KWAME NKRUMAH UNIVERSITY OF SCIENCE AND TECHNOLOGY,

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COLLEGE OF HEALTH SCIENCES

SCHOOL OF PUBLIC HEALTH

ASSESSMENT OF TRACE METAL LEVELS IN SELECTED MARINE FISH SPECIES LANDED IN GHANA AND THEIR POTENTIAL HUMAN HEALTH RISK

BY

BOATENG CHARLES MARIO

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DECLARATION

I, Boateng Charles Mario, hereby declare that this work is the result of my own research and that this dissertation has neither in whole or in part been submitted to this University or elsewhere for another degree. All references to other people's work which served as a source of information in this research have been duly acknowledged.

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HEAD OF DEPARTMENT

DEDICATION

This work is dedicated to God Almighty the giver of life.

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ABSTRACT

The study examined the levels of six (6) heavy metals; Zinc (Zn), Lead (Pb), Copper (Cu), Cadmium (Cd), Arsenic (As) and Mercury (Hg) in four marine fish species (*Sardinella maderensis, Dentex angolensis, Sphyraena sphyraena and Penaeus notialis*) and their potential health risks to potentially exposed populations in Ghana in the Gulf of Guinea (GOG) region. The concentrations of Zn, Pb, Cu, Cd and As in fish tissues were analyzed after microwave digestion of samples using an Inductively Coupled Plasma Mass Spectrometry. Mercury was measured directly in the solid samples using an Automated Mercury Analyzer. With the exception of Pb, all metals analyzed were detected in fish samples. Highest concentrations of Cu (12.08 ± 1.46), Zn (19.20 ± 2.27), As (8.46 ± 2.42) and Cd (0.03 ± 0.01) were observed in the muscle tissues of *P. notialis* while *D. angolensis* recorded the highest concentration of Hg (0.14 ± 0.03). Largely, significant variations ($p < 0.0001$) were observed in the concentrations of metals across the various fish species analyzed. Except for As, the levels of all metals were below the tolerable limits set by the Food and Agricultural Organization (FAO), United States Environmental Protection Agency (USEPA), the Australian and New Zealand Food standard code and the European Commission (EC).The study however reveals significant carcinogenic risk due to As intake for *S. maderensis* and *D. angolensis* in all age categories except for children between age 1 to 3 years, and all 9 age categories for *P. notialis* .It is therefore recommended that, the consumption of *P.notialis* , *D. angolensis* and *S. maderensis* caught from the Ghana coastal water is done with caution particularly among children and adolescents populations to avoid possible non-carcinogenic effects and long-term carcinogenic effects later in life.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

LIST OF ABBREVIATIONS

AAS ……………………………….Atomic Adsorption Spectroscopy

CR …………………………………Carcinogenic Risk

DMA ………………………………. Direct Mercury Analyzer

EC …………………………………. European Commission

EDI …………………………………Estimated Daily Intake

FAO …………………………………Food and Agricultural Organization

HI ……………………………………Health Index

IAEA ………………………………...International Atomic Energy Agency

ICP-MS ………………………………Inductively Coupled Plasma Mass Spectrometry

TE ……………………………………Trace metals

THQ …………………………………..Target Hazard Quotient

USEPA ………………………………..United State Environmental Protection Agency

WHO …………………………………..World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Fish is a major source of protein and fundamental micronutrients for about a quarter of the world's population (Béné *et al*., 2015). The global production of fish as indicated by the Food and Agriculture Organisation (FAO) has risen in the last few years (Bartley, 2015; AOUNFD, 2000). In 2016, the world produced 162,646,576 tons of fish and fishery products (FAO, 2016). Fish is considered a healthy food source because of its high quality of protein composition, desirable lipid composition, valuable minerals, vitamins and low cholesterol which are required for brain development, cell repair and growth and neurodevelopment functions (Oken *et al.*, 2008, Sarkar *et al*., 2016). Despite these associated health benefits, their consumption may also serve as a primary route for metal ingestion to humans (Tchounwou *et al*., 2012).

The anthropogenic introduction of trace element pollutants into the aquatic environment has received worldwide attention due to the potential risks to ecosystem functioning, food security and safety. Trace metals is considered a threat to the physiology of marine organisms including fish as well people who consume seafood (Rahman *et al*, 2012; Copat *et al.* 2012). The tendency for trace elements to bio-accumulate in marine species which in turn, becomes biomagnified up the food chain pose even more human healthrelated threats as this increases the likelihood of terminal diseases to show up in both children and adults (Majed *et al.*, 2016). Trace metals such as Pb, As and Hg have no known significant biological roles either to marine organisms or humans, and their presence in aquatic systems is a mere threat to the ecosystem (Ahmed *et* al., 2016).

Cadmium is fatal even at extremely minute levels (Soderland *et al*., 2010). However, research shows that significant quantities of cadmium enter the environment each year through human activities ((Sany *et al*., 2013).In humans, prolonged exposure is characterized by renal dysfunction, followed by tubular proteinuria. Also, bone defects such as osteomalacia, osteoporosis have been associated with Cadmium. Lead is documented as a principal environmental peril with teratogenic effects (Duruibe *et al.*, 2007). The primary route of human exposure is through seafood and inhalation (Bustamante *et al*., 2008).

Lead toxicity destroys haemoglobin synthesis, causes kidney failure, elevates blood pressure and interfere with central nervous systems functions coupled with cardio disorders at elevated levels (Ogwuebgu and Muhanga, 2005 as cited in Duruibe *et al.*, 2007). In children it tends to interfere with their central nervous system, decrease intelligent quotient and cause mental retardation (Wani *et al.,* 2015, Radyminska *et al.*, 2019). Exposure to arsenic alters several sulfhydryl-containing proteins and enzyme systems and it is considered to be carcinogenic (Saei-Dehkordi, Fallah & Nematollahi, 2010). Researchers have found out that marine species accumulates substantial amounts of arsenic compared to other foods and high quantities have been found in fish muscles from the Gulf of Guinea and the Mediterranean (Bozkurt, Eliri & Kesiktas, 2014). Studies have documented the toxicity of mercury on some fish species and its subsequent potential health hazards to consumers (Singare *et al*., 2013). Adsorption of high amounts of methyl mercury from the surrounding water by fishes leads to bioaccumulation and subsequently causes damage to kidneys and intestines in fishes, reproductive failure and DNA alteration. In humans, mercury poisoning causes intoxication to the nervous system, coordination difficulties, gastrointestinal toxicity and dementia ((Addo, 2017).

Although metals exist naturally, human activities including mining, smelting, domestic sewage and industrial processing, may increase their concentrations beyond threshold limits in the environment (Ju *et al.*, 2017). These metals are getting either deliquesce in the water or participate in sediments and suspended particles in the water. Eventually, they are taken in by either directly or indirectly by organisms through bioaccumulation and subsequently biomagnified up the food chain (Yi, Yang & Zhang, 2011).

Fish (finfish and shellfish) are more susceptible to metal bioaccumulation via direct absorption through gills, feeding and digestion of sediment particles which could present significant development and health implications to the fish (Ju *et al.*, 2017) and subsequently human health. The issue of trace metal accumulation in fish is of worldwide concern as it has negative implications on health. The primary reason being that, the consumption of seafood is the principal route for human exposure to trace elements as opposed to inhalation and dermal contact (Saha *et al.*, 2016). The magnitude of trace metal accumulation in aquatic organism is influence by the feeding habit, age, sex, respiration, chemical form, affinity, absorption rate, excretion and habitat (Bustamante *et al*., 2006). Marine benthic organisms or bottom dwellers may accumulate metals from sediment through feeding which act as a reservoir for pollutants discharged into the ecosystem (Cohen *et al.*, 2005).

1.2 Problem Statement

The marine coastal environment is extensively recognized on account of its infinite resources as a contributing factor to socio-economic development. The health and sustainability of the coastal ocean are increasingly in jeopardy due to the rapid intensification of human activities (Diop & Scheren, 2016). Rapid urbanization and industrialization in recent years have led to the release of organic and inorganic substances into the coastal environment thereby, upsetting and disrupting the natural biological balance (Förstner & Wittmann, 2012). A better understanding of the status of trace elements in coastal waters of Ghana is of utmost importance to marine ecosystem functions, the seafood industry, public health and the sustainable developments of marine resources (Langston, 2017). Various of studies have reported the status, dimension and levels of trace metal pollution in freshwater, coastal and lagoon water bodies in Ghana (Fianko *et al*., 2007; Armah *et al*., 2010; Mahu *et al*., 2015; Afum & Owusu, 2016;).

In Ghana, the activities of small scale gold mining sector and other industrial developments along the coast have contributed significantly to metal pollution of major water bodies and their adjoining estuaries and subsequently the ocean (Afum &Owusu, 2016). In support to the above consensus, Mahu *et al*., 2016, Botwe *et al*., 2017, Nyarko *et al*., 2014 & Klubi *et al*., 2017 in their assessment of trace metals pollution in sediment from the near shore and estuaries in Ghana recorded high levels above international sediment quality guidelines. These activities may result in the contamination of local seafood with metals. However, much research has not gone into assessing the state of contamination of fish with trace metals and their possible public health risk.

1.3 Justification

Fish is an important component in the Ghanaian diet due to its nutritional benefit and affordability as compared to meat. The Food and Agricultural Organization (2016) stated that Ghana's current per capita fish consumption stands at 28 kg, higher than Africa's current 10.5 kg and the world's current 18.9 kg. Also, fish contributes to about 60% of protein intake and 22.4% of household food expenditures, thus making Ghana a major fish consuming nation. Several studies have reported the concentration of trace elements in fish for Ghana's coastal environment and their possible health risk (Nyarko *et al*., 2103). However, studies focusing on risk assessments to a sensitive population like children and the adolescent age group is scant. There is, therefore, the need to provide consumers with information on the status of trace metals levels in fish from Ghanaian coastal waters and any associated health risk through local seafood consumption.

1.4 Aim

This study aims to evaluate the levels of Pb, Cd Hg, Cu, Zn and As in Sardinella *maderensis*, *Sphyraena sphyraena, Dentex angolensis and Penaeus notialis* from the coastal waters of Ghana and their potential human health risk.

1.4.1 Specific Objectives

1. Determine the levels of Pb, Cd, Hg, Cu, Zn and As in the fish tissues.
2. Estimate the daily intake of heavy metals and compare with regulatory limits
3. Assess any potential carcinogenic and non-carcinogenic human health risks associated with Cu, Zn, Hg, As, Pb and Cd levels in the fish species.

1.5 Null Hypothesis

1. Trace metal (Cu, Zn, As, Hg, Pb and Cd) levels in *Sardinella maderensis*, *Dentex angolensis*, *Penaeus notialis and Sphyraena sphyraena* from Ghanaian coastal waters are within recommended levels for human consumption.
2. Consumption of *Sardinella maderensis*, *Dentex angolensis*, *Penaeus notialis and Sphyraena sphyraena from* Ghanaian coastal water present no carcinogenic and non-carcinogenic health risk to Ghanaians.

CHAPTER TWO

2.0 LITERATURE REWIEW

2.1 Introduction

The continental shelf of Ghana is relatively narrower with a total area of about 24, 500 km^2 (Atta-Mills *et al*, 2004). The fisheries division is a very significant factor to consider in the development of Ghana, both socially and economically. Ghana's fisheries sector contributes significantly towards sustainable livelihoods, food security and poverty reduction (FAO, 2016).There is quite a wide range of fisheries resources in Ghana's waters which can be tapped for development. Ghana's fisheries sector is composed of artisanal fishers who fish mainly for subsistence to semi-industrial and industrial fleets. Fish stocks are harvested from inland and marine waters. The artisanal sector constitutes more than 76 percent of the total fish production in Ghana. The sector also employs over two million women involved in fish trade, processing and other fish related activities (Nunoo *et al*., 2014).

The fisheries sector contributes significantly to the economy, taking about 4.5 percent of Ghana's GDP and 10 percent of labour force (FAO, 2016). This shows that the fisheries sector employs a significant amount of people, brings foreign exchange to the country, aids in poverty alleviation and most importantly provides food security for the average Ghanaian. In Ghana, fish serves as a renowned source of animal protein and is consumed by the vast majority of locals from the provincial poor to the urban rich (Darkwa & Smardon, 2010). Fish provides vitamins, minerals, potassium and polyunsaturated fats in human diet (Bourre & Paquotte, 2008).

2.2 Trace metals in the marine environment

The occurrence of trace elements in the marine ecosystem has become an important subject of concern to human health due to the potential dangers they pose to humans through bio-accumulation in the food chain (Furness, 2017). Some trace metals generally occur at background levels in the environment but may elevate due to anthropogenic activities

(Morel and Price, 2003). These metals are released naturally into the marine ecosystem via volcanic eruption, weathering processes and forest fires (Cipro *et al*., 2018).

Atmospheric deposition and continental overflow are the primary sources of trace metals pollution in the marine system (Halstead, Cunninghame & Hunter, 2000). Biogenic sources and forest fires are of lesser significance (Karl *et al*., 2007). Nevertheless, metals can be deposited into the marine sediments via human activities such as mining, smelting, burning of coal and wastewater disposal (Guillot *et al*., 2018). Other imperative landbased human sources of heavy metals result from the development of mechanical, agricultural and urban exercises since the mid-60s (Tanaka, 2006).Trace elements can be categorize as essential and nonessential. Nonessential metals such as mercury lead, cadmium and arsenic have no biological role and maybe toxic even in minute concentrations (Wood, 2011).

2.2.1 Copper

Cu is introduced into the marine ecosystems through anthropogenic sources such as coal mining, fertilizer production, smelting of ore and effluent discharge from surrounding industries. (Lenntech, 2015). Cu is an essential trace element found in marine organism (Nelson *et al*., 2014) which often accumulates in some fish species at elevated levels that apprehend growth and development (Hall *et al.,* 1988). This may, in turn, have adverse effects such as olfaction (Baldwin *et al.,* 2003) and reduced sperm and egg production in the fishes (Taub, 2004). According to CDA (1998), the normal level of copper in whole fish tissue is one to two parts per million.

The mean Cu levels in the fish species varies from 5.27 ppm in *Sarotheron galilaeus* to 144.93 ppm in *Parachanna* fish in the Weija Lake, Ghana (Ansa-Asare, 1999). Mansour and Sidky (2012) reported mean copper levels in a fish sample obtained from a marine water body to be 1.1 ± 0.4 mg/L in a study conducted in fayoum Governorate, Egypt. Akter *et al*., (2015) reported mean copper levels in tilapia obtained from freshwater in India to be 5.2 ± 0.11 mg/kg. Ahmed *et al*., (2012) conducted a study in copper levels in salmonella fish obtained in a lagoon in Bangladesh and the average copper concentration in the stomach of fish was reported to be 12.00 mg /kg dry wt. Concentrations were 6.32 mg/ kg dry wt in the gills and 4.24 mg /kg dry wt. in the muscle. The copper levels in most fish samples obtained from the United States marine waters ranged from 0.382.35mg/kg with an overall average of 0.65 mg/kg, with the maximum being 23.1 mg/kg (Ahmed et al., 2010).

