DYNAMICS OF HEAVY METALS IN SEAWATER, SEDIMENT, MUDPRAWNS AND FISH TISSUES CAUGHT OF DURBAN BASIN IN SOUTH AFRICA: IMPACTS AND IMPLICATIONS

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I further declare that I have not previously submitted this work, or part of it, for examination at UNISA for another qualification or at any other higher education institution.

24.07.2021

SIGNATURE DATE

DEDICATION

This dissertation is dedicated to my supervisor Prof. Richard Naidoo and all residents of Durban that consume locally harvested seafood.

PUBLICATIONS AND PRESENTATIONS

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- **Sanjeev Debipersadh**, Timothy Sibanda, Ramganesh Selvarajan & Richard Naidoo (2018) Investigating toxic metal levels in popular edible fishes from the South Durban basin: implications for public health and food security. *Environmental Monitoring and Assessment*, 190:476 https://doi.org/10.1007/s10661-018-6862-5
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SUMMARY

Durban Basin is highly prone to anthropogenic contamination, particularly heavy metals (HM). This is a critical environmental concern having a ramification on declining fish populace and quality of seafood prompting public health apprehensions in the region. However, there is no data in the literature on HM levels in the edible fish species, including the potential health risk of consumers. Therefore, this study aimed at determining baseline levels of HM accumulation in popular edible fishes and the potential public health risk that may be associated with their consumption. Further, the study assessed the trophic level transfer and the suitability of the studied fish species as bio-indicators that could be used for the systematic and periodic monitoring of toxic metal pollution in the marine environment. Results indicated that anthropic HM levels in fish species in the Durban basin exhibited both spatial and interspecific variability with Durban South and Harbour reporting higher values than other sites. Studied fish species also had higher mean levels of lead (Pb) beyond maximum allowable limit levels of 0.5 mg/kg prescribed by the South African Department of Health (DOH). Among edible fishes, Slinger had significantly ($p<0.05$) high accumulation patterns of arsenic (As), chromium (Cr), Nickel (Ni) and Pb exceeding the permitted regulatory levels in seafood. Intraspecific regional differences in HM levels in both maasbanker and slinger from the pristine (Cape Vidal) and polluted (Durban basin) marine environments were observed, indicating that the two species are potentially suitable for heavy metal pollution biomonitoring. Risk assessment revealed that all fish species had THQ>1 for Cr, implying a significant potential non-carcinogenic health risk in the consumption of fish caught in the Durban basin.

Keywords: Heavy metal, fish muscle, bioaccumulation, edible fishes, Durban Basin, food safety, Public health risk.

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LIST OF ABBREVIATIONS

BAF	Bioaccumulation Factor
CVCCRZ	Cape Vidal Controlled Catch and Release Zone ().
CVCZ	Cape Vidal Controlled Zone
DOH	Department of Health of South Africa
DWAF	Department of Water Affairs and Fisheries
EDI	Estimated Daily Intake
FAO	Food and Agriculture Organization
GES	Good Ecological Status
HI	Hazard Index
HM	Heavy metals
ICP-OES	Inductively coupled plasma optical emission spectrometry
KZN	KwaZulu Natal
MAL	Maximum allowable limit
MANOVA	Multivariate analysis of variance
MPA	Marine Protected Area
MPI	Metal pollution index
MSFD	Marine Strategy Framework Directive
NMPMP	National Marine Pollution Monitoring Programme
RSPCA	Royal Society for the Prevention to Cruelty to Animals
SASSI	Southern African Sustainable Seafood Initiative
SBM	Single Buoy Mooring
TDI	Tolerable Daily Intake
THQ	Target hazard quotient
TR	Target Carcinogenic Risk
TR_{lim}	Maximum allowable daily fish consumption limit
TR_{mm}	Maximum allowable fish consumption rate (meals/month)
USEPA	US Environmental Protection Agency
WHO	World Health Organization

CHAPTER 1:
INTRODUCTION

1.1 Background of the study

Coastal environments are fluctuating and complicated ecological units that are exposed to various anthropogenic activities that may result in fish population declines, and thus impacts coastal communities that rely on them as a food source (Gusso-Choueri *et al.*, 2015). Furthermore, there is increased concerns on the quality of seafood's and public health benefits from fish due to the presence of toxic metals and metalloids, mainly attributed to increased pollution of marine ecosystem by anthropogenic activities (Rajeshkumar & Li, 2018).

