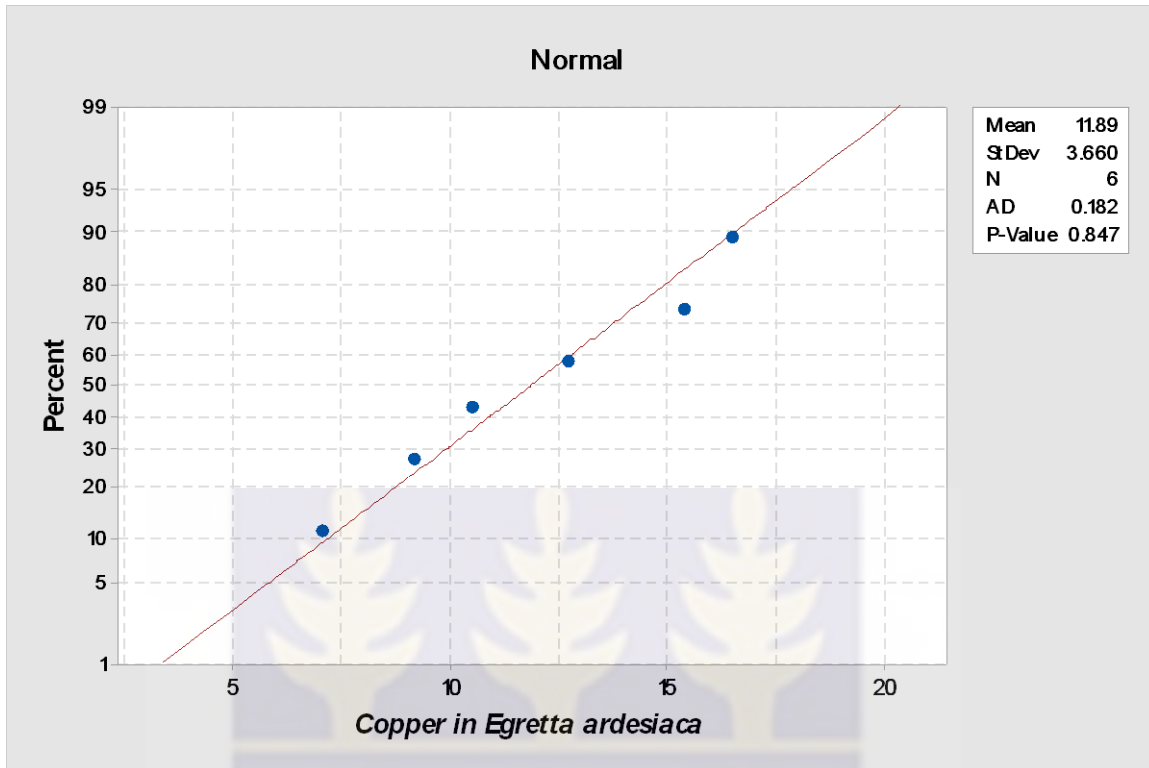


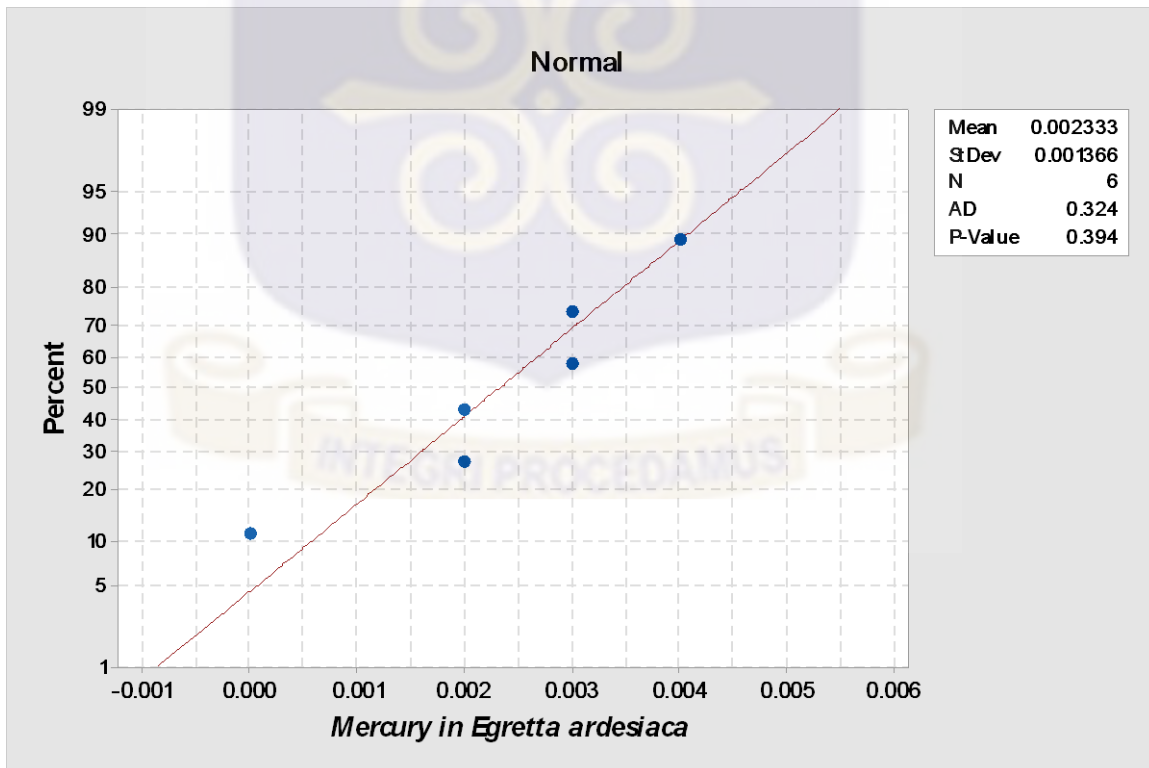