In Ghana, Gbogbo *et al*, 2018 reported mean concentrations of 6.76 mg/kg, 4.45 mg/kg and 10.52 mg/kg in Sardinella, Dentex and Penaeus respectively. Another study by Armah *et al*, 2016 on the trace metals accumulation on selected marine fish sold in the

Ghanaian market reported 3.01 mg/kg and 6.67 mg/kg for tuna and barracuda.

2.2.2 Zinc

Zinc occurs naturally in air, water and soil but in the marine environment, it occurs mainly through anthropogenic sources such as mining, coal, waste combustion and steel production (Lenntech, 2015). It accumulate even in minute concentration in organisms and considered to be relatively non-toxic, especially when taken orally (Qu *et al*., 2014). Fishes may also bioaccumulate and bio-magnify zinc in their bodies when exposed to zinc-polluted waterways (Lenntech, 2015). Giardina *et al.* (2009) in their study on the heavy metal levels in fish samples observed that high levels of zinc in fishes may lead to physiological effects, growth retardation and effect on populations and kill adult species. Ahmed et al., (2013) reported average Zn concentration in stomach, gills and muscle of fish to be 12.74, 9.91 and 5.05 mg /kg dry wt., respectively in a study on induced toxicity and histopathological changes of freshwater fish, tilapia (Oreochromis mossambicus). Ansa-Asare, (1999) reported Zn levels in fish samples taken from the Weija reservoir, Ghana to range from 5.87-18.5mg/kg. Mansour and Sidky (2012) reported mean Zn levels in fish sample obtained from a freshwater body to be 0.75 mg/kg in a study conducted in Egypt.

The level of Zn in marine species in Ghana is within permissible limits with few exceptions. Nyarko *et al.*, 2012 study the accumulation pattern of trace metals in marine species landed in the coastal communities in Ghana and reported an average concentration of 2.04 mg/kg. Other findings by Armah et al., (2016), Bandowe et *al*., (2014) and Hogar et al, (2018) reported Zn levels to be within the WHO permissible

limits.

2.2.3 Arsenic

Arsenic is introduced into the marine environment through weathering procedures (Zeitoun & Mehana, 2014). Human sources include smelting activities, mining and mechanical emissions from coal-consuming electric producing facilities (Schwarzenbach *et al*., 2010). The toxicity of arsenic is based on the compounds and the valence state of the arsenic atoms. Inorganic arsenic compounds (trivalent) are detrimental to health than organic arsenic compounds (pentavalent) (Jomova *et al*., 2011). Fish is a key source of arsenic exposure in the human diet (Mohammed, Kapri & Goel, 2011). Notwithstanding, over 90% of arsenic contained in edible parts of fish is present as the arsenic-containing natural compound arsenobetaine with no human threat (Kjelland *et al*., 2015).

The amount of arsenic in fishes might be high due to the intake of phytoplankton which is a primary producer in marine ecosystems. Due to harmful natural of arsenic, fish that contains significant levels of inorganic arsenic may posed risk to human health (Ebrahimi & Taherianfard, 2011). Marine vertebrates inhabiting As polluted environment may accumulated elevated concentrations

Ahmed *et al*., (2013) studied arsenic induced toxicity and histopathological changes in gill and liver tissue of freshwater fish, tilapia. The levels ranged from 0.19 to 65 mg/kg in gills, 0.2 to 125.9 mg/kg in the liver. Koch *et al*. (2011) also reported total arsenic concentration of 0.28 to 3.1 mg/kg in Sardinella from Mediterranean.

Arsenic pollution is a major environmental challenge comforting developing countries due to the release of arsenic residues from Arsenopyrite ore during gold mining (Armah *et al*, 2012) for which Ghana is no exception. Previous studies have shown elevated levels of Arsenic in sediments from mining communities, estuaries and near shore sediments in Ghana. Previous studies on As in Ghanaian waters revealed elevated levels

(5.7 -94.0 µg/g) in sediments from coastal waters (Mahu *et al*. 2015) and 3.45 – 142 µg/g estuarine sediments (Mahu, 2014).

Another study by Klubi *et al.*, (2017) on the impact of gold mining activities on trace metals enrichment from selected estuaries in Ghana reported (35-75 ug/g) for Ankobra and (23-54 ug/g) for Pra estuary respectively which is above the sediment probable effect level. Botwe *et al*., (2108) on their study on chemical contamination for sediment from the Tema harbour in Ghana reported arsenic levels (23 mg/kg – 89 mg/kg) above the sediment quality criteria

2.2.4 Cadmium

Cadmium exist naturally in the environment at extremely low concentrations (USEPA, 2016). Shellfish can accumulate high levels of cadmium compared to other marine species due to their high affinity for cadmium. Natural processes such as weathering of rocks, forest fires and volcanic eruptions release cadmium into the atmosphere (Lenntech, 2018). Mining activities and the use of agricultural products such as pesticides and fertilizers are anthropogenic ways through which cadmium are released into water bodies (Lenntech, 2018; USEPA, 2016). Industries release cadmium into the environment as a by-product of zinc, lead and copper extraction (Lenntech, 2018).

Aquatic organisms such as mussels, shrimps, lobsters, oysters and fish are more susceptible to cadmium bioaccumulation (Lenntech, 2018). Acute exposure of aquatic organisms to cadmium toxicity causes increased mortality, growth impediment and destruct reproductive systems (USEPA, 2016). Human toxicity to Cd includes bone marrow deformation, elevated blood pressure, brain damage and blurred vision. In sensitive populations like pregnant women high Cd levels may destroy placenta formation and lead to bone deformation in the fetus. (Lenntech, 2018).

Cornejo-Ponce *et al*. (2011) reported cadmium levels in gills of fish samples obtained from Bangladesh lagoon water in Bangladesh to be 0.0017– 0.0151 ug/g. The mean Cd value reported by Koch *el at*, (2011) varies from 0.031-0.042 ug/g, and 0.024 -0.032 ug/g in Sardinella and horse mackerel obtained from the Atlantic Ocean in eastern Portugal. Elevated levels of cadmium (0.94 ± 0.036 mg/kg, ww) were also reported in chub mackerel in a study conducted on cadmium-induced toxicity in marine species (Akter *et al*., 2015).

Gyimah *el al*, (2018) studied the health risk from the consumption of contaminated fish obtained from Barekese reservoir in Ghana and reported 6.09 ± 1.03 ug/g ww, 6.09 ± 0.83

ug/g ww and 110.5 ± 7.85 ug/g ww for Oreochromis, *Tilapia Zilli* and *Heterotis niloticus* respectively. These concentrations are extremely above the permissible limit for Cd in seafood set by WHO. Another study by Nyarko *et al*., (2013) in trace metals assessment from selected marine fishes in Tema-Ghana reported Cd levels below detection limits for *Chloroscombrus chrysurus* and *Sardinella maderensis*.

2.2.5 Mercury

Over 90 percent of mercury pollution comes from human activities such gold mining, coal production, by-products of industrial processes and dental amalgam (Sonke *et al*., 2013). In aquatic environments, the mobility and bioavailability of Hg are significantly influenced by processes such as the solubility, acidity and alkalinity as well as the organic matter content (Randall and Chattopadhyay, 2013).

In the aquatic environment, Hg exists in an elemental volatile form, Hg^{o}, which is relatively non-reactive and several toxic mercuric species such as $Hg2^{+,}$ and organic Hg, mainly monomethyl mercury (MeHg), dimethylmercury (Me_2Hg) and some ethyl (EtHg) mercury. Wetland and estuarine sediment commonly have lower oxidation-reduction potential (ORP) which is one of the routes of Hg speciation. Decreasing ORP promotes microbial-mediated sulfur reduction, which promotes the methylation of Hg (Randall and Chattopadhyay, 2013). There is no biological requirement for Hg 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).

Higher levels of mercury were observed in catfish recording as high as 0.5±0.01 ug/g which exceeded the permissible limit of 0.0001mg/l recommended by the European

Union for human consumption in a study conducted in Northeast and Eastern Central Atlantic Ocean in Portugal. High concentrations of mercury in sediment (2.18 mg/kg) and fish tissues such as liver muscles and gills of mudfish (0.723 mg/g) have been reported in a study by Newman (2012). This is so because these fishes are bottom feeders and feed on sediments and can accumulate higher concentrations of heavy metal.

2.2.6 Lead

According to Lenntech (2018), Pb is not usually found alone in its metallic form naturally. It bonds in ore with zinc, silver and copper and it is extracted together with these metals (Lenntech, 2018). Concentrations of Pb found in the environment are mostly as a result of human activities such as combustion in car engines, waste from batteries and paints as well as other industrial effluents (Karrari *et al.*, 2012). Lead has been used throughout history for applications ranging from metal products, cables, pipelines to paints and pesticides. The widespread use of Pb has increased its residues throughout the environment (Raeisi *et al.*, 2014). In Ghana, indiscriminate electronic waste disposal is the leading cause of Pb contamination in the environment. Till date, there is no known biological function of Pb (Agusa *et al.,* 2015; Lenntech, 2018). However, when aquatic organisms ingest Pb in water, it bioaccumulates in their bodies (Lenntech, 2018). It affects body functions of phytoplankton on which numerous organisms in the aquatic ecosystem depend on.

Accumulated Pb in fish causes health effects to humans when consumed, these include; disruption of the biosynthesis of haemoglobin and anaemia, nervous and brain damages, declines in fertility in male organisms (Lenntech, 2018). Lead is non-essential trace metals and tends to bioaccumulate in organisms through the food chain (EFSA, 2010). Lead may articulate with the natural structures, for example, tetraethyl Pb seems to have the best potential for bioaccumulation in fish (Doney *et al*., 2011). High concentration of Pb has been found in marine bivalves and finfish from estuaries and marine waters (Mitra & Zaman, 2017). The United States Environmental Agency (USEPA) characterises lead as perilous to most types of life and open to aquatic organisms (Huang *et al*., 2014). Pb levels in Ghana coastal waters has decreased slightly over the past decade owing to the ban on the use of lead fuels, lead paints, lead base pesticides and proper management, control and disposal of electric waste (Nyarko *et al*., 2013). Ansa-Asare (2014) reported lead levels to range from 0.09- 04.28 mg/kg in a study conducted in Sakumono estuary in Ghana. Another Study by Nyarko *et al*., (2013) reported lead concentration below detection (<0.04 ug/g) in selected marine species from Tema fishing harbour.

2.3 Factors Influencing Bioaccumulation of Trace Metals

2.3.1 Six and Age

The size and age of an organism have a significant effect on its vulnerability, sensitivity and susceptibility to trace metal toxicity. In a review article, Alavian-Petroody *et al*. (2106) studied the correlation between metals accumulation and age of rocky oysters (*Saccustrea cucullata*). The results show that Cd, Pb and Ni accumulation was significantly higher in juvenile oysters than matured once. Another study by Amisah *el al*. (2009) on the toxicity of heavy metal accumulation on clam size from the Volta estuary in Ghana also reported higher concentrations in immature clam compere to mature once.

These censuses are in agreement with previous works by Yap *el at*. (2009), Hedouin *et at*.(2006) and Lui *et al*.(2015) who stated that, juvenile marine organisms are more sensitive and less tolerant to metal accumulation due to high growth, feeding and metabolic rates than adult organisms, and also spawning lead to sudden loss of heavy burden and weight loss in mature organisms. However, the relationship between metal accumulation and fish size is inconsistent. Other authors have reported a positive correlation between age and size with metal bioaccumulation. Jie *et al*. (2107) on their study on the effect of heavy metal in freshwater fish fishes: species, tissue and size revealed that Pb, Cd and Zn bioaccumulation increase with size and age. Other findings by Ji & Zhang (2012) on the relationship between metal concentration and fish size established a strong correlation between Hg bioaccumulation with size and age. The continuous and longtime exposure of aquatic organisms to a polluted environment could lead to elevated concentration of metals in the older organisms (Yi & Zhang 2012).

2.3.2 Species

Different marine fish species living in the same ecosystem may accumulate different concentration of heavy metals. This interspecies variations in metal bioaccumulation could be attributed to feeding pattern, ecology and habitat of the organism. Pouil *et al*. (2108) Observed that piscivorous species accumulated higher Hg concentration than planktivorous species due to the ingestion of contaminated preys. Elevated levels of total mercury have also been reported in carnivorous species contrast to non-predatory once (Renedo *et al.* 2017). This differences in Hg interspecies bioaccumulation could be related to the accumulation and inability of Hg to biodegrade in prey tissues as well as the continuous ingestion of contaminated preys in the aquatic food chain over time.

Vieira *et al*. (2011) wrote that organisms that feed on primary producers appear to bioacumulate higher arsenic concentration from planktons than predacious species. This is because, marine planktons ingest a large amount of arsenic and contributes to the accumulation, speciation and transfer of arsenic in the food chain (Bustamante *et al*. 2008). This is in agreement with Bawuro *et al*. (2018) who linked the accumulation metals to feeding habitat and concluded that plankton feeding species accumulate high Zn and Cu concentration contrary to predatory once.

Marine benthic organisms accumulate higher levels of As, Zn and Cd than pelagic species (Bodin *et al*., 2017) since sediments contain higher metal load than the water column. Metals released from either anthropogenic or natural sources into water column may bind with suspended particles and enriched in sediments through sedimentation (Caplat, 2015). The static equilibrium of the sediment-water interface may disintegrate owing to changes in environmental conditions and caused the released of metal into the overlying waters. This could relate the reason why benthivorous species may accumulate higher arsenic and cadmium than pelagic species.

2.3.3 Habitat

Fish habitat greatly influences the accumulation of heavy metals in the marine environment. A study by Bustamante *et al*. (2008) on the bioaccumulation of heavy metals in giant squid reported that total mercury bioaccumulation increase in deep oceans contrast to open waters due to the low levels of dissolved oxygen concentration, low pH and lack of solar radiation which influence mercury methylation process.

In support to the above affirmation, Mille *et al*. (2018) studied trace metals bioaccumulation in seven marine fish species in the Gulf of Lion and reported that benthivorous species accumulates higher concentration of Pb and Hg compared to pelagic species indicating bioaccumulation and transfer of metals in the aquatic food chain over time.Yi and Zhang (2102) in their studies, “heavy metal accumulation and fish size” also reported elevated levels of Mercury and Arsenic in yellow head catfish (Benthic species) contrary to Sardinella which a pelagic. Ahmed *et al*., (2014), Islam *et al*., (2015) and Copat *et al*., (2012) also reported similar findings. This interspecies variation in metals bioaccumulation could be linked to the habitat of the organism in the aquatic environment

2.3.5 Salinity

The mobility and toxicity of trace elements decreased with increase in salinity in aquatic systems due to cation exchange complexity on metal speciation (Acosta *et al*, 2011). Salinity increase will improve metal bioavailability and mobilization from solid sediment to the water phase due to the interference of excess cation effect on metal deposition (Verlycke *et al.,* 2003). Zhao *et al*. (2103) studied the effect of salinity on metal mobility in estuarine sediments and reported a significant increase in Cd availability with an increase in salinity. It is evident that Chloride anion concentration in salt increase with increasing salinity. These anions react with Cadmium ions to form complex compounds which interfere the stability and solubility of Cd in the solid phase, thus resulting in higher mobility of Cd in water for accumulation by aquatic organisms (Du Laing *et al*., 2009)

It is documented that the inclusion of salt solutions could steer a pulse of elevated acidity. The replacement of adsorbed protons on the surface of the negatively charged colloids by salt cations and divalent ion displaces reduced acidic metal cations (e.g., Al^{3+} and Fe^{2+}) from sediment exchange sites, with subsequent oxidation and hydrolysis causing acidification (Wong et al., 2010). Acidification influence the mobility of metals trapped in sediment phase especially those with high affinity for the carbonate fraction

Salinity variations affect the toxicity and bioaccumulation of Cu in marine organisms. Lee *et al*. (2010) studied the Influence of salinity on Cu accumulation and toxicity on estuarine organism in south China and reported high accumulation of Cu with increasing salinity.