It is estimated that marine ecosystems will be three times more polluted in the next 50 years compared to the last 50 years (Jacobs *et al.*, 2015), with only 13.2% of the world's ocean waters as still pristine state and unspoiled by human activity (Jones *et al.*, 2018). The increase in human population and industrialisation have made the ocean susceptible to severe pollution contrary to the historical belief that the ocean is immune to pollution due to its vastness (Pradervand *et al.*, 2004). Such environmental pollution results from a range of human-induced environmental disturbances which could be once-off or cumulative; and includes a range of terrestrial, industrial and domestic waste discharges (Palmer, Van der Elst & Parak, 2011; Vikas & Dwarakish, 2015; Kibria *et al.*, 2016; Kroon *et al.*, 2016). Among the major pollutants, there have been increased concerns on the potential adverse effects of wastes laden with high contents of toxic heavy metal (HM) pollutants such as cadmium (Cd), nickel (Ni), lead (Pb), chromium (Cr) and mercury (Hg). The major sources of these heavy metal contaminants in the environment include industrial and agricultural effluents (El Zrelli *et al.*, 2018), acid mine drainage (Leppänen, Weckström and Korhola, 2017), and transportation (Hassan, 2017). Ultimately, the marine ecosystem becomes the final sink for all riverine or land based contaminants

(Nazir *et al.*, 2015; Kroeze *et al.*, 2016; Hassan, 2017; Barrows, Cathey & Petersen, 2018).

Generally, heavy metals in the aquatic environment are persistent, non-degradable and are considered hazardous to biological systems due to their oxidative and carcinogenic potential (Moodley *et al.*, 2014). Under certain environmental conditions, heavy metals can accumulate to toxic level and cause ecological damage (Al Naggar *et al.*, 2018) . However, heavy metals such as copper (Cu), zinc (Zn) and manganese (Mn) are essential micro-nutrients which play an important role in biological systems at lower concentrations (Damodharan & Reddy, 2013), and generally decay into harmless or less harmful forms during their metabolism. In contrast, non-essential and non-biodegradable metals like Cd, Hg, Cr, Ni and Pb are believed to have no known role and are largely toxic at elevated concentrations (Canli and Atli, 2003). Contamination of surface and ground water sources and oceans by heavy metals such as arsenic (As), Pb, Cd, Zn, Mn, Cu and mercury (Hg) may have ecosystem-wide implications due to their toxicity even when present at trace levels (Ozyurt *et al.*, 2016). The greatest concern related to these toxic metals are the ease of bioaccumulation by marine organisms (Ahdy, Aly Abdallah & Tayel, 2007) and consequent bio-magnification in aquatic food chains (Ahmed *et al.*, 2016). This may eventually be deleterious to human health primarily through consumption of contaminated fish.