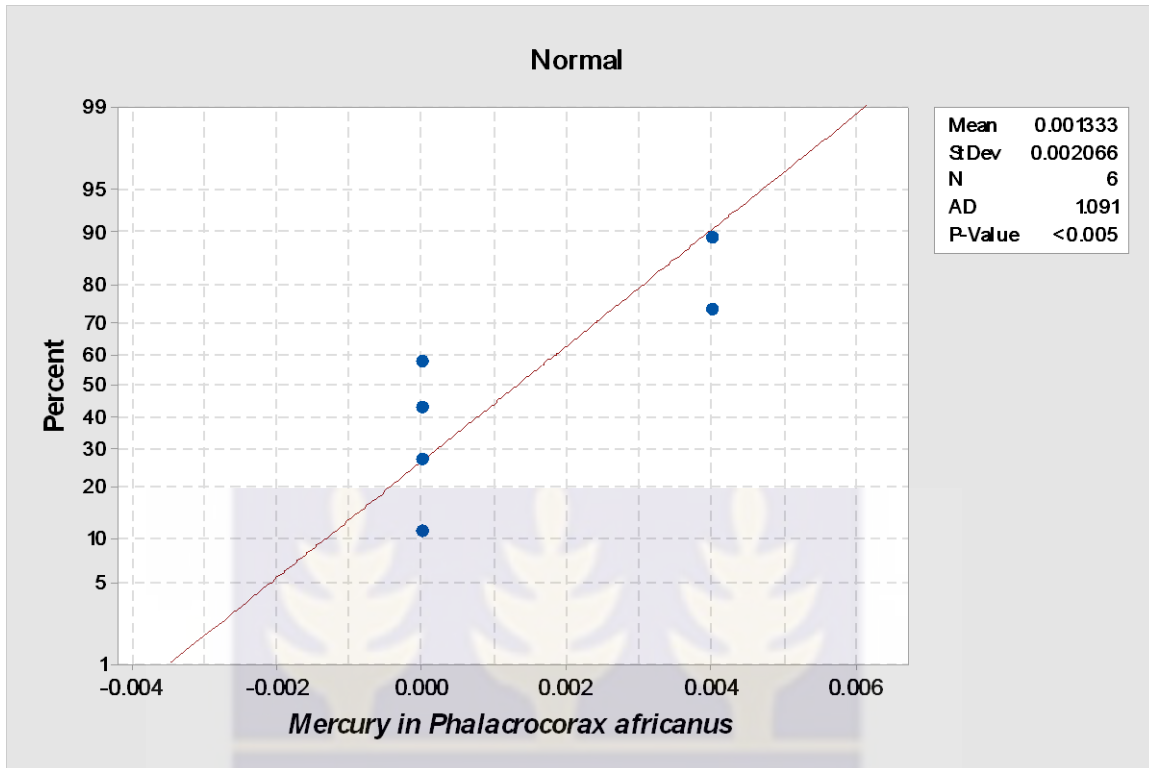