Other studies by Mario *et al*. (2013), Boateng *et al*. (2015) and Mahu *el al*. (2016) also reported similar findings. The increase in Cu accumulation with salinity could account from the increase in the acidification caused by excess Na+ cations and the removal of Cu ions from CuSo42+ in sediments into water column under oxidation conditions (Diana *al et.* 2014).

2.3.5 pH

The effect of pH on chemical processes of trace elements is a significant factor that influences the mobility, availability and transformation of metals within the aquatic system (inmaculade *el at*., 2016). Ocean acidification caused by a decrease in pH will impact on the mobility and improve the availability of metals for adsorption. [16]. Tehervand & Jalali (2016) studied the impact of pH change on Cd speciation and mobility and reported that different speciation of Cd varies with the change of pH while the ionic reactivity of Cd decreased with the increase in pH indicating that, acidification enhanced the mobility of Cd.

Smolders & Mertens (2013) established that pH is the predominant factor that influences the assimilation properties of trace elements, which controls the stability of bicarbonates, and ionic characteristics of heavy metals in marine sediment. Previous work by Yobuet *et al*., (2010) reported that the metal toxicity and accumulation in aquatic ecosystems increase with increasing mobility in low pH medium. Contrary to Cd mobility and adsorption which increase with decreasing pH, Cu and Ni adsorption capacity increase with increasing pH. Zhang *et al*., (2016) investigated the correlation between acidification and Cu accumulation and recounted that the Cu mobility is weak in acidic medium owing to the formation hydroxonium ion and the presence of positively charged cations interaction with carbonate composition in sediment.

Mercury methylation describes the fundamental process that facilities the conversion of the various species from Hg to methylmercury (Bustamante *et al.*, 2008). $MeHg^+$ is the most toxic form among mercury species and has the propensity to bio-magnify through the aquatic food chain (Scheuhammer *et al*., 2007). The occurrence of methylation is enhanced by pH change, micro-organisms and organic matter composition (Schartup *et al*., 2015). Kelly *et al*. (2003) studied the "Effect of pH on mercury uptake by an aquatic bacterium and its impact on Hg cycling" and reported that the less change in pH by acidification accounted in a significant increase in Hg accumulation. This perceived correlation between MeHg+ levels in fish and acidification was due to the effect of pH in the methylation process.

Other studies by Yang *et al*. (2007), Jingying Xu *et al*. (2014), and Dunham *et al*. (2104) also reported similar findings and stated that the mobility, transformation, adsorption capacity and the conversion of Hg to MeHg+ in marine sediments is influenced by the complexation of hydrogen ions in acidic medium. The solubility and mobility of arsenic speciation in sediments are greatly influenced by pH Change (Sharma & Sohn. 2009). Feng *et al*. (2012) studied the behaviour characteristics of arsenic speciation and pH change in estuarine sediments. The result showed that the conversion of organic arsenic (predominant form) in marine waters is into inorganic arsenic occur mostly in slightly acidic to alkaline conditions accompanied by the reduction reactions. Prieto *et al*. (2018) on their studies on arsenic mobilization in polluted sediments and its consequences on bioaccumulation in the food chain reported similar findings.

2.4 Trace metals and Bioaccumulation

Trace metals are hazardous because they tend to bioaccumulate through the various trophic levels (Etim & Mbakara, 2017). Bioaccumulation suggests an increment in the concentration of a chemical in an organism after some time, contrasted with the chemical's concentration in the earth (Sabine and Wendy, 2009). Trace metals aggregate in living things whenever they are ingested and amass quicker than they are broken down (metabolised) or discharged (Pepper, Gerba & Brusseau, 2011). The bioaccumulation of trace metals emerges from serval environmental sources including air, water and diet (Wuana & Okieimen, 2011).

There are a number of physiological procedures and mechanisms that influence accumulation, sequestration, detoxification and storage of trace metals (Georgescu *et al.*, 2011). These physiological mechanisms control the bioaccumulation of trace metal via feedback structures that respond to environmental concentration and support homeostasis (Sigel, 2017). Although fish can regulate trace metal concentrations within their habitat, they are limited to specific levels after which bio-accumulation may occur (Chiarelli & Roccheri, 2014).

2.5 Effects of Trace metals accumulation In Fish.

A major global concern has been created about the various effects that heavy metals poses to the environment, animals, plants and human beings. Human take in most metals mainly through seafood such as fish (Lenntech, 2015). Cadmium accumulation in the marine organisms affects sensitive organs such as the liver, kidney, gonad development and hormone synthesis (Castro-González and Méndez-Armenta, 2008).

Although arsenic toxicity mainly occurs through drinking of arsenic-polluted waters, fish can also be a key source of arsenic exposure to human health (Chapman, 2013). Arsenic found in edible part of fish is an organic form with less human health risk However, fish may contain some proportion of inorganic arsenic which may cause malignant growth of the skin, bladder, lung and liver cancer depending on the level of exposure. (Mudgal *et al*., 2010). Lower level exposure of humans to arsenic through ingestion can also lead to decreased production of red and white blood cells, abnormal heart rhythm, damage of blood vessels, nausea and vomiting (Sabine and Wendy, 2009).

Moreover, mercury (Hg) and its compounds are highly toxic, especially methylmercury - a potent neurotoxin which accumulates in fish and the food chains that they are part of (Lenntech, 2015). High concentrations of methylmercury through the intake of fish can cause spontaneous abortion in pregnant women, congenital malformation and other disorders (Lenntech, 2015). It has caused a significant number of human fatalities in several parts of the world (Carr and Neary, 2008). For instance, the methylmercury poisoning incident involving fish was reported in Niigata, Japan during 1965 and it affected almost all the fish consumers who lived there (U.S.E.P.A, 1997c).

Furthermore, excess amounts of copper through fish intake by humans can cause system dysfunctions that result in impairment of growth and reproduction (Lenntech, 2015). However, researches that have been done in the past and recent times have reported that copper is not related to a high incidence of cancer to biological systems through fish consumption (Perrault, Buchweitz & Lehner, 2014).

2.6 Ecology of study organisms

2.6.1 Dentex angolensis (Poll and Maul 1953)

Dentex belongs to the Sparidae family commonly knowns as sea beams. Its main graphical distribution is from the coast of Morocco to Angola (FAO, 2014). It's the most dominant fish species landed in the western coast of Ghana mainly from Elmina, Sekondi to Axim by artisanal fishermen. Due to high market value and demand, Dentex is mostly preferred by populace from the middle-income class (Nunoo *et al*., 2014).The species is demersal and mostly caught with bottom trawl (FAO, 2014).

This species has a maximum length of about 37 cm but is commonly found to be 24 cm in length (FAO 2014; De Morais *et al.,* 2015). *Dentex angolensis* has an oval body which is moderately deep and compressed. The head profile is straight and its interorbital space is narrow with suborbital space being wide. It has a low mouth which is slightly oblique. It has several rows of canine-like teeth and that of the outer row is the strongest (FAO, 2014; De Morais *et al.*, 2015).

The scales are present on the cheeks and anterior part of preopercle and a lateral line has 45 to 49 scales. It is red in colour with silvery reflections with head darker and belly lighter. The dorsal and anal fins are also red except on their bases and pelvic fins are light coloured. The pectoral fin and caudal fin are also reddish (DeMorais *et al*., 2015; Aheto *et al.,* 2011).

Dentex angolensis is carnivorous and feed mainly on preys. Preferentially feed on crustaceans and prey on juvenile pelagic fishes as well. Previous study on the feeding habit of *Dentex angolensis* by Hamida *et al*. (2009) showed crustaceans and worms as the dominant food composition. The adult Dentex also feeds on shrimps from the family Decapoda and some species of cephalopod.

Plate 2.1 Dentex angolensis (Oceanbase.ca)

2.6.2 Sardinella maderensis (Lowe, 1838)

Sardinella maderensis is a small pelagic fish species of high commercial importance in Ghanaian waters and throughout the Western Gulf of Guinea (Tous *et al*., 2015; Koranteng, n.d.). It is also distributed along the Mediterranean Sea in the Southern and Eastern parts, penetrating also the Suez Canal and is in the family Clupeidae (Tous *et al*., 2015). It is mainly exploited by the artisanal and inshore purse seiners and also by industrial trawlers (Nunoo *et al.,* 2015).

Catches of *Sardinella maderensis* increased significantly when the purse seine net especially the poli net was introduced (Koranteng, n.d.). Coastal upwelling affects catches of sardinellas in the Western Gulf of Guinea (Nunoo *et al.,* 2015). *Sardinella maderensis* has an elongate body which is fairly strongly compressed in some and grows to a length of 25-30cm. The belly has a moderately sharp keel of scutes. *Sardinella maderensis* has no postopercular spot, but a golden or sometimes blackish area just behind the gill opening

(Froese & Pauly, 2017). The body is covered with cycloid scales in a longitudinal series to the base of the caudal fin (Tous *et al*., 2015). Breeding in *Sardinella maderensis* occurs once a year and this is during the warm season which is July-September. Sexual maturity is known to occur during its third year of life. Fertilization is external and shows no parental care (Tous *et al*., 2015).

The trophic level in which marine organisms belongs to determine their sustainability, survival and relative position within the marine food hierarchy (Tsikliras. 2005). Sardinella species are categorized into group three in aquatic food rating which classifies them as herbivores (Pauly *et al*., 2000). Sardinella predominantly feeds on crustaceans, marine plankton and fish larvae. Previous study on dietary composition, feeding pattern and trophic level of *Sardinella maderensis* by Tsikliras et al. (2005) showed that crustaceans from the family copepods, amphipods and decapods form 52% of vacuity index followed by zooplanktons in which diatoms and blue-green algae were the main prey. Other studies by Morote *et al*., (2008), Shah *et al*., (2019) and Bahar *et al* (2015) also reported crustaceans and zooplanktons as the dominant food preference.

Plate 2.2: *Sardinella maderensis* (oceanbase.Com)

2.6.3 Sphyraena sphyraena (Linnaeus, 1757)

Sphyraena sphyraena can be found in the Eastern Atlantic, from the Bay of Biscay to Mossamedes, Angola, including the Mediterranean and Black Sea, Canary Islands, and Azores. In the Western Atlantic, it also occurs at Bermuda and off Brazil" (Froese & Pauly, 2017; Carpenter & De Angelis, 2016). *It belongs to the family* Sphyraenidae, and the species is harvested mainly with nets such as bottom or pelagic trawls among others (De Morais *et al.,* 2015).

Sphyraena Sphyraena has a maximum length of 165 cm but is commonly found to be about 60 cm in length. It has an elongate, cylindrical body and head is large with a long pointed snout. It possesses teeth which are strong, conical and erect, with the width of their bases less than the interspace between adjacent teeth. Teeth are also present on the roof of mouth. Its caudal fin is deeply forked and the posterior margin of each lobe is straight. It has a series of about 20 to 22 angled cross-bars along its upper sides. The bony edge of its opercle ends in a single point and the tip of the lower jaw has a distinctive fleshy tip (Carpenter & De Angelis, 2016).

The maxilla does not reach the anterior eye margin. The body is dark above and silvery below (Marine Species Identification Portal, 2016) with the upper part of the head and maxilla being black as well as the fins. The pelvic have white anterior margins. Scales are present with lateral line scales being 120 to 150 in number. It has a well-developed keel which is formed by the lateral-line scales at the posterior region. The gill cover is also completely scaled. The first dorsal fin is directly above, or slightly in front of, pelvic-fin origins (Carpenter & De Angelis, 2016).

Sphyraena species are predominantly piscivorous and prey typically on small pelagic fish mainly *Engraulis encrasicolus* and some demersal species (Ragheb 2000). Seasonal variation influences its feeding pattern which is relatively high in the dry season. As top predators, the continuous prey on contaminated prey species increases its propensity to accumulate contaminants within the food chain (Bustamante *et al* 2008). A study on feeding habit of Sphyraena barracuda by Akadje *et al*. (2012) showed that Sardinella, Penaeus species and Engraulis were the main prey which represented 68% of it vacuity index while crustaceans were the minor prey. Barracudas are opportunistic, prey and feed as scavengers on dead remains of fish from shark kill (Nelson, 2007).

Plate 2.3: *Sphyraena sphyraena* (fishbase.org)

2.6.4 *Penaeus notialis*

Penaeus notialis belongs to the family Penaeidae which is the largest of the superfamily Penaeoidea. Penaeidae, also known as penaeid shrimp or penaeid prawn, is a family of marine crustacean in the suborder Dendrobranchiata (Richmond, 2002). *Penaeus notialis* is distributed along the West African coast from Mauritania to Angola (East

Atlantic) and in the Greater Antillers from Cuba to the Virgin Islands and on the Atlantic coast of Middle and South America from southern Mexico to Brazil. They are one of the most valuable fishery resources, particularly in areas where conditions are favourable such as the Gulf of Mexico, some part of West Africa and in Southeast Asia from the West coast of India to the Gulf of Carpentaria (Adelugba & Edah, 2014). They are fished extensively by trawls, seine nets, traps and artisanal gears (Lawal-Are & Akinjogunla, 2012).

The maximum carapace length for a male is 4.1 cm and that of the female 4.8 cm (Palomares & (Pauly, 2017; Lawal-Are & Akinjogunla, 2012). *Penaeus notialis* can be found at depths from 3 to 700 m and most common at depths from 10 to 75 m. It inhabits bottom mud or sandy mud, and sandy patches among rocks in the marine environment (Palomares & Pauly, 2017; Lawal-Are & Akinjogunla, 2012). Generally, the majority of penaeids are omnivorous, feeding on varying proportions of sediments, detritus, algae and benthic organisms (Adelugba & Edah, 2014).

Plate 2.4: Penaeus notialis (crustiesoversea.free.fr)

2.7 Previous Works

Over the years, there has been a growing interest of researchers in the area of heavy metal concentration in the aquatic environment due to the risk these metals pose to human health through consumption of fish and other aquatic resources. Though heavy metal studies are still in its infancy across Africa, largely due to lack of adequate equipment, there have been a number of research works on heavy metal accumulation. Developed countries are however well advanced in their study of trace metal contamination and their related toxicities. Some research works from across the world will be cited below.

Molina (2011) reported lead as the most urgent pollutant among the other heavy metals analyzed in terms of its high non-carcinogenic health risk values recorded in the fishes. He also reported the carcinogenic health risks of arsenic in the fish species because it was the only confirmed human carcinogen through the route of ingestion among all the other metals he analyzed and concluded that fish products from Laguna de Bay were not fit for human consumption.