Oceans and seas cover over two-thirds of the earth's surface, and it an important habitat for numerous life forms ranging from invisible microbes to earth's biggest known living creatures. In addition, it harbours organisms that form an important food resource for humanity. Fish is one of the major food resources from the ocean and is considered a healthy food owing to its richness in proteins of high biological quality, valuable mineral compounds and vitamins (Kovekovdova & Simokon', 2002; Jennings *et al.*, 2016). Nutritionally, marine fish are rich in essential ω-3 polyunsaturated fatty acids (PUFAs), especially eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA) while being low in cholesterol (Sea *et al.*, 2015). Globally, many populations depend on fish for food and nutrition security It is estimated that fish and other aquatic food products provide more than 15% of animal protein to a third of the planet's population, and that fishing-based activities contribute to the livelihoods of over a half-billion people, with global trade worth more than US$100 billion a year (Fisher *et al.*, 2017; Bosch *et al.*, 2016b). The Food and Agriculture Organization (FAO) estimates that fish are the most widely traded foods in the world, with about 50% coming from developing countries, with a net value of fish export of over $20 billion in 2011 (USAID, 2016), which was greater than the net exports of rice, coffee, tea, tobacco, and meat combined. These figures show that the contribution of wild fish to food security may even be higher than previously thought in many developing countries. With the global human population projected to increase by more than 30% to exceed 9 billion by 2050, and assuming an average adult weight of 60 kg represents an increase in demand of more than 365 million tonnes of dietary protein (Rice and Garcia, 2011) with approximately 20% coming from fish. By 2014, capture fisheries and aquaculture were estimated to provide about 3 billion people with almost 20% of their average per capita intake of animal protein, and a further 1.3 billion people with about 15% of their per capita intake (HLPE, 2014). Despite the important role played by fish in terms of food security and numerous health benefits, they are vulnerable to environmental contaminants like toxic heavy metals bestowed in their environment. These contaminants may be absorbed by fish from the surrounding water, sediment and diet, raising a possibility of detrimental health defects to populations that consume fish on a regular basis (Bosch *et al.*, 2016b) since accumulation of toxic contaminants may exceed regulatory levels (Vandermeersch *et al.*, 2015). Detrimental health defects that are associated with this may include serious conditions such as renal failure, liver damage, cardiovascular disease and even death (Alissa & Ferns, 2011; Kim *et al.*, 2015; Lentini *et al.*, 2017; Debipersadh *et al.*, 2018; Rajeshkumar and Li, 2018).

Due to the accumulation of heavy metals in water and sediment in the marine ecosystem, marine organisms including fish have been effectively used as biological indicators of coastal pollution, and in assessing the influence of waste disposal operations on the marine environment (Authman *et al.*, 2015). Increasing water pollution has hogged the limelight of the scientific community and public onto environmental and public health issues (Fleming *et al.*, 2015; Hamilton & Safford, 2015; Jacobs *et al.*, 2015; Hartley *et al.*, 2018). Fishes at higher trophic levels in polluted ecosystems can accumulate toxic heavy metals to detrimental concentrations (Xia *et al.*, 2019). Therefore, levels of heavy metals in fish is a function of the levels of these contaminants in sediment and water of the particular aquatic environment from which they are sourced together with the duration of exposure (Rajeshkumar & Li, 2018). It is also believed that the accumulation of heavy metals at higher trophic levels in pristine environments is low compared to polluted systems (Hadzi, Essumang & Adjei, 2015). Monitoring the heavy metal accumulation in fishes is therefore critical to better manage the negative impacts of anthropogenic activities on the environment. Towards this, different efforts and strategies are being employed by various bodies to address the issue of environmental pollution. For instance, the Marine Strategy Framework Directive (MSFD, 2008/56/EC) seeks to establish a framework for the development of marine strategies designed to achieve Good Ecological Status (GES) in marine environments in the European Union by the year 2020 using eleven qualitative descriptors (Zampoukas *et al.*, 2012). Similarly, the Department of Agriculture, Forestry and Fisheries in South Africa tasked with different strategies for the development and sustainable use of marine and coastal resources, maximizing the economic potential of the fisheries sector; and protecting the integrity and quality of the country's marine and coastal ecosystems. Key to these strategies is continuous monitoring and assessment of concentrations and effects of contaminants including heavy metals in the marine environment considering the impacts and threats to the ecosystem.