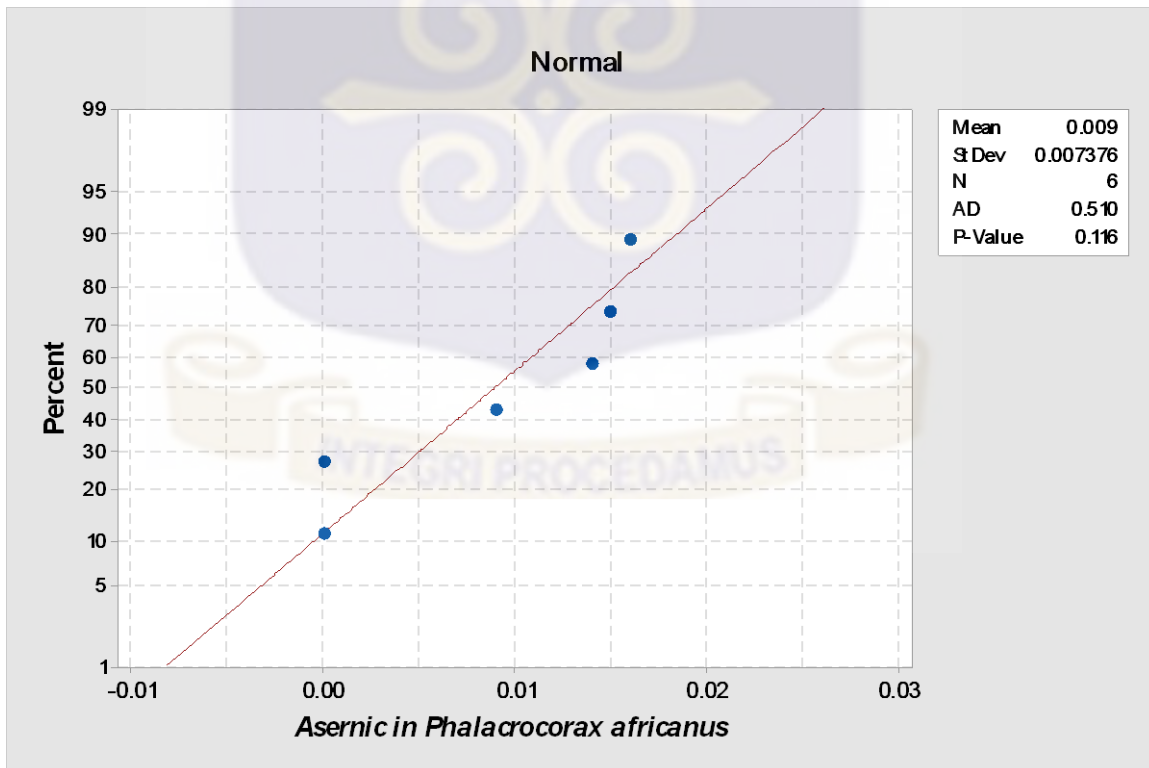
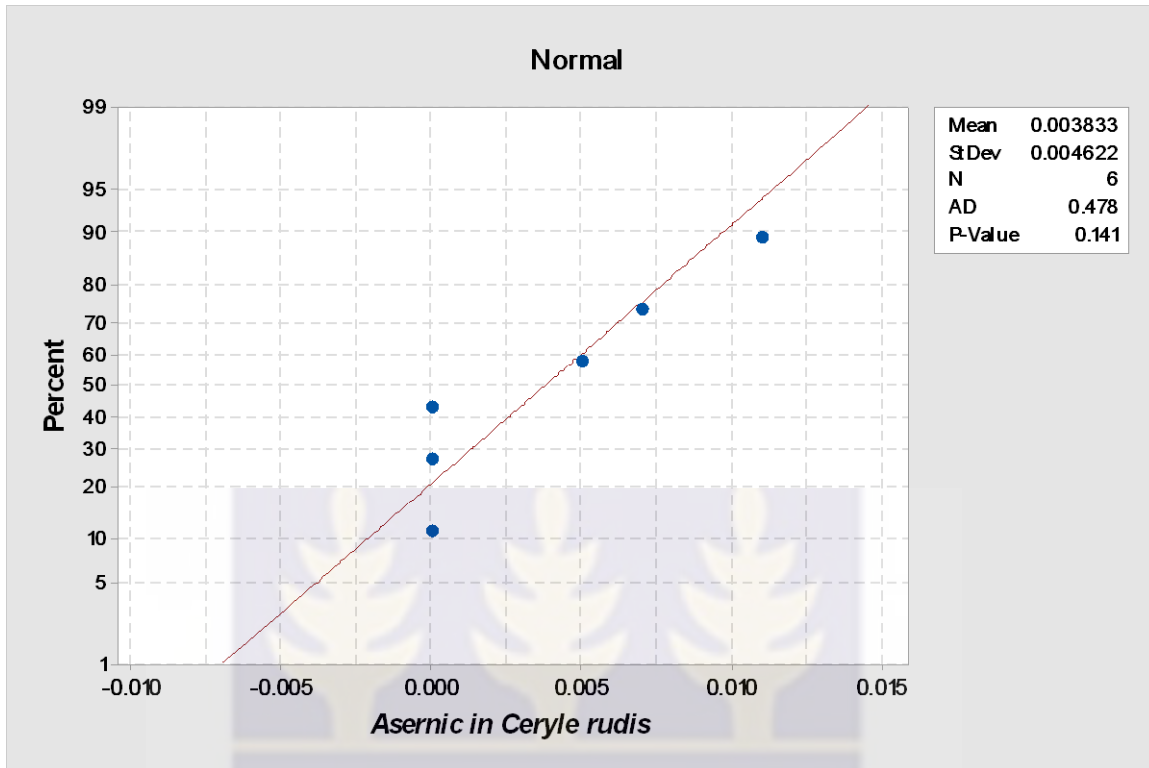