Bhupander & Mukhejeree (2011) assessed heavy metal levels in muscle tissues of fish from Kolkata wetland and estimated the human health risk posed by fish ingestion. This study concluded that the non-carcinogenic health risks for individual metals were below 1, however, the carcinogenic health effects of As, Cu, Ni and Zn were found to be marginally high.

Agusa *et al.* (2015) assessed the concentration of heavy metals in the liver and muscles of different marine species in Malaysia found out that trace metal concentrations were higher in the liver than the muscles. They also observed that some of the fish species had higher levels of Hg due to oil contamination in the area. Apart from the concentrations of the trace metals, they also estimated the health risk to the Malaysian population through the consumption of fish by estimating intake rates based on the concentrations of trace metals in fish muscles and daily fish consumption. Levels of heavy metals were compared with guideline values of the USEPA. Some species had higher levels of Hg, indicating that consumption of such species at the estimated rate may be hazardous to the Malaysian population.

Bandowe *et al.* (2014) in their research, estimated trace metal levels in the muscle of three demersal fishes along the coast of the Ghana. "They observed that the trace metal concentrations in the fish tissues were in the medium range when compared to fish from other parts of the world, however, the concentrations of some trace metals (Cd, Cu, Fe, Mn, Zn) were higher in guts and gills than in muscle tissues". The calculated THQ was less than 1, indicating that consumers were safe. They concluded that health risk arising from the consumption of the studied fish species is minimal. In another advancement, Nyarko *et al*. (2013), studied the concentration of metals in two commercially important marine fish landed in Ghana. The levels of Cd, Hg, As and Pb reported in their studies were within the permissible limit set by WHO and the European Commission. The estimation of their risk didn't reveal any potential health implications to the exposure population.

2.8 Analytical methods for the determination of trace metals

Modern methods that can be used to determine the concentrations of trace elements in environmental matrices include Anodic Stripping Voltammetry (ASV) and the use of Ion-Selective Electrodes (ISE) which are based on electrochemical principles (Yikpo, 2014). Other methods also employ Nuclear Proton-Induced X-ray Emission (PIXE), Instrumental Neutron Activation Analysis (INAA), X-ray Fluorescence (XRF), Atomic

Absorption Spectroscopy (AAS), Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Yikpo, 2014).

Inductively Coupled Plasma Mass Spectrometry or ICP-MS is an analytical technique used for elemental determinations. The technique was commercially introduced in 1983 and has gained general acceptance in many types of laboratories. Geochemical analysis for environmental samples is preferred using ICP-MS technology because of its superior detection capabilities, particularly for the rare-earth elements (REEs). ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICPAES),

2.8.1 Determination of Mercury by Direct Mercury Analyzer (DMA 80)

The milestone DMA -80 is the most successful mercury analyzer for environmental samples (solids, liquids, gas). Dried samples are chemically decomposed under oxygen within the decomposition furnace. The decomposed products are carried out to the catalytic section of the furnace where oxidation is completed with halogens, nitrogen and sulfur oxides trapped. Mercury present in the remaining decomposition product is selectivity trapped on an amalgamator after flushing the system with pure oxygen. The mercury vapour is released by rapid heating of the amalgamator and carried through the absorbance cell in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance is measured at 253.7 nm as a function of mercury quantity (ng) (USEPA 2007).

2.9 Health risk assessment

Trace metal contamination, especially for non-essential metals, has the potential of causing health issues. Health risk assessment, after evaluating metal concentration in the environment, is important because it tells whether human consumption of aquatic resources from a contaminated area could pose health problems. The U.S Environmental Protection Agency (2012) defines human health risk assessment as the characterization of potential health risks to humans as a result of exposures to environmental hazards.

Health risks posed by trace metals through fish consumption is classified as carcinogenic or non-carcinogenic effects (Peng *et al.*, 2016 as cited in Yi *et al*., 2017). Carcinogenic effects are estimated by comparing exposure concentrations with thresholds for adverse effects, as determined by dose-effect relationships (Solomon et al., 2013 as cited in Yi *et al*., 20170. Non-carcinogenic effects are determined using the Target Hazard Quotient (THQ) model created by the U.S Environmental Protection Agency (U.S.E.P.A).

The THQ takes estimates of the maximum permissible risk on human population through daily exposure, taking into consideration a sensitive age group during a lifetime (Li and Zhang, 2010 as cited in Mahfuza *et al.,* (2017). THQ does not give estimates of the probability of experiencing adverse health effects for an exposed population, however, it indicates the risk level associated with pollutant exposure (Yi *et al.*, 2017).

CHAPTER THREE

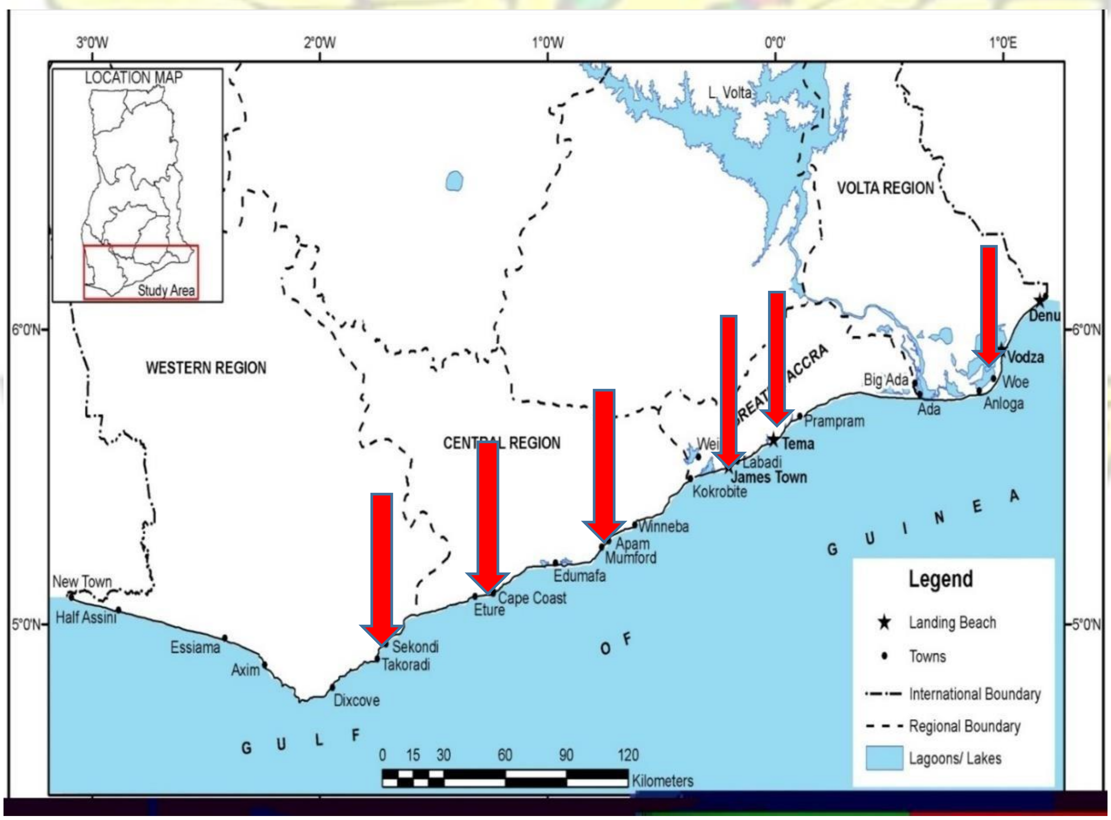
3.0 MATERIALS AND METHODS

3.1 Study Area

The Tema fishing harbour is situated in the eastern coast of Ghana along the Gulf of Guinea in Accra the capital of Ghana with an estimated population size of over four million inhabitants (GOG, 2019). The harbour consists of two main segments, the fishing sector which comprises of the inner and outer fishing harbour as well as the canoe basin and the main shipping port (GPHA. 2016). The harbour serves as a primary route for import and export of goods and services into the county as well as neighbouring countries in the northern part of Ghana. Also known as the industrial city, Tema harbour is noted for its heavy industrial activities due to the situation of numerous companies around its vicinity. The occupation of these industries constitutes pollution due to the discharge of industrial waste into ways which eventually enters the ocean (Nyarko *et al.*, 2011). Beside industrialization, maritime activities such as shipping at the harbour pollute the coastal environment through oil spillage and leakage during and after the discharge of oil for transportation to the Tema oil refinery at the oil berth. (Nyarko *et al*., 2011).The recent establishment of the power barge for electricity generation at the fish harbour also contribute to the pollution of heavy metals.

The Albert Bosomtwe Sam fishing harbour popularly known as Secondi-Takoradi fishing market is located at the western coast of Ghana in Takoradi the capital of the western region with over two million inhabitants (Ghana Statistical Service. 2012). The fishing harbour consists of industrial, semi-industrial and a canon section with fish processing and preservation facilities. Located a few meters from the Takoradi main harbour which is the second largest port in Ghana serves a center of transportation of raw materials and crude oil within Ghana. Other sampling stations involved in these studies includes the Elmina fish market, James town, Apam and Kate fishing market in the Volta region.

Fish samples were obtained from canoe fishermen as soon as they were landed. Fish landed at the Tema fishing harbour are caught from the near-shore and offshore areas in Tema, Sukumo, Teshie, Osu, Prampram and its environs those from Apam fishing market are caught from Winneba, Apam, Mumford, Ekumfi-narkwa and salt pond. Fish Keta are mostly caught from Dzita, Anloga, Woe Keta, Kedzi and Adina whereas those from Sekondi fishing harbour are caught from nearshore and offshore areas of Shama, Aduesi, Aboadza, Sekondi and Takoradi. Final fish from Elmina fish landing beach are mostly caught from offshore and nearshore areas of Biriwa, Anomabo, Moree Elmina and Komenda. These areas have been impacted through various anthropogenic activities such as shipping, fishing, industrialisation, mining and urbanisation.



Map of Ghana showing study locations

3.2 Field Sampling

3.2.1 Fish collection

Freshly caught *Sardinella maderensis, Sphyraena sphyraena, Dentex angolensis and Penaeus notialis* from Ghanaian coastal waters were purchased from Six (6) major landing harbours (Fig. 1) along the 560 km coast of Ghana from July to September 2018. Fish landed in these major landing sites represent fish from the nearshore and offshore areas of the Ghanaian EEZ as well those of neighbouring countries such as Cote D'Ivoire, Togo, Benin and Nigeria. These fish species are among the most heavily consumed fish by the Ghanaian population and are of great economic importance (kwei & Ofori, 2005). Fish of different sizes were selected for analyses as size influence bio-accumulation of metals. A total of 200 individuals (10 individuals per species at each landing site) were used for the analysis. The fish specimen was washed with distilled water to remove adhering particles, wrapped in well labelled sterile polyethylene bags, and transported on ice to the Wet Laboratory of the Department of Marine and Fisheries Science, University of Ghana. Sample preparation was performed as per the EPA Guide No. 823-B-00-007 (EPA 2008).

3.2.2 Sample Preparation

In the laboratory, vital information such as weight and standard length were used in computing the condition factors of the different fish species (Table 1). Fish samples were placed on a PTFE cutting board and scales removed by scrapping using titanium knife.

Cross contamination was avoided by rinsing the blade with ultra-pure water between fish. Exactly 20 g of muscle tissue was removed from each individual fish of the same species from each landing beach to form a composite sample.

The samples were freeze-dried at -80°C for 48 hours to constant weight and homogenized. The moisture content of the fish samples was also determined. The estimation of moisture content was relevant for converting dry weight concentration to wet weight concentrations for comparison with international guidelines and regulatory limits which are set on wet weight bases. The dried samples were homogenized using a high-speed stain steel blender. The processed samples were sealed in an airtight plastic bag for trace metal analysis at the Research Centre of Toxic Compounds in the
Environment, Masaryk University, Czech Republic.

3.3 Analytical methods

3.3.1 Sample digestion

A dry weight of 0.2 g of a homogenised sample was weighed in labelled DPA-K60 pressure vessels made up tetrafluoromethoxylene (TFM). Concentrated nitric acid (4 ml Merck p.a) was added and samples were left at room temperature for at least 1 hour after which 2 ml of hydrogen peroxide (Merck p.a) was added. The reactor tubes were firmly closed and placed in a microwave oven (Berghof-MWS3, Bergdorf speedwave®, Eningen, Germany) for digestion using the program below.

Table 3.1 Program sequence for microwave digestion

Step	Power (W)	% power	Ramp time (min sec)	PSI	°C	Hold time (Min sec)
1	1200	100	5	600	50	5
2	1200	100	5	600	100	5
3	1200	100	10	600	200	8

The digested samples were cooled at room temperature after which the valves were cautiously opened to enable the pressure in the reactor to expel. The samples were then transferred into labelled 50 ml polypropylene graduate cylinders and diluted to 50 ml with Milli-Q water and shaken. (USEPA Method 2003). Two blanks and one certified reference material was digested with each batch of sample digestion. Certified reference material of similar composition was used.

Plate 3.1 Microwave digestion of fish samples

3.3.2 Analysis of Metals

The concentration of trace metals (Pb, Cu, As, Cd and Zn) in the samples were analysed utilising an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent 7700 series) at Research Centre for Toxic Compounds in the Environment, Masaryk University, Brno-Czech Republic. Multi-component Standard XTC-13 (Spex CertiPrep®, Metuchen, USA) solutions were utilised to set up a calibration curve.

Plate 3.2 Analysis with ICP-MS

Mercury was analyzed using Solid Thermal Decomposition Atomic Absorption Spectrometry by the automated mercury analyzer (AMA - 254) at Research Centre for Toxic Compounds in the Environment, Masaryk University, Brno-Czech Republic. About 200 mg dried homogenized sample was weighed into a tared sampling boat and preheated for 60s at 100^{o} C. The samples were further heated for 160 s at 780^{o}C to vaporize mercury. With the continuous flow of oxygen, the vaporized mercury was trapped in a gold amalgamator tube and heated at $355\ ^{o}$ C to release the trapped mercury into the atomic absorption spectrophotometer detector at a wavelength of 257.3 nm of its concentration to be detected and quantified. The mercury concentrations were recorded on mg/kg dry weight (EPA Method 7473).

3.3.3 Quality assurance

Super pure reagent grade chemicals (Merck PA) were used in all analytical methods. Milli-Q water was used for solution preparation. The methodology was validated by analysis of certified reference material DORM-2 Dogfish Muscle (National Research Institute of Canada -CNRC) and by the analysis of samples spiked with a known concentration of analytes. Results of analysis of certified reference material, spike recoveries and method quantification limits can be found in (table 1). Typical relative standard deviations for replicate analysis were in a single unit of percents.