Heavy metals are widely pervasive in marine fish, and can accumulate *via* different routes such as the gills, absorption through the skin, as well as ingestion of sea water and food (Damodharan & Reddy, 2013). Furthermore, accumulation of heavy metals in fishes may be correlated to fat content, food sources, the physiological state of the individual and the toxicological dynamics of the specific metal (Sea *et al.*, 2015). Consequently, a high variability in heavy metal concentrations may exists among fishes, and their habitats. A recent study reported a relationship between water contamination and toxins absorbed in fish tissue (Malik *et al.*, 2010). Additionally, similar relationships may occur as a function of the species feeding habits (Zrnčić *et al.*, 2013). Generally, heavy metal pollutants are transported from near shore to deep sea by ocean currents, diffusion due to concentration gradients and transposition up the food chain (Pérez-Moreno *et al.,* 2016). Some studies have documented changes in the internal organs of deep-sea fish resembling those seen in shallow-water fish exposed to human pollutants including heavy metals and industrial chemicals, such as polychlorinated biphenyls (PCBs) (Oosthoek, 2015). Heavy metals have also been implicated in exacerbating microbial fish diseases; for instance copper have been associated with increasing fish susceptibility to vibriosis (e.g. from *Vibrio anguillarum*) (Austin, 1999), depending on concentration and duration of exposure. Consequently, pollution of such nature may have the potential to result in massive fish kills, reduced fecundity and, ultimately to reduced yields. The rise in ocean pollution is, therefore, a massive threat to the fishing industry and a great concern to the global economy as loss of productivity of wild fisheries will certainly influence communities and have a knock-on effect on their food security. Due to public health concerns, heavy metal contaminants in fish and other seafood must not exceed levels established by legislation or other relevant standards (Descriptor 9; Directive 2000/60/EC) (Zampoukas *et al.*, 2012). Hence, continuous monitoring of seawater, sediments and seafood against heavy metal contamination and subsequent accumulation is highly important to safeguard public health. Towards this initiative, there have been extensive researches done to study bioaccumulation patterns of heavy metals in edible fishes from different coastal environments around the world in the last two decades (Mansour *et al.,* 2013; El Shafay *et al.,* 2016; Iqbal *et al.,* 2017; Mziray & Kimirei, 2016; Velusamy *et al.,* 2014; Qiu, 2015; Damodharan & Reddy 2013; Xia *et al.,* 2019).

In recent years, countries like South Africa have extended their coastlines (approximately 3 000 km) facilitating access to large areas of ocean which can support commercial, recreational and subsistence fisheries (Bosch, 2015). According to Oceanographic Research Institute, South African marine environment is home to a multitude of popular edible fishes (Mann, 2013) that include the catface rock cod (*Epinephelus andersoni*), slinger seabream (*Chrysoblephus puniceus*), santer seabream (*Cheimerius nufar),* bronze seabream (*Pachymetopon grande*), grunter *(Pomadasys commersonnii),* maasbunker *(Trachurus trachurus)* and atlantic chub mackerel *(Scomber japonicas)* which are popular and are heavily consumed by human population along the shoreline and all over the country.

Durban is one of the major industrial and commercial hub along the Indian ocean coastline that are characterized by several sites of major marine metal pollution ranging from industrial activity runoff, wastewater outfalls, river mouths (where metal pollutants are carried downstream from agricultural activity and industrial or urban developments) or harbours (where oil spills or pollution from shipping activity cause increased metal concentrations in marine water). For instance, bathing, surfing and fishing was banned in Durban in the year 2019 due to raw sewage flowing into the water. This was investigated by Water and Sanitation and reported as the failure of the mechanical rakes at the entrance to the pump station allowing an ever-increasing amount of foreign objects to enter the pumping system. This resulted in the pumps tripping and failing mechanically leads to an uncontrolled sewage flow in to the marine system. Similarly, in early 1960 and 2005 South African marine environment faced tanker accidents resulted in oil spills and affected marine biodiversity including the African penguin (*Spheniscus demersus*) and other species (Wepener and Degger, 2012). According to Donoghue and Marshall, (2003), most of the investigation before 1960 in marine regions of the country (Western Cape, followed by the Eastern cape and KZN) studied different pollutant types including industrial effluent and storm-water run-off, specifically, hydrogen sulphide, fluoride, titanium dioxide. Later, between 1960 and 1990, metals were by far the most commonly measured contaminants in South African marine pollution studies (Wepener and Degger, 2012). More recently, a renewed interest in marine pollution research has been rekindled in the form of exposure studies to various marine biota. For example, assessment of hydrocarbon in mussels (Degger *et al.*, 2011), plastic debris in sharks (Kim *et al.*, 2019), heavy metals in fishes (Genthe, 2013; Borrell *et al.*, 2016; Cammilleri *et al.*, 2018). Unfortunately, very few studies targeting heavy metal contamination of marine fish caught within the Durban basin have been reported in South Africa (Guastella, 1994; Thawley, Morris & Vosloo, 2004; Taylor *et al.*, 2010; Olaniran, Naicker & Pillay, 2014; Moodley & Pillay, 2015). These studies are limited in scope not taking into account the localized hotspots of chronic metal pollution affecting the basin. In order to increase the knowledge on different localized hotspots and its pollution, our study does consider the hotspots of Durban basin based on its unique point of source. For example, South Durban basin whose biological balances have been modified in relation to the anthropogenic development and, in particular, to great industry settlement and untreated sewage release. The intensive shipping and cargo development increased release of difference wastes in the harbour region. Whereas, the north Durban basin was contaminated by treated effluents that discharged directly from the local treatment plants. Furthermore, the comparison of heavy metal bioaccumulation in edible fishes from pristine and polluted marine environments along the KZN coastline is very limited.