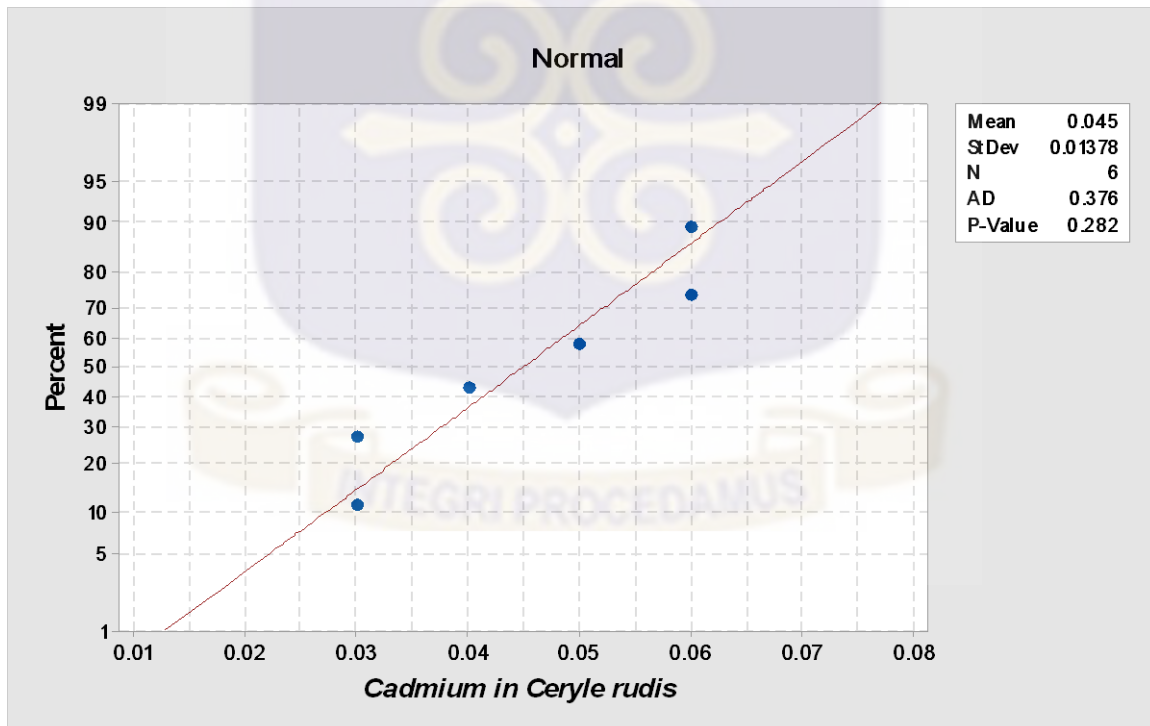
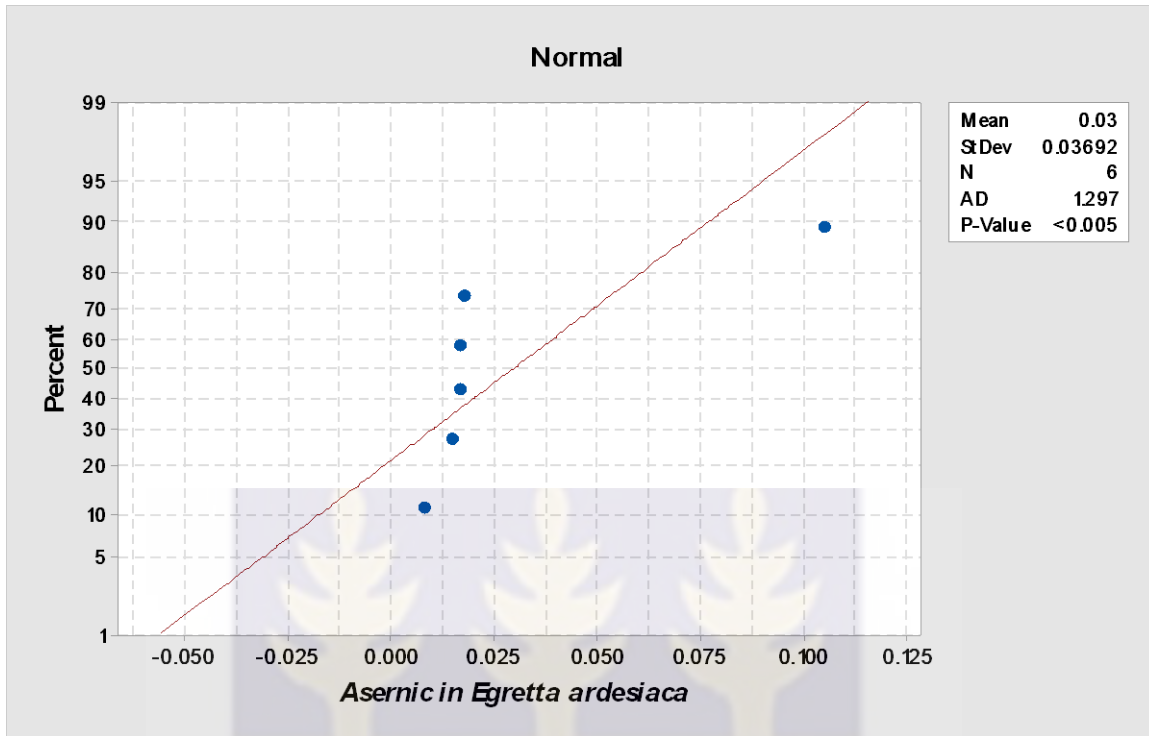
Appendix 4: Normality test for heavy metal concentrations in shorebirds samples according to species