Table 2.3 Quality assurance of trace metal analysis determined by the use of certified reference material DORM-2 Dog fish Muscle, NRC-CNRC

Elements	Limit of quantification (mg/kg)	Measured Concentration (mg/kg)	Certified Concentration (mg/kg)	Spiking recoveries (%)
Pb	0.3	0.078 ± 0,041	0,065 ± 0,007	101±1
Cu	0.08	2,17 ± 0,08	2,34 ± 0,16	96±6
Zn	2	26,4 ± 2,3	25,6 ± 2,3	97±2
As	0.004	17,3 ± 0,8	18,0 ± 1,1	108±6
Cd	0.0006	0,043 ± 0,003	0,043 ± 0,008	99±1
Hg	0.0003	4,48 ± 0,08	4,64 ± 0,26	n/a

3.4 Statistical analysis

The data was analysed utilising the MATLAB 9.4.0 (MATLAB, USA) statistical tool. The average concentration and standard error of the metal in fish species were determined. Multivariate post hoc Tukey tests were utilised to analyse the statistical significance of the distinctions among mean concentrations of trace metals among various fish species for each metal. The interrelationship between trace metal bioaccumulation in fish species were determined using Pearson correlation analysis.

3.5. Human health assessment risk

3.5.1 Estimated daily intake of metal

The dietary exposures of trace metals for children and adults were calculated using average trace metal concentrations in fish species. "Nine different age-categories, children 1-3years (14 kg), 4-6 years (21 kg), children 7-10 years (32 kg), adolescents 11-14 years (51 kg), adolescents 15-19 years (67 kg), adults 25-54 years (77 kg), adults 5564 years (77 kg) and seniors > 65years (72 kg) were used in the estimation of health risks (USEPA, 2008). "The estimated dietary intake was compared with the current provisional maximum tolerable daily intake (PMTDI) ug/person/day) of the Joint FAO/WHO Expert Committee on Food Additives" (JECFA, 2009: FAO, 2016). "The estimated daily intake (EDI) of each metal per meal of fish consumption was estimated for the various age categories" (Copat *et al*. (2012).

$$EDI = \frac{\mathrm{FIR} \times \mathrm{C}}{\mathrm{BWa}} \quad (1)$$

Where, *FIR* is the fish ingestion rate which, set at 76.7g/day for Ghana (FAO, 2016), *C* is the metal concentration in fish [ug/g w.w)] and Bw is the average body weight of the different age groups ranging from 14 kg to 77 kg.

3.5.2 Non-cancer-causing hazard

While the method for estimating target hazard quotient (THQ) does not provide a quantitative estimate of the probability of an exposed population experiencing adverse health effect, it does provide an indication of the risk level due to pollutant exposure (USEPA, 2010). The THQ measures the ratio of a single substance exposure level over a specified period (e.g., sub-chronic) to a reference dose (RfD) for that substance derived from a similar exposure period (USEPA, 2010). THQ assumes a level of exposure (i.e., RfD) below which it is unlikely for even sensitive populations to experience adverse health effects. If the exposure level (E) exceeds this threshold (i.e., if THQ = E/RfD exceeds unity), there may be concern for potential non-carcinogenic effects (USEPA, 2010). If the THQ value is less than 1, the exposed population may not experience any adverse health effect. However, if the value of the THQ is above one, it means the exposed population through the consumption of contaminated fish is likely to experience toxic effects. The higher the THQ value, the higher the probability of the hazard risk on the exposed population. The THQ was estimated from the following equation

$$THQ = \frac{EF \times ED \times FIR \times C}{RfD \times WAB \times TA} \times 10^{-3} \quad \text{(USEPA 2011)} \qquad (2)$$

Where EF is exposure frequency (365 days/year); ED is exposure duration for the 9 diverse age classifications. The ED is set at 4 years (ages 4 through 6), 7 years (kids 7 to

10 years), 11 years (young people 11 to 14 years), 15 years (youth 15-19 years), 25 years (adults 25 to 54 years) and 55 years (adults 55 to 64 years) and 66 years (Vieira *et al*., 2011). FIR is the fresh food ingestion rate (fish = 76.7 g/individual/day) (FAO 2016); C is the metal concentration in fish (ug/g ww); RFD is the oral reference dose, which represents an estimation of the daily exposure to which human populace might be consistently exposed to a contaminant over a lifetime without an obvious danger of harmful impacts. The oral reference dosages of 0.003, 0.04, 0.005, 0.0003, 0.001 and 0.0035 mg/kg/day for Hg, Cu, Zn, As, Cd and Pb, individually were utilised in evaluating the THQ. WAB is the normal body weight and TA is the normal introduction time for non-cancer-causing agents (365days/year × ED).

3.5.3 Hazard index

For the combined effect of trace metal damage in fish, a total Hazard Index (HI) was utilised. The HI from THQs is shown as the total of the hazard quotients.

HI=THQ (Hg) +THQ (Cd) +THQ (Cu) +THQ (As) +THQ (Zn).

3.5.4 Carcinogenic risk (TR)

For cancer-causing agents, risks were evaluated as the steady likelihood of a person to develop cancer over a lifetime, because of presentation to a potential cancer-causing agent TR was analysed using the formula;

$$TR = \frac{EF \times ED \times FIR \times C \times CSFo}{BW \times TA} \text{(Storelli, 2008)} \qquad (3)$$

Where: TR = a unitless probability of an individual developing cancer over a lifetime and CSFo is the oral carcinogenic slope factor from the Integrated Risk Information System database, which is 1.5 (mg/kg/day) $^{-1}$ for Arsenic.

Note: THQ and TR Consumption limits estimations for arsenic were made on the presumption that the harmful inorganic arsenic was 3% of total arsenic (Copat *et al.*, 2013).

CHAPTER FOUR

4.0 RESULTS

4.1 Concentration of trace metals in assessed fish species

Mean concentrations and standard deviations of trace metals in *Sardinella maderensis, Dentex angolensis, Sphyraena barracuda, and Penaeus notialis* from Ghanaian coastal waters are shown in figure below. With the exception of Pb, which was below method detection limit of (0.3 ug/g) in all fish species, Copper, Zinc, mercury, cadmium, and Arsenic were detected in all the four species analyzed. Statistically, there exist significant differences (Anova: p=0.000) in concentrations of trace metals among the different fish species. *P. notialis* recorded the highest concentration of Cu, Zn, As, and Cd whereas *S. sphyraena* recorded relatively low concentrations of these metals. Significant differences were observed in metal concentrations across all four fish species. These variations may be attributed to differences of ecology, accumulation capacity, sex, age and feeding pattern of the species (Ahmed *et al.* 2015).

Figure 4.1 shows the mean concentration of copper estimated from the assessed fish species. The concentrations of Cu in the studied fishes ranged from of 0.31 - 12.08 µg/g. In an increasing order, Cu concentrations in the fish species followed the pattern *D. angolensis* < *S. sphyreana* < *S. maderensis* < *P. notialis*. Using one-way ANOVA, difference in copper concentration among the assessed fish species was significant (p (0.000) < 0.05). Post doc analysis (using Tukey test) revealed significant differences between *Penaeus notialis* and the other fish species (Appendix 1).

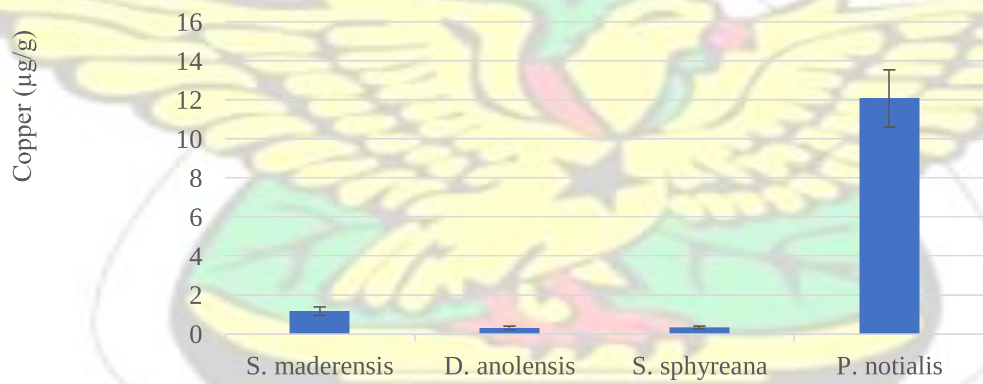


Figure 4.1 Mean concentration of copper in assessed fish species

Figure 4.2 shows the mean concentration of zinc estimated from the assessed fish species. Zinc concentrations in the studied fish species ranged from 4.23 – 19.21 µg/g. In an increasing order, Zn levels in the fish species followed the pattern *S. sphyreana* < D. *angolensis* < *S. maderensis* < *P. notialis.* Here also, significant differences (p=0.000) in

Zn concentrations were observed between *P. notialis* and all other three fish species. Post doc analysis (using Tukey test) revealed significant differences between *Penaeus notialis and* the other fish species (Appendix 2).

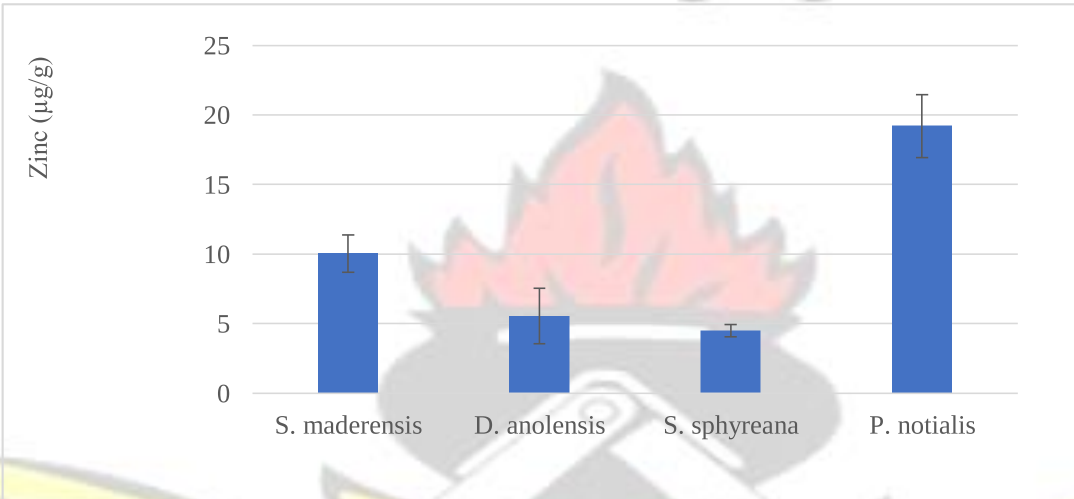


Figure 4.2 Mean concentration of zinc in assessed fish species

Arsenic concentration in the studied fish species ranged from 0.8 – 8.5 µg/g. In an increasing order, As in the fish species followed the pattern *S.sphyreana* < *S.maderensis* < *D. angolensis* < *P. notialis*. Significant differences (p=0.000) in As concentrations were observed between *P. notialis* and all other three fish species. As levels in *P. notialis* largely exceeds the maximum permitted sea food levels of 2.0 µg/g set by the Australian and New Zealand Food standard code. Using one-way ANOVA, difference in arsenic concentration among the assessed fish species was significant (p (0.000) < 0.05). Post hoc analysis (using Tukey test) revealed significant differences between *Penaeus notialis* and the other fish species (Appendix 3).

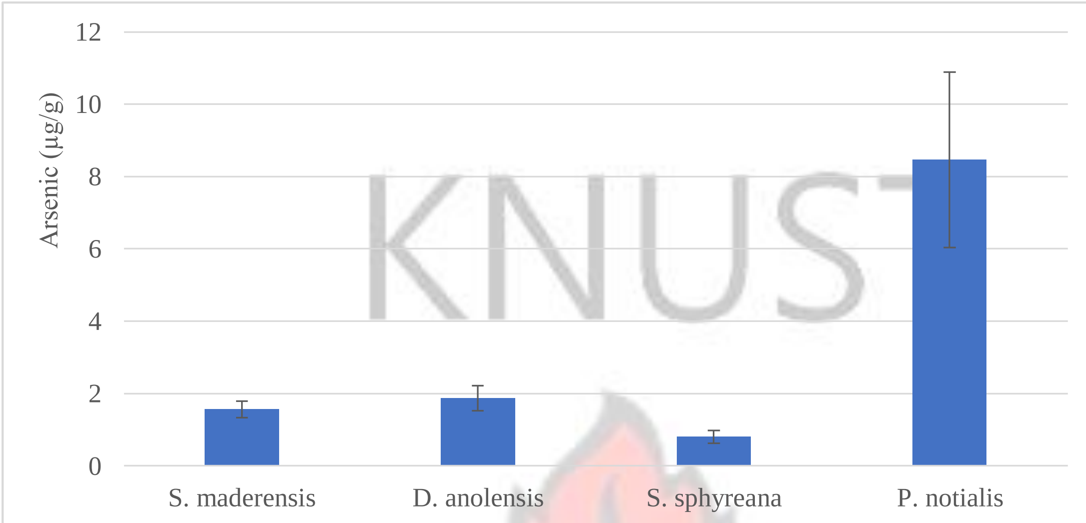


Figure 4.3 Mean concentration of arsenic in assessed fish species

The concentration of Cd in the studied fish species ranged from 0.002 - 0.026 µg/g and followed the order *S. sphyraena* < *S. maderensis* < *D. angolensis* < *P.notialis*. Using oneway ANOVA, difference in cadmium concentration among the assessed fish species was significant (p (0.000) < 0.05). Post doc analysis (using Tukey test) revealed significant differences between *Penaeus notialis* and the other fish species (Appendix 4).