ISimangaliso Wetland Park is the largest marine protected area (MPA) and pristine (undisturbed and pollution free) environment in South Africa with Cape Vidal being an attractive tourist spot for fishing and diving, situated within the iSimangaliso Wetland Park. iSimangaliso Marine Reserve is home to around 1200 fish species including some of the edible fishes common to the Durban basin. Therefore, monitoring of heavy metal contamination in fishes from both pristine and polluted environment may aid in formulating a proficient environmental management strategy aimed at mitigating marine pollution and its knock-on effects on human health(Qu *et al.*, 2016).

1.2 Problem statement

The coast of KwaZulu Natal, stretching for 640 km and supports a greater number of marine species than any other equivalent length of South African coastline. According to Attwood *et al*. (2002), the South African marine environment is a rich and diverse national asset which promotes economic and social opportunities. KwaZulu Natal supports a high density of coastal population (30% of total population) whose extensive urbanization and industrialization activities resulted in generation of wastes rich in organic and inorganic pollutants that enter the ocean through the large number of rivers and estuaries with consequent threats to fish populations. This region is also very susceptible to global environmental issues such as climate change (Schleyer, Kruger & Celliers, 2008; Mcclanahan, Maina & Muthiga, 2011) and changes in marine biodiversity (Chown, 2010). Apart from these challenges, the rich marine environment with vast numbers of fish species is heavily harvested for food, resulting in many line-fish species being over-exploited (Palmer *et al*., 2011).

Heavy metal discharge from industrial areas into the environment, and the chemical persistence of heavy metals in marine ecosystems are serious environmental problems including Durban Basin (Indian Ocean) which is confronted with spatial and/or temporal high levels of heavy metals (Expansion and Port, 2012). Fish is an essential part of the human diet, however, they may also bio-accumulate these toxic heavy metals (Dórea, 2008) through the fluvial flow of contaminated water (Fernandes & Pillay, 2012), which translates into a public health problem. However, there is no recent data on how pollution levels influence the toxic metal levels in important fish species along the Kwa-Zulu Natal coastline. To characterize the potential risk of heavy metals in fish to consumers, it is essential to obtain contemporary data on the levels of a range of toxic heavy metals in a variety of fish species, which can be compared with fish from a pristine environment. In addition, there is also a need to understand how environmental conditions and biological factors might influence metal levels in fish from the KwaZulu Natal coast to identify fish species of which consumption may be a threat to human health.

1.3 Justification

It is erroneous to believe that heavy metals entering the sea simply become diluted and negligible as postulated by Järup (2003). This attitude changed when 43 people died and 70 others became permanently paralysed due to mercury poisoning resulting from sea food consumption in Minamata Bay and the Shiranui Sea (Molony, 2003). The pioneering monitoring programme in South Africa was the National Marine Pollution Monitoring Survey Programme established in 1974 to assess pollutant concentrations, sources and impacts along the coast to establish a baseline (Cloete & Oliff, 1975). This then gave rise to the first National Marine Pollution Monitoring Programme (NMPMP) to monitor pollutants and their status at recognized impact sites, however in 1982 the programme was terminated (Wepener & Degger, 2012). Post 1990, no pollution monitoring programmes exists and research initiatives are predominantly driven by tertiary institutions or private consultancies focusing on ecotoxicology and bio monitoring (Donoghue & Marshall, 2003).