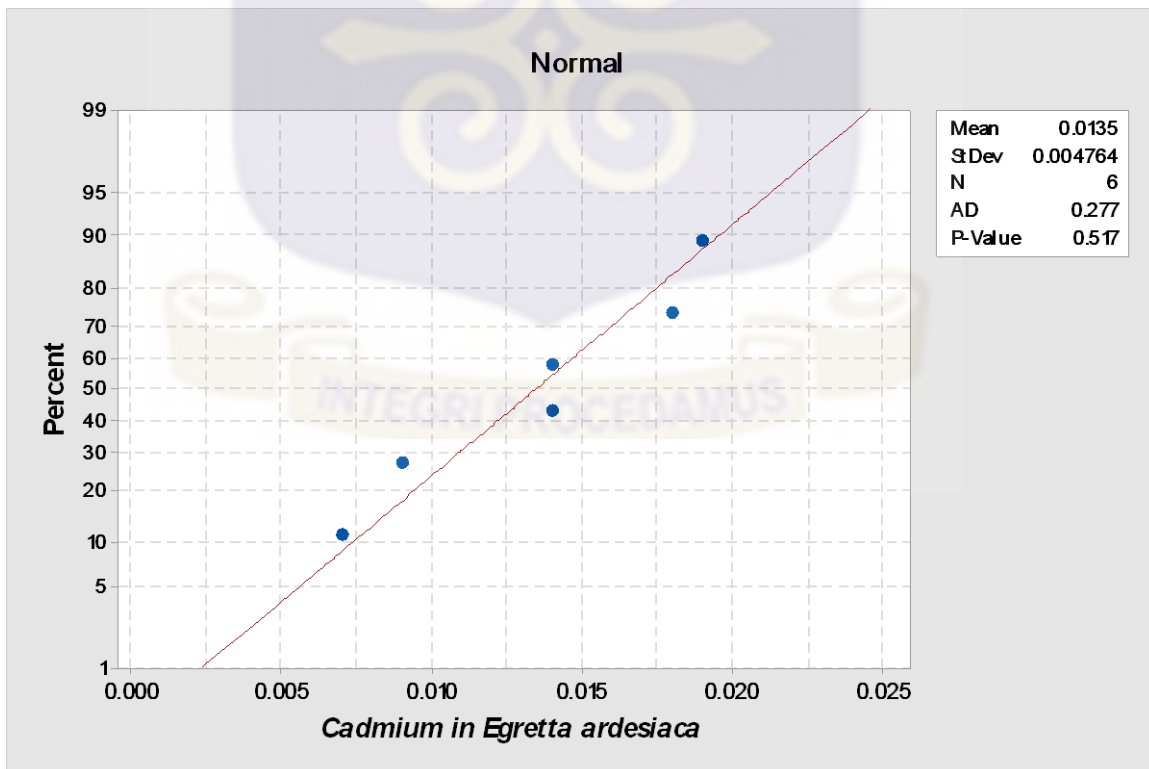
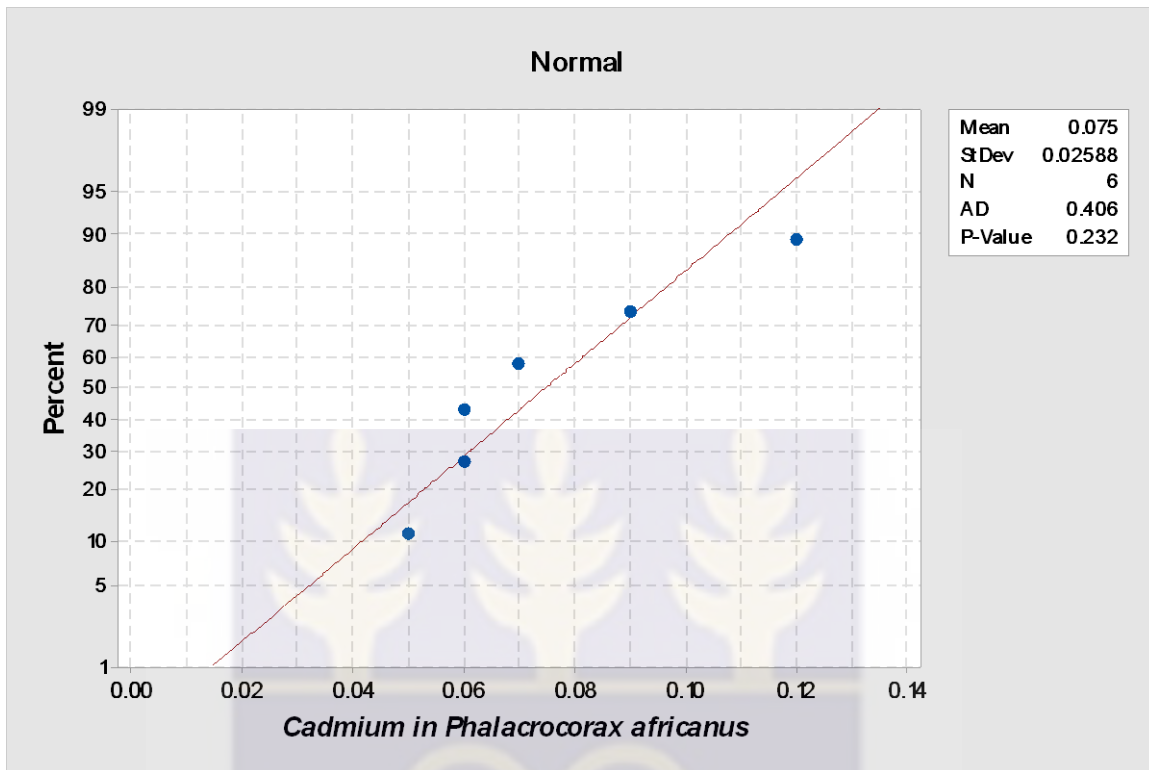