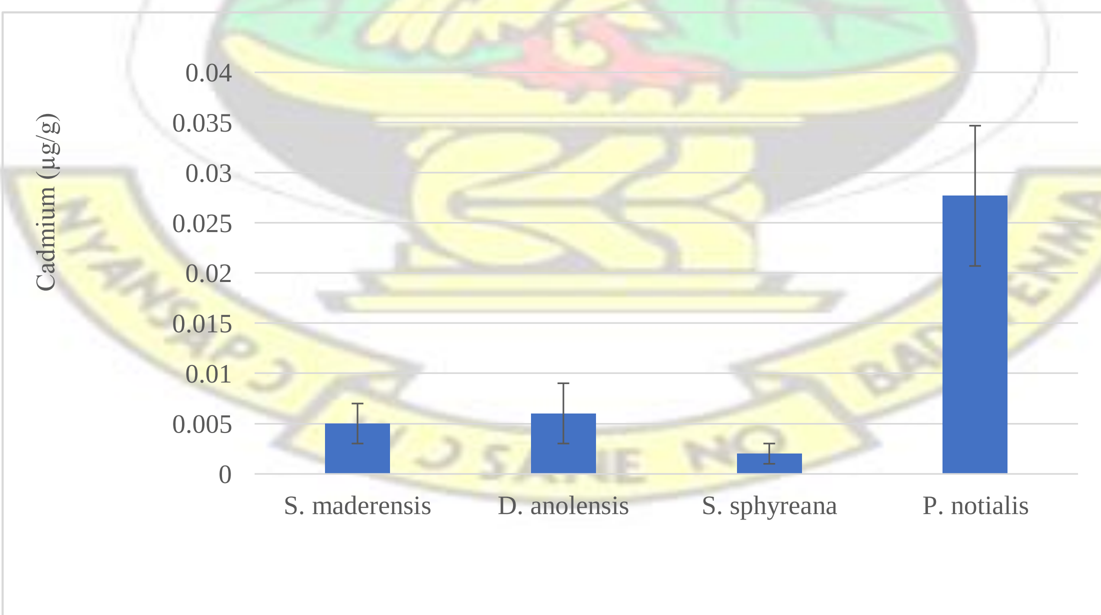


Figure 4.4 Mean concentration of cadmium in assessed fish species

The concentrations of Hg in the studied fish species ranged from 0.020 – 0.137 µg/g, following the order *S. maderensis* < *P. notialis* < *S. sphyraena* < *D. angolensis*. Contrary to the patterns observed for all the other metals in which *P. notialis* recorded the highest levels of all Cu, Zn, Cd and As, *D. angolensis* records the highest Hg level. No significant differences in Hg concentration existed between any of the fish species studied

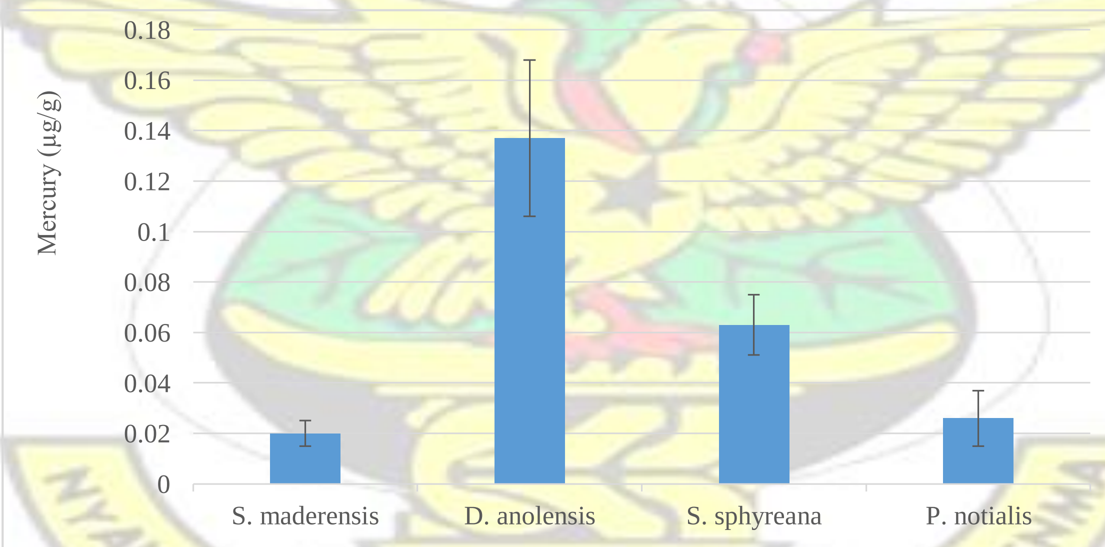


Figure 4.5 Mean concentration of mercury in assessed fish species

4.2 Intake of trace metals

Table 4 outlines the intake of trace metals on a daily basis from the consumption of the assessed fish species. From Table 4, the intake of copper ranged from 0.38 ug/per/day in Dentex sp. to 66.18 in Penaeus sp ug/per/day. Intake of zinc fluctuated from 4.48

ug/per/day in Dentex sp. sp. to 105.12 ug/per/day in Penaeus sp. (Table 4). Regarding intake of Arsenic, intake ranged from 0.78 ug/per/day in Sphyraena sp. to 44.34 in Penaeus sp. ug/per/day (Table 4). Intake of Cadmium ranged from 0.01 ug/per/day in Sphyraena sp. to 0.15 in Penaeus sp. ug/per/day (Table 4).

Intake of Mercury ranged from 0.03 ug/per/day in Penaeus sp. to 0.75 in Dentex sp. ug/per/day (Table 4). Using One Way ANOVA, a significant difference in intake of trace metal was not observed for the assessed fish species (One Way ANOVA, df = 3, p-value = 0.18) as shown in Appendix 7.

Table 3.1 Estimated daily intake (ug/person/day) compared with Provisional Maximum Tolerable Daily Intake (PMTDI) suggested by joint FAO/WHO Expert committee on Food and Additive

Age Group			**Estimated Daily**		
Intake					
				Zn	
S.maderensis	Cu	Cd	As		Hg
Children 1-3 yrs	6.409	0.027	8.457	55.005	0.110
Children 4-6 yrs	4.273	0.018	5.698	36.670	0.073
Children 7-10 yrs	2.804	0.012	3.739	24.065	0.048
Adolescent 11-14 yrs	1.759	0.008	2.346	15.099	0.030
Adolescent 15-19 yrs	1.339	0.006	1.789	11.494	0.023
Adult 20-24yrs	1.247	0.005	1.662	10.695	0.021
Adults 25-54yrs	1.165	0.005	1.554	10.001	0.020
Adults 55-64yrs	1.165	0.005	1.554	10.001	0.020
Seniors >64yrs	1.246	0.005	1.662	10.995	0.021
D.angolensis					
Children 1-3 yrs	1.698	0.033	10.245	30.351	0.752
Children 4-6 yrs	1.132	0.022	6.830	20.234	0.501
Children 7-10 yrs	0.743	0.014	4.482	13.279	0.325
Adolescent 11-14 yrs	0.466	0.009	2.812	8.331	0.206
Adolescent 15-19 yrs	0.355	0.007	2.414	6.342	0.157
Adult 20-24yrs	0.330	0.006	1.992	5.902	0.146
Adults 25-54yrs	0.309	0.006	1.863	5.518	0.136
Adults 55-64yrs	0.309	0.006	1.863	5.518	0.136
Seniors >64yrs	0.330	0.006	1.992	5.902	0.146

S.sphyraena					
Children 1-3 yrs	1.808	0.011	4.383	24.655	0.345
Children 4-6 yrs	1.205	0.007	2.922	16.436	0.230
Children 7-10 yrs	0.791	0.005	1.918	10.786	0.151
Adolescent 11-14 yrs	0.496	0.003	1.203	6.768	0.095
Adolescent 15-19 yrs	0.378	0.002	0.916	5.151	0.072
Adult 20-24yrs	0.325	0.002	0.852	4.794	0.067
Adults 25-54yrs	0.329	0.002	0.797	4.482	0.063
Adults 55-64yrs	0.329	0.002	0.797	4.482	0.063
Seniors >64yrs	0.352	0.002	0.825	4.794	0.067
P.notialis					
Children 1-3 yrs	66.181	0.148	44.349	105.189	0.142
Children 4-6 yrs	44.121	0.099	30.899	70.126	0.095
Children 7-10 yrs	28.954	0.065	20.278	46.020	0.062
Adolescent 11-14 yrs	18.167	0.041	12.723	28.875	0.039
Adolescent 15-19 yrs	13.829	0.031	9.685	21.980	0.030
Adult 20-24yrs	12.869	0.029	9.012	20.453	0.028
Adults 25-54yrs	12.033	0.027	8.423	19.125	0.026
Adults 55-64yrs	12.033	0.027	8.423	19.125	0.026
Seniors >64yrs	12.869	0.029	9.012	20.453	0.028
PMTDI	300	0.83	2.14	500	0.57

4.3 Target hazard quotient (THQ)

Table 5 shows the risk associated with consumption of the assed fish species. From Table 5, the THQ of copper ranged from 0.008 in Sphyraena sp. to 1.655 in Penaeus sp. THQ of zinc fluctuated from 0.015 in Sphyraena sp. to 0.351 in Penaeus sp. (Table 3). Regarding THQ of Arsenic, Target hazard quotient ranged from 0.080 in Sphyraena sp. to 4.635 in Penaeus sp. (Table 3). THQ of Cadmium ranged from 0.002 in Sphyraena sp. to 0.148 in Penaeus sp. (Table 3).

THQ of Mercury ranged from 0.066 in Sardinella sp. to 2.502 in Dentex sp. (Table 3). Using One Way ANOVA, significant difference in Target hazard quotient was observed for the assessed fish species (One Way ANOVA, df = 3, p-value = 0.56) as shown in Appendix 8. The results revealed that *P. notialis* recorded the highest health risk values among the four fish species studied. From Table 5, hazard index ranged from 0.209 - 159 in Sardinella, 0.673 - 3.72 in Dentex, 0.314 to 1.727 in Sphyraena and 1.321 -7.264 in Penaeus respectively.

Table 4.2 Target hazard quotient for different trace metals and their hazard index (HI) from the consumption of four fish species from the coastal waters of Ghana

Age	Target Hazard Quotient					HI
S. maderensis	Cu	Cd	As	Zn	Hg	
Children 1-3yr	0.160	0.027	0.855	0.183	0.365	1.590
Children 4-6yr	0.107	0.018	0.570	0.122	0.243	1.060
Children 7-10yr	0.070	0.012	0.347	0.080	0.160	0.669
Adolescent 11-14yr	0.044	0.008	0.235	0.050	0.100	0.437
Adolescent 15-19yr	0.033	0.006	0.179	0.038	0.076	0.332
Adult 20-24yr	0.032	0.005	0.166	0.036	0.071	0.310
Adult 25-54yr	0.030	0.005	0.155	0.033	0.066	0.289
Adult 55-64yr	0.030	0.005	0.155	0.033	0.066	0.289
Seniors>64	0.032	0.005	0.166	0.036	0.071	0.310
D. angolensis						
Children 1-3yr	0.042	0.033	1.024	0.101	2.502	3.720
Children 4-6yr	0.028	0.022	0.683	0.067	1.668	2.468
Children 7-10yr	0.019	0.014	0.448	0.044	1.095	1.620
Adolescent 11-14yr	0.012	0.009	0.281	0.028	0.687	1.017
Adolescent 15-19yr	0.009	0.007	0.214	0.021	0.523	0.774
Adult 20-24yr	0.008	0.006	0.199	0.020	0.486	0.719
Adult 25-54yr	0.008	0.006	0.186	0.018	0.455	0.673
Adult 55-64yr	0.008	0.006	0.186	0.018	0.455	0.673

Seniors>64	0.008	0.006	0.199	0.020	0.486	0.719
S. Sphyraena						
Children 1-3yr	0.045	0.011	0.438	0.082	1.151	1.727
Children 4-6yr	0.030	0.007	0.292	0.055	1.008	1.392
Children 7-10yr	0.020	0.005	0.192	0.036	0.503	0.765
Adolescent 11-14yr	0.012	0.003	0.120	0.023	0.316	0.474
Adolescent 15-19yr	0.009	0.002	0.092	0.017	0.240	0.360
Adult 20-24yr	0.009	0.002	0.085	0.016	0.224	0.336
Adult 25-54yr	0.008	0.002	0.080	0.015	0.209	0.314
Adult 55-64yr	0.008	0.002	0.080	0.015	0.209	0.314
Seniors> 64yr	0.009	0.002	0.085	0.016	0.224	0.336
P.notialis						
Children 1-3yr	1.655	0.148	4.635	0.351	0.475	7.264
Children 4-6yr	1.103	0.099	3.090	0.254	0.317	4.863
Children 7-10yr	0.724	0.065	2.028	0.153	0.208	3.178
Adolescent 11-14yr	0.454	0.041	1.272	0.096	0.130	1.993
Adolescent 15-19yr	0.346	0.031	0.968	0.073	0.099	1.517
Adult 20-24yr	0.322	0.029	0.901	0.068	0.092	1.412
Adult 25-54yr	0.301	0.027	0.843	0.064	0.086	1.321
Adult 55-64yr	0.301	0.027	0.843	0.064	0.086	1.321
Seniors> 64yr	0.322	0.029	0.901	0.068	0.092	1.412

Table 4.3 Target Cancer Risk (TR) of trace metals from consumption of four fish species collected from the coastal waters of Ghana

Age ***S. maderensis***	Target carcinogenic risk (inorganic) As
Children 1-3yr	5.49×10^{-6}
Children 4-6yr	1.47×10^{-5}
Children 7-10yr	1.68×10^{-5}
Adolescent 11-14yr	1.66×10^{-5}
Adolescent 15-19yr	1.73×10^{-5}
Adult 20-24yr	2.14×10^{-5}
Adult 25-54yr	2.50×10^{-5}
Adult 55-64yr	5.49×10^{-5}
Seniors>64	7.05×10^{-5}
D. angolensis	
Children 1-3yr	6.59×10^{-5}
Children 4-6yr	1.76×10^{-5}
Children 7-10yr	2.02×10^{-5}
Adolescent 11-14yr	1.99×10^{-5}
Adolescent 15-19yr	2.06×10^{-5}
Adult 20-24yr	2.56×10^{-5}
Adult 25-54yr	2.99×10^{-5}

Adult 55-64yr	$6.59×10^{-5}$
Seniors>64	$8.45×10^{-5}$
S. Sphyraena	
Children 1-3yr	$2.82×10^{-6}$
Children 4-6yr	$7.51×10^{-6}$
Children 7-10yr	$8.63×10^{-6}$
Adolescent 11-14yr	$8.51×10^{-6}$
Adolescent 15-19yr	$1.10×10^{-5}$
Adult 20-24yr	$1.28×10^{-5}$
Adult 25-54yr	$1.28×10^{-5}$
Adult 55-64yr	$2.82×10^{-5}$
Seniors>64	$3.62×10^{-5}$
P.notialis	
Children 1-3yr	$2.98×10^{-5}$
Children 4-6yr	$7.95×10^{-5}$
Children 7-10yr	$9.12×10^{-5}$
Adolescent 11-14yr	$9.00×10^{-5}$
Adolescent 15-19yr	$9.34×10^{-5}$
Adult 20-24yr	$1.16×10^{-5}$
Adult 25-54yr	$1.35×10^{-5}$
Adult 55-64yr	$2.98×10^{-5}$
Seniors>64	$3.82×10^{-5}$

Table 4.4 shows the correlation matrix for trace metals observed in *Dentex angolensis* during the study period. Zinc & Copper, arsenic & copper, cadmium & copper, zinc and cadmium, arsenic and cadmium exhibited a positive correlation (0.58, 0.59, 0.95, 0.46, 0.51).However, mercury showed a negative correlation with all the other metals.

Table 4.4: Correlation matrix of trace metals in *Dentex angolensis* from coastal waters of Ghana.

	Cu	Zn	As	Cd	Hg
Cu	1.00				
Zn	0.58	1.00			
As	0.59	-0.15	1.00		
Cd	0.95	0.46	0.51	1.00	
Hg	-0.77	-0.65	-0.03	-0.88	1.00

Table 4.5 shows the correlation matrix for trace metals observed in *Sardinella maderensis* during the study period. Zinc & Copper, arsenic & zinc, cadmium &copper, mercury and copper, arsenic & mercury, zinc & mercury exhibited a positive correlation (0.14, 0.21, 0.71, 0.15, 0.87, and 0.34) while cadmium & zinc, arsenic & copper, cadmium & arsenic was negative (-0.13, 057, -0.24 – and 0.56)

Table 4.5: Correlation matrix of trace metals in *Sardinella maderensis* from coastal waters of Ghana.