Significant quantities of heavy metals in wastewater are discharged into rivers and drained into the coastal system. These metals can accumulate and become biomagnified in water, sediment, and aquatic food chains resulting in sub-lethal effects or death in local fish populations (Hollis *et al.*, 2000; McGeer *et al.*, 2000). For normal metabolism of fish, essential metals must be taken up from water, food, or sediment, however, non-essential metals are also absorbed by fish where they ultimately accumulate in the tissues (Yi & Zhang, 2012). Therefore, it is important to better understand the relationships between the concentrations of both essential and non-essential metals in water, sediment, mud prawns and in fish tissues. Furthermore, monitoring the levels of toxic heavy metals in fish are of interest not only because of the potential effects on the fish themselves, but also because of the negative health effects on human population that consume them.

Recently, there has been renewed interest in marine pollution research in the form of exposure studies that assessed metals in water, sediment and accumulation in biota (Vermeulen & Wepener, 1999; Wepener, 2008; Boyd, 2010a)***.*** The South African Government has also started to address this issue through principles contained within the White Paper for Sustainable Coastal Development in South Africa, although in practical terms, not much has been achieved in terms of research. To the best of my knowledge, and literature studies relating the heavy metal concentrations relationship between water and popular edible fishes are scanty or non-existent in the Durban Basin, South Africa. Therefore, this study sought to cover that essential information gap on the heavy metal levels in common line fishes and assess the health risks associated with the consumption of such fish in the area. This research was motivated by the need to investigate through site audits, toxicological and physicochemical studies the migration and accumulation of heavy metals in sea water, sediment, mud prawn and edible fish species in the Durban Basin. In addition, a comparison of heavy metals in selected fishes between two different coastal ecosystems namely, pristine and polluted was done together with a health risk assessment.

1.4 Hypothesis

The study tested the null hypothesis (H_o) that (i) there are no species and locational differences of toxic heavy metal contamination in edible fishes (ii) there are no differences between the pristine and polluted marine ecosystem in toxic heavy metal contamination in same fish species caught along the KZN coastline.

1.5 Research questions

The study sought to address the following research questions:

1. Are the heavy metal concentrations in both seawater and fish within acceptable limits? What can we expect in the future?
2. What is the relationship between the heavy metal concentration in the seawater, sediment, mud prawns and the fish species?
3. Could any species sampled be used as bio-indicators in an early warning/monitoring system?
4. Does the feeding habits and capture location influence the accumulation of heavy metal concentration in fish species?
5. What are the health risks associated with the consumption of edible fish species accumulated with toxic heavy metals?
6. What interventions are taken at both national and international levels concerning anthropogenic disturbances and heavy metal accumulation in fishes from marine environments?

1.6 Aim and Objectives

The main objective of the research was to determine heavy metal concentrations in seawater, sediment, and different fish species from the Durban Basin and Cape Vidal to correlate heavy metal contamination in these physical and biological matrices.

The specific objectives of the study were to:

1. Determine heavy metal concentrations in sediment, seawater and fish and possibly use the results in a modelling scenario.

2. Determine the relationship between the heavy metal concentration in the seawater and the fish species.
3. Determine the usefulness of any species as bio-indicators in an early warning/monitoring system.
4. Determine if the concentration of heavy metal contamination is related to fish feeding habits.
5. Determine the possible health risks associated with the consumption of contaminated fish.
6. Suggest interventions that can be taken at both national and international levels with regards to contaminated fish from marine environments.

CHAPTER TWO:
LITERATURE REVIEW

2.1 Introduction

Durban is a port city on the eastern shore of Africa that is administered by the Thekwini Municipality. The city perceived as a worldwide biodiversity hotspot has been adversely influenced by urban development that caused huge natural wellbeing challenges (Roberts, 2008). These environmental challenges are the consequences of minor attention given to environmental management. The South Durban Basin (SDB) contains a blend of modern and abutting neighborhoods created because of a lack of foresight going back to the late 1950's, 1960's and 1970's. Topographical and meteorological complexities experienced in the area brings about poor dispersion of toxins. These pollutants cause several diseases such as asthma, leukemia, cancer and other respiratory problems to South Durban communities (Aylett, 2010). Little to no consideration was given to the total impacts of contamination and its effect to the wellbeing of the encompassing communities. It is consequently not shocking that this outcomes in strife among industry and communities who demand a right to reasonably healthy environmental conditions (Guastella & Knudsen, 2007).