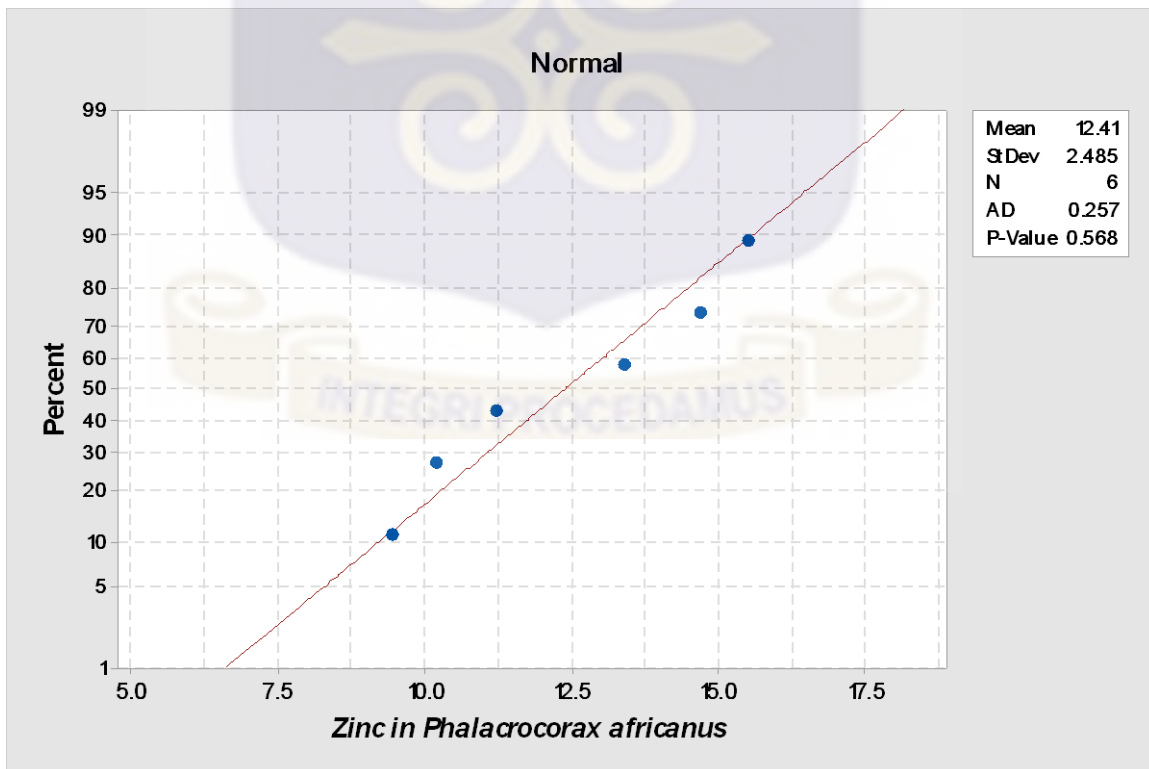
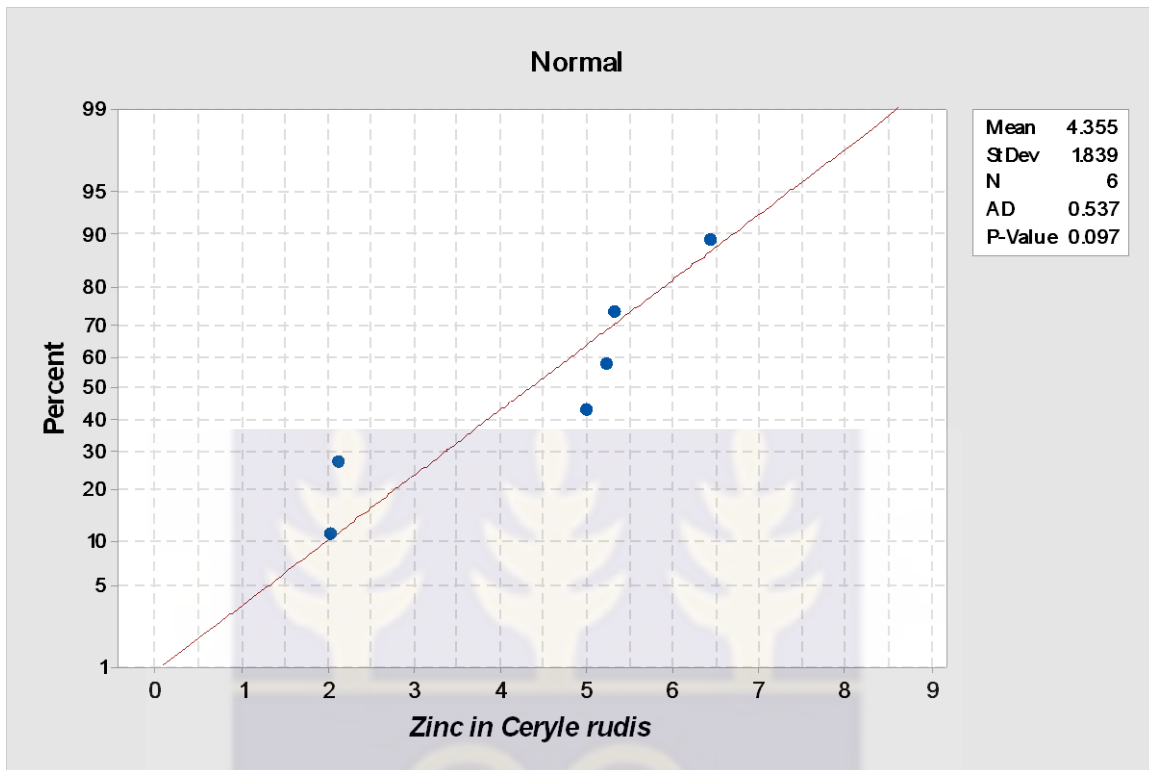