	Cu	Zn	As	Cd	Hg
Cu	1.00				
Zn	0.14	1.00			
As	-0.13	0.21	1.00		
Cd	0.71	-0.57	-0.24	1.00	
Hg	0.15	0.87	0.34	-0.56	1.00

In *Penaeus notialis*, a positive correlation was observed between copper & zinc, arsenic& copper, cadmium & copper, mercury &cadmium (0.50,0.58, 0.04, 0.08, 0.3 and 0.14) whiles copper & mercury, cadmium & mercury exhibited a negative correlation as shown in table 4.5

Table 4.6: Correlation matrix of trace metals in *Penaeus notialis* from coastal waters of Ghana

	Cu	Zn	As	Cd	Hg
Cu	1.00				
Zn	0.50	1.00			
As	0.58	0.04	1.00		
Cd	0.08	-0.14	-0.53	1.00	
Hg	-0.49	0.30	-0.89	0.41	1.00

In *Sphyraena Sphyraena,* copper exhibited a negative correlation with all metals whereas arsenic

& zinc, cadmium & zinc, arsenic & cadmium was positive (0.88, 0.93, and 0.68)

Table 4.7: Correlation matrix of trace metals in *Sphyraena sphyraena from* coastal waters of Ghana

	Cu	Zn	As	Cd	Hg
Cu	1.00				
Zn	-0.14	1.00			
As	0.08	**0.88**	1.00		
Cd	-0.12	**0.93**	**0.68**	1.00	
Hg	-0.09	-0.33	-0.27	**-0.52**	1.00

5.0 DISCUSSIONS

5.1 Trace metals in fishes

The purpose of this study is to estimate the concentrations and potential human health risks associated with lead, cadmium, mercury, copper, zinc and arsenic through the consumption of *Sardinella maderensis*, *Sphyraena sphyraena*, *Dentex angolensis and Penaeus notialis* from the coastal waters of Ghana. The specific objectives of the study includes determining the concentrations of zinc, copper, mercury, lead, arsenic and cadmium in the fish tissues, estimating the provisional tolerable daily intake of trace metals and assessing any potential carcinogenic and non-carcinogenic human health risks related with Cu, Zn, Hg, As, Pb and Cd levels in the fish species.

In decreasing order, trace metal concentrations in studied fish species followed the pattern *Penaeus notialis* > *Sardinella maderensis* > *Dentex angolensis* > *Sphyraena sphyraena*. Among all the sampling stations, Tema recorded the highest concentrations for Cu, As and Cd followed closely by Elmina where Zn recorded their highest concentrations respectively. The station with the least trace metal concentration was Apam which recorded the lowest concentrations for Cu, Zn, and Hg. There was however no significant statistical difference between all the stations in terms of concentration of heavy metals at $p<0.05$.

5.1.1 Arsenic

Currently, there is no recommended limit for arsenic consumption in seafood and other food-related products. The food and agriculture organization/ World health organization expert committee on food and additives in 2014 redrew the maximum permissible daily intake for arsenic owing to deleterious effect on health even at minute concentration and concluded that there is no safe level to arsenic exposure (WHO/FAO, 2014). The levels for arsenic has increased progressively over the past years in sediments, water and biota from the coastal waters of Ghana (Horgah, 2015). Previous studies on As in Ghanaian waters revealed elevated levels (5.7 -94.0 μg/g) in sediments from coastal waters (Mahu *et al*. 2015) and 3.45 – 142 μg/g estuarine sediments (Mahu, 2014).

Another study by Klubi et al., (2017) on the impact of gold mining activities on heavy metals enrichment from selected estuaries in Ghana reported (35-75 ug/g) for Ankobra and (23-54 ug/g) for Pra estuary respectively which is above the sediment probable effect level. Botwe et al., (2108) on their study on chemical contamination for sediment from the Tema harbour in Ghana reported arsenic levels (23 mg/kg – 89 mg/kg) above the sediment quality criteria. With regards to water contamination, Akabzaa *et al*., (2009), Bhattacharya et al., (2012), Kusimi &Kusimi (2012), Akabzaa &Yidana (2012) and Asante *et al*., (2107) in their studies in arsenic contamination in surface waters from estuaries in Ghana reported concentrations above the WHO recommended limit of arsenic in water. This calls for a better management policy to address the issue of arsenic pollution in Ghana.

Total arsenic was the trace metal detected in the highest concentration in the tissue of the accessed fish spices. The toxicity of arsenic compounds depends on the valence state, molecular form and the chemical speciation of the arsenic compound. Inorganic arsenic is carcinogenic and poses significant toxicity to human health. (ATSDR, 2003). In increasing order, As in the fish species followed the pattern *S.sphyraena* < *S.maderensis* < *D. angolensis* < *P. notialis*. Significant differences (p=0.000) in As concentrations were observed between *P. notialis* and all other three fish species.

Feeding habit, ecology, salinity and habitat influence the bioaccumulation and trophic transfer of As in the marine environment. Rahman *et al*; 2012 in their study on "bioaccumulation, biotransformation and trophic transfer of arsenic in the aquatic food" chain stated that marine primary producers such as Phytoplanktons and algae play a significant role in arsenic distribution, speciation and transfer in the aquatic ecosystem. These primary producers can hold concentration much higher than their surrounding waters which may contribute to the trophic transfer of arsenic to higher levels of the marine food chain. In support of the assertion, Vieira *et al*, 2011 wrote that organisms feeding on primary producers appear to bio accumulate higher arsenic concentration than predacious once. Also, marine benthic (organisms that live on the seabed) accumulate higher levels of arsenic than pelagic species due to the fact that sediments contain higher arsenic levels than the water column. Since *Penaeus notialis* is bottom dweller and mostly feeds on primary producers (plankton and algae) could account for the high levels of arsenic bioaccumulation than the other fish species.

As levels in *P. notialis* largely exceeds the maximum permitted seafood levels of 2.0 μg/g set by the Australian and New Zealand Food standard code. Generally, crustaceans contain high naturally occurring arsenic levels than other marine organisms. Also As levels in all fish species except *S. Sphyraena* exceeded the recommended maximum value of 1.3 μg/g in tissue residue set by the USEPA (Burger & Gochfeld, 2005). The exceedingly high levels of As in the fish species studied implies a potential environmental As pollution in Ghanaian waters. Arsenic pollution in Ghanaian waters have been attributed to the mobilization of As through Arsenopyrite oxidation exacerbated through mining activities in the Region (Smedley and Kinniburgh, 2002), and use of arsenic-based herbicides in agricultural processes (Mahu *et al.* 2015). Arsenic problem is not only limited to Ghana, but also to most African Countries. Studies have for instance found high levels of As (0.02 and 1760 μg L^{-1}) in groundwater with values ranging up to 10,000 μg L^{-1} in surface water from different parts of Africa (Ahoulé *et al.* 2015).

Nevertheless, the level of Arsenic in assessed fish species was much lower compared to findings from other research conducted elsewhere. Storelli & Marcotrigiano (2001) in their study on total organic and inorganic arsenic in some commercial species of crustaceans from the Mediterranean sea, Italy recorded arsenic concentration 45 mg/kg and 15.45mg/kg respectively. In another study by Anacleto *el al*, (2009) on total arsenic content in seafood consumed in Portugal reported concentration of arsenic in *Nephrops norvegicus* as 32 ± 8.2 mg/kg.

5.1.2 Mercury

Mercury is classified among metals with potential health concern due to its tendency to biomagnify along the food chain. The toxicity of mercury depends on the chemical speciation, duration and level of exposure. Seafood is a predominant source of methylmercury exposure to humans. Over 85% to 90% of total mercury content in fish tissue is methylmercury which is detrimental to human health. Generally, muscle tissues of predatory species (Dentex and Sphyraena) contain higher levels of mercury contrary to non-predatory once indicating biomagnification and trophic transfer of mercury through the aquatic food chain. In support of the assertion, Kensova *et al*, (2009) stated that mercury levels in predacious fish are higher due to mercurys inability to degrade in body tissues.

In this study, the concentration of Hg ranged from 0.020 ug/g to 0.137 ug/g respectively. The highest Hg concentration was found in Dentex *angolensis* (0.137 ug/g) and the lowest (0.020 ug/g ww) observed in *P. notialis*. Hg concentration found in this study was below the permissible limit of 0.5 ug/g recommended by both FAO (2004) and the European Commission (2006). However, the mean concentration of mercury observed in this study is lower than previously reported by other studies in Ghana. Ntow & Khwaja (1998) on mercury pollution in Ghana (West Africa) commercial fish reported 0.14 ug/g to 0.48 ug/g ww. Another study by Oppong *et al*., 2010 on total mercury in fish from Pra estuary in Ghana reported mercury (0.62 ug/g -1.24 ug/g) a level above FAO (2006) permissible limit of 0.5 ug/g. Doke &Gohlke, (2014) on health risk estimation from methylmercury exposure in Ghana reported 0.21ug/g to 0.84 ug/g. Compare with the above previous works, the low levels of mercury recorded in this study could be attributed to the proper handling, uses and disposal of mercury as well as the regulation of small scale gold mining in Ghana which is a key source of mercury pollution in water bodies.

5.1.3 Copper

One important element of concern is also copper. It is a micronutrient for numerous enzymes and helpful for the overall formation of an iron-containing pigment called hemoglobin (Islam *et, al*, 2015). However, excessive accumulation of copper has been reported to cause adverse health problems. The Cu concentrations in the studied fishes ranged from 0.31 - 12.08 μg/g. The highest Cu concentration was found in *Penaeus notialis* (12.08ug/g) and the lowest (0.31 ug/g) observed in *Dentex angolensis*. The concentration of Cu in fish samples analyzed were all below the FAO recommended guideline of 30ug/g (FAO, 2004). However, the mean concentration of Cu in *P. notialis* (12.08 ug/g) exceeded the regulatory limit of 10 ug/g set by Australia Food Standard Code.

Similarly to As accumulation, our results indicate that non-predatory species (Penaeus and Sardinella) accumulated higher Cu levels than carnivorous ones suggesting poor biomagnification and transfer of Cu through the aquatic food chain. In support of the above, Cardwell *et al*, 2013 in their study on "Do Cu, Zn, Cd, Pb and Ni Biomagnify in aquatic ecosystems" stated that Cu does not biomagnify in food web comprising of primary producers and fish. Another study by Croteau *et al*, 2005 concluded that whether an organism is sorted by food chain or treated with a taxonomic basic within discrete food webs, Cu enrichment does not biomagnify. Cu enrichment in the aquatic organism may emanate from industrial discharges into sediment and surrounding water bodies (Ahmed, 2014). Cu concentrations detected in this study are higher than those reported by Akoto *et* *al*, 2014, Bandowe *et al*, 2014, Ansah *et al*, 2018, and Gbogbo *et al*, 2018 in commercial fish from the coastal waters of Ghana.

5.1.4 Lead

Lead a well-documented environmental pollutant owing to its detrimental effects on sensitive pollutions. In children, lead has the tendency to interfere with their central nervous system, decrease intelligent quotient and mental retardation (Wani *et al.*, 2015, Radyminska *et al.*, 2019). The level of lead in Deep Ocean waters vary from 0.01 -0.02g u/l but slightly higher in open waters (0.3ug/l) due to human influence (Castro-Gonzalez and Mendez-Armenta 2008).

Pb levels in Ghana coastal waters has decreased slightly over the past decade owing to the ban on the use of lead fuels, lead paints, lead base pesticides and proper management, control and disposal of electric waste (Nyarko *et al*., 2013). The concentration of Pb in all fish species analyzed was below the method detection limit of 0.3ug/g. This is in accordance with previous works by Ansah *et al*, 2018, Bandowe *et al,* 2014 and Akoto *et al*, 2014 who reported Pb levels less than 0.3ug/g. In support to the above submission, Mahu *et al*., 2016, Klubi *et al*., 2017, Botwe *et al*., 2018 and Nyarko *et al*., 2014 in their assessment of heavy metal pollution in coastal sediment from Ghana recorded lead levels below the sediment quality guidelines

5.1.5 Cadmium

The least trace element detected in the tissues of the accessed species was cadmium. It has been documented that, Cd is among other heavy metals that occur in aquatic organism and marine habitat in trace concentration (Vieira *et al.*, 2011). There is proof for Cd bioaccumulation in marine organism particularly those that feed on primary producers such as algae and cephalopods, but the process of biomagnification and trophic transfer of Cd in the marine food chain is inconsistent (Falco *et al*., 2006).

The concentration of Cd ranged from 0.002 -0.026 ug/g. The highest 0.026 ug/g and lowest 0.002 ug/g Cd concentration were found in *P. notialis and S. maderensis* respectively. The variation in Cd interspecies levels could be attributed to feeding habit, rate of absorption, habitat and diet. The maximum Cd level permitted by the European Commission through fish consumption is 0.05 ug/g (EC, 2006). However, none of the investigated fish species in this study exceeded the acceptable limit of Cd.

The mean Cd value recorded (0.01 ug/g) was similar to mean values found in fishes from the waters of Ghana (Akoto *et al,* 2014). Nevertheless, Cd levels estimated in this study were quite less than those reported by Copat *et al*., (2013) who encountered mean concentrations of 0.96 µg/g in fish muscles from Easter Mediterranean Sea, Italy.

5.1.6 Zinc

Zinc is an essential trace element with rare toxicity but, at above to 30 µg/g, it may induce toxicity to humans. The maximum concentration of Zn recorded in the samples was 15.99 µg/g recorded in *Penaeus notialis* and the lowest concentration was 3.64 µg/g in *Sphyraena sphyraena*. Zn recorded the highest concentration at all the sampling stations. The concentrations of Zn in all the fish samples were below the FAO permissible limit of 30 µg/g for safe human consumption (FAO, 1983). The levels of Zn recorded in this study agrees with previous studies in Ghana by Nyarko (2013) and Akoto (2014).

5.2 Correlation of Trace Metals in Fish Species

Generally, not all trace elements increase in concentration with an increase in length and size as reported in literature. This is due to the differences in affinity, absorption rate and homeostatic control. To envisage the interrelationship between the metal accumulation pattern in individual fish species, Pearson correlation analysis was performed. Our results showed that Cu, Zn and As accumulation in tissues of *Penaeus notialis* and *Sardinella maderensis* exhibited a strong significant correlation. This species are planktivorous and may accumulate Cu and Zn from planktons which use those metals for their physiological and enzymatic activities. Again As concentration varies significantly in primary producers (phytoplankton and microalgae) which forms the basis of the marine food chain. Planktons take in total arsenic in place of phosphate from marine waters during feeding due to its chemical similarities with phosphate (Rahman *et al.,* 2012). This may elucidate the positive correlation between Cu, Zn and As among planktivorous species. The result is consensus with finding by Liu *et al*., 2014 who reported that, Zn bioaccumulation increase with Cu accumulation in planktivorous marine organisms. However, the relationship between Hg and As accumulation in Dentex and Sphyraena showed an inverse correlation. The negative correlation between Hg and As concentration insinuates the relative dilution effect of the lipid content on metal accumulation in the tissues as reported by Liu *et al*., (2014).