The rising allure for coastal residence and recreation combined with international tourism popularity acts as a driver for further improvement along the Durban coast. Together with the regular stressors, for example, environmental change and people playing a lavish part on pressurizing the beach front strip by induced coastal pollution. Majority of developments in Kwa-Zulu Natal (KZN) is in the southern region built around the railway that extends the railroad thus broadening the length of the coastline with the central focal region and the underdeveloped northern districts that comprises of unspoilt beaches. This advancement increased ecological burden that could deteriorate the surrounding marine water quality and in this way undermining human and environment wellbeing (O’Connor *et al.*, 2009). The port of Durban has been the catalyst for extensive industrial and urban development resulting in an increase in the point source pollution for sewage and storm water. Furthermore, shipping forms another major venture which could lead to the release of hazardous materials to the environment (Vetrimurugan *et al.*, 2018).

Overuse of fertilizers may result in anthropogenic enrichment in agricultural soils that run off into rivers and ultimately find their way to the ocean to accumulate and contaminate the toxic components in tissues of oceanic animals. In view of this, more research focus is warranted on the interaction between contaminant concentrations in tissues of species from various trophic levels as well as water and sediment (Vilches *et al.*, 2019). Marine environments are increasingly becoming prone to chemical contamination arising from diverse sources such as oil spillages and discharge of effluents containing toxic metals (DeForest, Brix & Adams, 2007; Malik *et al.*, 2010; Bosch *et al.*, 2016a). When toxic metals invade marine environments, they readily bind to particulate matter and settle down to the sea floor (Hedge, Knott and Johnston, 2009). The occurrence of some heavy metals was confirmed in water, silts and a few popular fish species from Turkey (Gomgmt & Tezt, 1994). The authors further pointed out that despite the low levels of these metals from water bodies, heavy metal concentrations were high in the sediments and that the sampled fish contain high concentrations of a few metals especially Cu, Ni and Zn in their liver due to its multifunctional role in detoxification and storage. This suggested that the metals travel from polluted sediments via fish concomitant with the sediments and advance through the food chain. A recent study from Guo & Yang (2016) also pointed that the accumulation of heavy metals in residual cores from East China Sea were 150 years old and signifies the heavy metals deposits are the characteristic sources of anthropogenic tainting. Focused on the varieties of geochemical components and grain size of principal residues to locate of heavy metals were inspected and the level of enhancement surveyed found that:

- Pre-1950, industrial activities were very weak therefore, human activities exerted a marginal influence on heavy metal accumulation in sediments while the normal eroding of rocks principally affirmed the chemistry of sediment.
- 1950–1980, showed growing tendencies comparative to pre-1950s because China moved into an era of social modernization and fast socioeconomic development. The industrial revolution gave rise to the release of huge quantities of heavy metals, which caused the enrichment in sediments.

- 1980 to present, showed rapidly increasing trends which positively correlated with socioeconomic advances, for example, unreserved power utilization, aggregate provincial production and steel fabrication.

Scrutiny of sediments revealed that the change of the quality and heavy metal buildup in China are firmly identified with financial improvement. Gusso-Choueri *et al.* (2016) hypothesized that different genotoxic end points would be emphatically connected with heavy metal pollutants (Cu, Mn, Zn, Cr, Co, Ni, Cd, Pb) and poly aromatic hydrocarbons (PAHs). This was experimented on catfish from marine secured zones in Brazil and the outcomes endorsed that contaminants from land-based exercises will in general give genotoxic consequences for fish and showed that connections between bio-accumulated metals and genotoxic impacts existed. These impacts could trigger an injurious procession of natural changes, for example, propagation unsettling influences, development hindrance and carcinogenesis, which may be disseminated onto future generations.