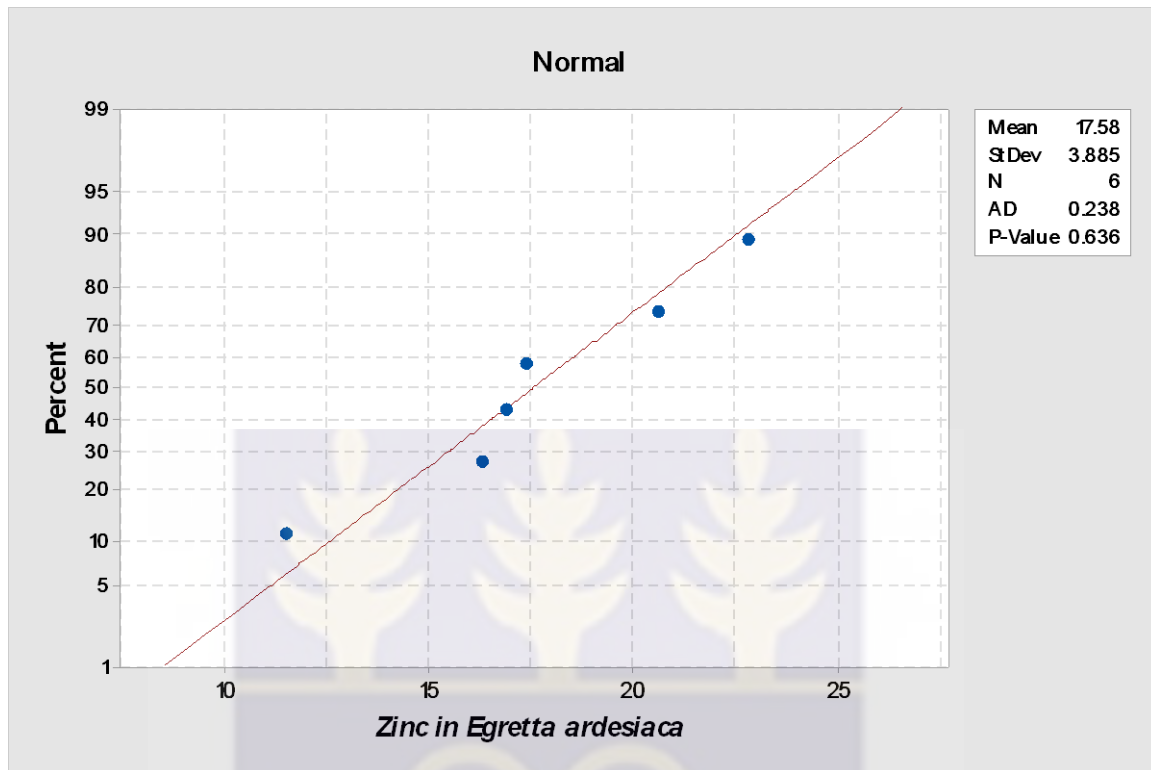












Appendix 5: Fish species used in the study



(a) *Sarotherodon melanoptheron* (Blackchin tilapia)



(b) *Coptodon zillii* (formerly known as *Tilapia zillii*) (Red belly tilapia)

Appendix 6: Significance of heavy metals concentration

(a) Sediment samples

Trace metal	p-value	Remarks
Cu	0.04	Significant
Zn	0.47	Not significant
Cd	0.87	Not significant
As	0.07	Not significant
Hg	0.008	Significant

(b) Water samples

Trace metal	p-value	Remarks
Cu	0.002	Significant
Zn	0.0002	Significant
Cd	0.062	Not significant
As	0.000	Significant
Hg	0.000	Significant

(c) Fish samples

Trace metal	p-value	Remarks
Cu	0.18	Not significant
Zn	0.276	Not significant
Cd	0.196	Not significant
As	0.379	Not significant
Hg	0.873	Not significant

(d) Shorebirds samples

Trace metal	p-value	Remarks
Cu	0.000	significant
Zn	0.000	significant
Cd	0.000	significant

Appendix 7: GPS coordinates of sampling locations.