5.3. Estimation of Potential Human Health Risks

The concentrations of all trace metals analyzed in fish species did not exceed the recommended levels set by recognized regulatory bodies with the exception of As. The toxicity of these metals depends on the exposure dose. Thus, estimating the daily consumption which depends on the metal concentration and amount ingested by an individual is considered a tool for evaluating the balance between benefits and risk (Copat *et al.* 2012). EDIs were compared with the provisional maximum tolerable daily intake (PMTDI) (µg/person/day) suggested by joint FAO/WHO Expert Committee on Food and

Additive (JECFA, 2009: FAO, 2016). Generally, higher EDIs were observed in the youngest population and vice versa. EDIs for Cu was within a range of 0.33 and 66.4 µg/person/day across all 9 age categories in the four fish species (Table 4). These values are far below the PMTDI of 500 µg/person/day, therefore implying no potential health threats from Cu with the consumption of these fish species. Computed EDIs for As were in the range of 0.8 µg/person/day and 44.3 µg/person/day across all 9 age categories in the four fish species. The EDI for As due to the consumption of *S. maderensis* exceeded the PMTDI of 2.14 µg/person/day in all three age categories of children and adolescent in the age group of 11 to 14 years. In *D. angolensis*, EDIs for As again exceeded the PMTDI of 2.14 µg/person/day in all age categories of both children and adolescents while that due to the consumption of *S. sphyraena* exceeded the PMTDI in children between ages 1 to 6 years. The EDI for As due to the consumption of *P. notialis* however, exceeded the PMTDI of 2.14 µg/person/day across all 9 age populations. The EDIs due to Zn exposure were in the range of 4.5 µg/person/day and 105.2 µg/person/day. Like Cu, the EDIs due to Zn exposure was far below the PMTDI of 300 µg/person/day across all 9 age categories in the four fish species, thus implying no penitential risks due to exposure to Zn from the consumption of all four fish species. EDIs due Cd exposure was within a range of 0.002 µg/person/day and 0.09 µg/person/day across all 9 age categories for all four fish species. These values are below the PMTDI of 0.85 µg/person/day Cd, thus implying no potential threats from Cd exposure in the four fish species. Finally, EDIs due to Hg exposure in the range of 0.02 µg/person/day to 0.4 µg/person/day were within PMTDI of 0.57 µg/person/day for Hg suggesting no potential threats from Hg exposure in the four fish species.

While computed EDIs suggest no risk to all 9 age categories due to Hg and Cu exposures, the estimated THQ of Hg due to consumption of *D. angolensis* and *S. sphyreana* exceeded 1 in all 3 age categories and 2 age categories of children population respectively, while that of Cu for *P. notialis* exceeded 1 in children between ages 1 and 7 years. Likewise, the THQ of As due to the consumption *P. notialis* exceeded 1 in all age categories of children and adolescents. These observations imply children and adolescents are the most likely to experience significant non-carcinogenic health risks from the intake of Hg, Cu and As in these fish species. The results of this study, therefore, support the European Commission's restrictions concerning the consumption of marine species especially predatory species by children, pregnant women, and breastfeeding mothers" (Falcó *et al.* 2006). Hazard Index (HI) which explains the combined effect from multiple trace metal consumption from a fish species exceeded 1 in children and adolescent populations for *S. maderensis, D. angolensis* and *S. Sphyraena* and all age populations for *P. notialis*. This implies that exposures to these fishes may result in some non-carcinogenic effects such as kidney damage.

Although Hg (methylmercury) and Cd are categorized in USEPA groups C (possible carcinogens to human due animal evidence and little or no human data) and B1 (probable carcinogen due to human studies), respectively, their TRs were not computed because the Ingestion Slope Factors (CSFo) are not established yet for these elements" (USEPA, 2010). For carcinogens, the USEPA sets a target risk level of 10^{-6} to denote negligible cancer risks for individual chemicals (USEPA, 2010). It is, however, recommended that the cumulative cancer risks for all potential carcinogenic contaminants do not have a residual cancer risk exceeding 10^{-4} "(USEPA, 2010). For this study, cancer risks due to the intake of As from *S. maderensis* and *D. angolensis* consumption exceeded the 10^{-6} threshold for all age groups but that of children between age range 1 to 3 years did not exceed the recommended level. Meanwhile, TRs exceeded the threshold value across all age categories for *P. notialis* and adolescents through seniors for *S. sphyraena* **CHAPTER SIX**

6.0 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Trace metal pollution is a global problem that threatens ecosystem functioning, global food safety and security. While extensive studies on trace metals level in seafood have been carried in many parts of the world to guide seafood consumption, little or no studies exist from other parts of the world including the Gulf of Guinea Region. The study, therefore, comes to fill an important gap in knowledge by providing information on trace metal levels in four (4) consumed fish species from the Gulf of Guinea and their possible human health risks.

Except for As, the levels of the studied metals (Zn, Cu, Cd and Hg) were below the permissible limits set by various regulatory authorities in the world. Arsenic levels were above permissible limits in fish species except for *S. sphyraena*. Even though, the concentrations of Cu and Hg and their computed EDIs point to no health threats, the THQs for exposures to these metals and As implied the possible manifestations of significant non-carcinogenic health risks in children and adolescents. Non-cancer risks due to As and Cu intake are higher for the consumption *P. notialis* while those for Hg intake are higher for the consumption of *D. angolensis* and *S. sphyraena.* The study further showed significant carcinogenic risks because of As intake from *S. maderensis* and *D. angolensis* in all age categories except for children between the age range 1 and 3 years and 9 years for *P. notialis*.

6.2 Recommendations

The study, therefore, recommends that to avoid non-carcinogenic risks that, the intake of these fish species by adolescents, children, pregnant women and nursing mothers is done with caution as risks are higher in these populations. These fish species, particularly *P. notialis* must be moderately consumed to avoid any likely carcinogenic risks in both children and adult populations. Considering the findings of the study, the accompanying recommendations are made to support policymakers and other concerned stakeholders in decision-making, planning policies and mitigating measures.

- For the avoidance of non-carcinogenic risks, the consumption of these fish species by adolescents and children should be eaten in moderation as risks was higher in these populations
- P. notialis must be moderately consumed to avoid any likely carcinogenic risks in both children and adult populations.
- The ministry of Fisheries and Aquaculture should make sure that educational and management programs are organised for the local fisherman to ensure compliance with good fishing practices.
- Continuous and regular monitoring programs for trace metals in other food products ought to be assessed, to protect the health of consumers against metal toxicities.

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APPENDICES

Appendix 1: Mean concentrations of copper in assessed fish species.

One-way ANOVA: Det, Sad, Pen, Shy

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Det, Sad, Pen, Shy

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	414.04	138.013	134.43	0.000
Error	20	20.53	1.027		
Total	23	434.57			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
1.01324	95.28%	94.57%	93.20%

Means

Factor	N	Mean	StDev	95% CI
Det	6	0.2608	0.0768	(-0.6020, 1.1237)
Sad	6	0.9554	0.1726	(0.0925, 1.8183)
Pen	6	10.067	2.017	(9.204, 10.930)
Shy	6	0.2733	0.0635	(-0.5895, 1.1362)

Pooled StDev = 1.01324

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping
Pen	6	10.067	A
Sad	6	0.9554	B
Shy	6	0.2733	B
Det	6	0.2608	B

Means that do not share a letter are significantly different.

Tukey Simultaneous 95% CIs

Interval Plot of Det, Sad...

Appendix 2: Mean concentrations of zinc in assessed fish species

One-way ANOVA: Det, Sad, Pen, Shy

Method

Null hypothesis	All means are equal
Alternative hypothesis	Not all means are equal
Significance level	α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	Det, Sad, Pen, Shy

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	562.71	187.570	103.41	0.000
Error	20	36.28	1.814		
Total	23	598.99			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
1.34680	93.94%	93.04%	91.28%

Appendix

One-

Method

	N	Mean	StDev	95% CI
Det	6	4.612	1.651	(3.466, 5.759)
Sad	6	8.617	1.167	(7.470, 9.764)
Pen	6	15.988	1.741	(14.841, 17.134)
Shy	6	3.717	0.371	(2.570, 4.864)

Pooled StDev = 1.34680

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping		
Pen	6	15.988	A		
Sad	6	8.617		B	
Det	6	4.612			C
Shy	6	3.717			C

Means that do not share a letter are significantly different.

Tukey Simultaneous 95% CIs

Means

Factor
Interval Plot of Det, Sad, ...

3: Mean concentrations of arsenic in assessed fish species way

ANOVA: D. puntactus, S. maderensis, P. ..notialis S. sphyreana

Null hypothesis All means are equal

Alternative hypothesis Not all means are equal

Significance level α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	D. angolensis, S. maderensis, P notialis, S. sphyreana

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	131.57	43.857	31.56	0.000
Error	20	27.79	1.390		
Total	23	159.37			

Model Summary

S R-sq R-sq(adj) R-sq(pred)

Appendix

One-

Method

1.17885	82.56%	79.94%	74.89%

	N	Mean	StDev	95% CI
D. angolensis	6	1.469	0.603	(0.465, 2.473)
S. maderensis	6	1.3654	0.2429	(0.3615, 2.3693)
P. notialis	6	6.521	2.244	(5.517, 7.525)
S. sphyreana	6	0.653	0.319	(-0.351, 1.657)

Pooled StDev = 1.17885

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping	
P. notialis	6	6.521	A	
D. angolensis	6	1.469		B
S. maderensis	6	1.3654		B
S. sphyreana	6	0.653		B

Means

Factor

Means that do not share a letter are significantly different.

Tukey Simultaneous 95% CIs

Interval Plot of D. angolensis, S. maderensis, ...

4: Mean concentrations of cadmium in assessed fish species

way ANOVA: D. angolensis, S. maderensis, P. notialis, S. sphyraena

Null hypothesis All means are equal

Alternative hypothesis Not all means are equal

Significance level α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor	Levels	Values
Factor	4	D. angolensis, S. maderensis, P. notialis, S. sphyraena

Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Factor	3	0.025707	0.008569	48.09	0.000
Error	20	0.003564	0.000178		

Appendix

One-

Method
Total 23 0.029271

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0133488	87.82%	86.00%	82.47%

	N	Mean	StDev	95% CI
D. angolensis	6	0.01872	0.00861	(0.00735, 0.03008)
S. maderensis	6	0.01725	0.00736	(0.00588, 0.02862)
P. notialis	6	0.08917	0.02364	(0.07780, 0.10053)
S. sphyraena	6	0.00697	0.00507	(-0.00440, 0.01833)

Pooled StDev = 0.0133488

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping	
P. notialis	6	0.08917	A	
D. angolensis	6	0.01872		B

Means

Factor

S. maderensis 6 0.01725 B

S. sphyraena 6 0.00697 B

Means that do not share a letter are significantly different.

Tukey Simultaneous 95% CIs

Interval Plot of D. angolensis, S. maderensis, ...

5: Mean concentrations of mercury in assessed fish species

way ANOVA: D. angolensis, S. maderensis, P. notialis, S. sphyraena

Null hypothesis All means are equal

Alternative hypothesis Not all means are equal

Significance level α = 0.05

Equal variances were assumed for the analysis.

Factor Information

Factor Levels Values

Factor 4 D. angolensis, S. maderensis, P. notialis, S. sphyraena

Analysis of Variance

Source DF Adj SS Adj MS F-Value P-Value

Appendix

One-

Method

Factor	3	0.07488	0.024961	8.03	0.001
Error	20	0.06215	0.003108		
Total	23	0.13704			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
0.0557457	54.65%	47.84%	34.69%

	N	Mean	StDev	95% CI
D. puntactus	6	0.1530	0.1023	(0.1056, 0.2005)
S. aurita	6	0.01557	0.00617	(-0.03191, 0.06304)
G. decadactylus	6	0.02177	0.01279	(-0.02570, 0.06925)
S. sphyreana	6	0.0873	0.0419	(0.0398, 0.1347)

Pooled StDev = 0.0557457

Tukey Pairwise Comparisons

Grouping Information Using the Tukey Method and 95% Confidence

Factor	N	Mean	Grouping

Means

Factor	N	Mean	Grouping	
D. angolensis	6	0.1530	A	
S. sphyraena	6	0.0873	A	B
P. angolensis	6	0.02177		B
S. maderensis	6	0.01557		B

Means that do not share a letter are significantly different.

Tukey Simultaneous 95% CIs

Interval Plot of D. angolensis, S. maderensis, ...

Appendix 6: **One Way ANOVA output for Trace metal intake**

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Dentex sp.	6	56.135	9.355833	189.5198
Sardinella sp.	6	85.912	14.31867	692.1975
Sphyraena sp.	6	37.471	6.245167	127.5199
Penaeus sp.	6	255.18	42.53	2689.997

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	4968.722	3	1656.241	1.790901	0.181334	3.098391
Within Groups	18496.17	20	924.8086			
Total	23464.89	23				

Appendix 7: One Way ANOVA output for Total Hazard Quotient

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
Sardinella sp.	6	0.525	0.0875	0.027118532
Dentex sp.	6	0.9561	0.15935	0.048900635
Sphyraena sp.	6	0.557	0.092833	0.013251235
Penaeus sp.	6	2.3878	0.397967	0.634438847

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.384073725	3	0.128025	0.70760226	0.558714462	3.098391
Within Groups	3.618546242	20	0.180927			
Total	4.002619966	23				

Appendix: 8 Trace metals in fish species from Sekondi

Species	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
Dentex	0.18	2.90	0.010	1.84	0.348
Sardinella	1.25	7.68	0.031	1.31	0.013
Penaeus	10.13	15.33	0.132	5.33	0.052
Sphyraena	0.26	3.58	0.009	0.21	0.101

Appendix 9: Trace metals in Fish species from Apam

Species	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
Dentex	0.18	2.70	0.018	1.08	0.109
Sardinella	0.78	0.83	0.020	1.28	0.010
Penaeus	9.55	14.65	0.073	7.15	0.014
Sphyraena	0.27	4.40	0.016	1.21	0.090

Appendix 10: Trace metals in Fish species from Elmina

Species	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
Dentex	0.24	6.98	0.018	0.92	0.158
Sardinella	1.00	8.78	0.017	0.98	0.016
Penaeus	7.10	16.58	0.079	4.75	0.043
Sphyraena	0.40	3.50	0.004	0.62	0.104

Appendix 11: Trace metals in Fish species from James Town

Species	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
Dentex	0.28	4.30	0.010	1.02	0.105
Sardinella	0.84	9.85	0.012	1.71	0.011
Penaeus	12.18	16.78	0.102	3.80	0.013
Sphyraena	0.26	3.55	0.003	0.61	0.057

Appendix 12: Trace metals in Fish species from Kate

Species	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
Dentex	0.31	5.65	0.024	1.14	0.052
Sardinella	1.02	9.65	0.012	1.45	0.027
Penaeus	9.00	13.88	0.078	9.13	0.011
Sphyraena	0.23	3.88	0.007	0.75	0.047

Appendix 13: Trace metals in Fish species from Tema

Species	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	As (mg/kg)	Hg (mg/kg)
Dentex	0.38	5.51	0.033	2.48	0.142
Sardinella	0.85	8.93	0.013	1.48	0.016
Penaeus	12.45	18.73	0.074	8.98	0.018
Sphyraena	0.22	3.40	0.003	0.49	0.066