Sampling Locations	Coordinates of the Four Main Sampling Location	Coordinates of all sampling areas	Coordinates of Biota (Birds)
	<i>Wet Season</i>		
Pambron	N5 ⁰ . 534608 ; W	N05 ⁰ 30.510 ; W000 ⁰	N05 ⁰ 30.969 ;
	0 ⁰ .27634	19.667	W000 ⁰ 18.371
		N05 ⁰ 30.552 ; W000 ⁰	N05 ⁰ 30.962 ;
		19.562	W000 ⁰ 18.371
		N05 ⁰ 30.555 ; W000 ⁰	N05 ⁰ 30.472 ;
	19.434	W000 ⁰ 19.805	
	N05 ⁰ 30.632 ; W000 ⁰	N05 ⁰ 30.980 ;	

		19.287	W000 ⁰ 18.334
		N05 ⁰ 30.705 ;	W000 ⁰
		19.306	
	N5⁰.520629 ;	W N05 ⁰ 30.805 ;	W000 ⁰
Aplaku	0⁰.315601	19.207	
		N 05 ⁰ 31.036 ;	W000 ⁰
		20.804	
		N05 ⁰ 31.432 ;	W000 ⁰
		20.502	
		N05 ⁰ 31.279 ;	W000 ⁰
		20.152	
		N05 ⁰ 31.521 ;	W000 ⁰
		20.924	
	N5⁰.509029 ;	N05⁰ 31.609 ;	W000⁰
Bortianor	W0⁰.326606	20.644	
		N05 ⁰ 32.000 ;	W000 ⁰
		20.442	
		N05 ⁰ 32.292 ;	W000 ⁰
		20.272	
		N05 ⁰ 32.275 ;	W000 ⁰
		20.988	
		N05 ⁰ 32.748 ;	W000 ⁰

20.992

N5⁰.551264 ; W N05⁰ 32.601 ; W000⁰

Oblogo

0⁰.292104

21.707

N05⁰ 32.579 ; W000⁰

21.804

N05⁰ 31.282 ; W000⁰

21.306

N05⁰ 30.952 ; W000⁰

18.379

N05⁰ 30.472 ; W000⁰

19.805

Dry Season

N05⁰ 31.818 ; W000⁰

Pambrons

19.621

N05⁰ 30.743 ; W000⁰

20.791

N05⁰ 31.537 ; W000⁰

19.442

N05⁰ 30.968 ; W000⁰

19.065



N05⁰ 30.889 ; W000⁰
20.657

Aplaku

N05⁰ 30.712 ; W000⁰
20.877

N05⁰ 31.789 ; W000⁰
19.016

N05⁰ 31.978 ; W000⁰
20.111

N05⁰ 31.228 ; W000⁰
20.081

N05⁰ 31.267 ; W000⁰
20.936

Bortianor

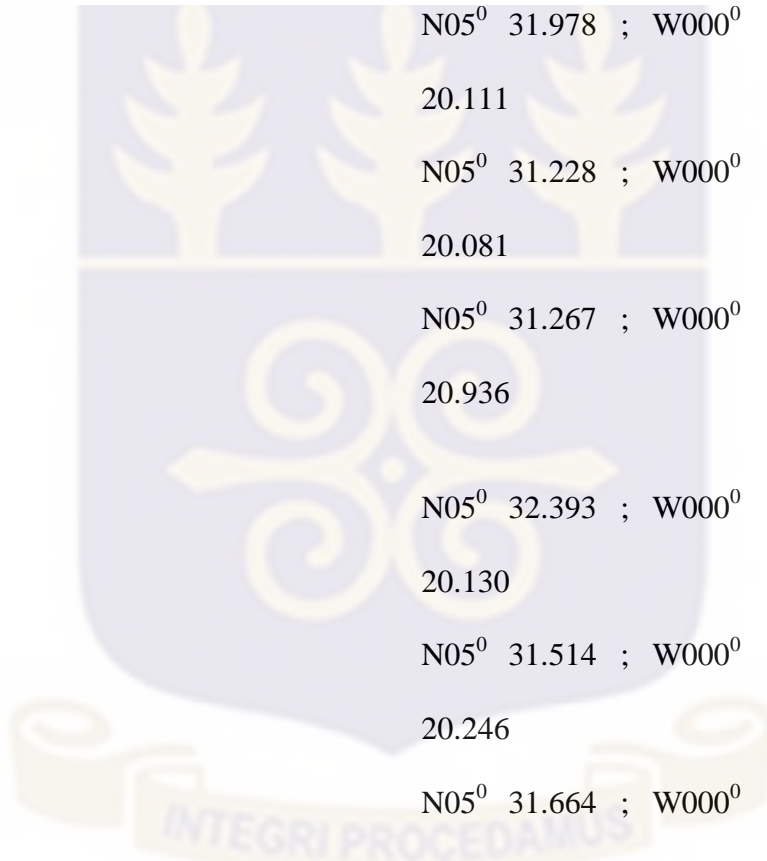
N05⁰ 32.393 ; W000⁰
20.130

N05⁰ 31.514 ; W000⁰
20.246

N05⁰ 31.664 ; W000⁰
21.269

N05⁰ 31.678 ; W000⁰
20.111

N05⁰ 30.903 ; W000⁰
21.123



Oblogo

N05⁰ 31.095 ; W000⁰

21.335

N05⁰ 31.190 ; W000⁰

21.050

N05⁰ 30.356 ; W000⁰

21.934

N05⁰ 32.365 ; W000⁰

20.792

N05⁰ 31.352 ; W000⁰

21.677

N05⁰ 31.581 ; W000⁰

21.578