It is appalling and stressing that financial advancement regularly prevails marine contamination through waste releases from agrarian exercises, pesticides, composts, businesses, sewage, effluents and transference, which can unfavorably influence the nature of seawater and human wellbeing. Ismail *et al.* (2016) captured the spatial variation and identified sources of metal contamination in surface water along the Straits of Malacca, Malaysia. Utilizing principal component analysis, the authors demonstrated that the presence of Cu and Cr was associated with mining and shipping activities while high levels of Pb was linked to land-based pollution, possibly originating from vehicular emissions (Ismail *et al.*, 2015). Carić, Klobučar & Štambuk (2016) indicated that overall development of tourism voyage is continually expanding on marine natural pollution. Heavy metal marine affliction dependent on cruise liners mooring in Croatia was affirmed by ecotoxicological studies of sediments, antifouling associated impose manifestation in banded murex (*Hexaplex trunculus*) and bio-examining of Mediterranean mussel (*Mytilus galloprovincialis*) (Carić, Klobučar & Štambuk, 2016). A recent study from Spanish Mediterranean coastline revealed that the sediments were predominantly accumulated with Cr, Ni, Zn and Cd (up to 28.93 mg Cr kg^{-1} dw, 15.80 mg Ni kg^{-1} dw, 57.13 mg Zn kg−1 dw and 0.293 mg Cd kg−1 dw) respectively and potential ecological risk (RI < 150) occurred in regions where population and industrial activities are concentrated along the coastline (Paches *et al.*, 2019). While rapid industrialization along with advanced agricultural activities lead to heavy metal contamination in aquatic ecosystems which ultimately passes to humans through the consumption of aquatic foods (Salam *et al.*, 2019).

Coastal societies that depend on fish as a wellspring of nourishment stand an expanded danger of bioaccumulating lethal amounts of pollutants which could prompt genuine medical problems (Grandjean *et al.*, 2010). The contribution of fish as a dietary and quality food has been offset concerning risk of unfavorable impacts from algae, microscopic organisms, infections and toxic elements in some segments of the globe (Ryckebosch *et al.*, 2014). With respect to the exposure, of these toxic pollutants, they are at higher risk of health issues (STAP, 2012) and thus the determination of metals in eatable fish is highly significant. To ascertain its conceivable hazard to human wellbeing as expressed by Cid *et al.* (2001) and Tüzen (2003), the consumption of foods and water containing high or even trace quantities of these elements may be deleterious to human health (Dural, Göksu & Özak, 2007). Exposing three different species of macroalgae to different concentrations of some heavy metals and measuring its phytotoxicity revealed that for all algae the total accumulation was proportional to the concentration of the aqueous metal, however, the accumulation in marine plankton was significantly lower (Kearns & Turner, 2016), which is contrasted for few metal accumulation. For example, metals such as Ba, Cr and Ni showed different phytotoxic effects against aquatic animals, which is logical to suspect that the phytotoxicity can do mild to severe damages to aquatic vegetation. Reports have also mentioned that the herbicides used in antifouling paints and in agriculture have caused concern over the possible effects on corals in nearshore areas (Jones and Kerswell, 2003). This is because the suspected pollutants have higher order s o f magnitude more toxic to plants than to animals. However, the food chain from primary producer to consumers will mediate the accumulation in aquatic animals. In the improvement of a fish model in China, bio-kinetics and bioaccumulation of copper, in the cultured marine rice fish medaka was measured and found that the hatchlings may be a reasonable indicator for the biomonitoring of waterborne metals because of their high waterborne take-up rate (Guo *et al.*, 2016).

Added consideration should be given to environmental monitoring since it was observed that significant differences in the levels of total polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HM) in corals and in the surrounding ecological medium exits. Contrasted with sediments, corals had greater significant levels of PAHs demonstrating bioaccumulation conceivably through nourishment and direct contact; however HM levels indicated that despite the fact, that aggregation could happen in corals it was a reduced amount in sediments. It was also noticed that PAHs showed greater bioaccumulation than HM but an association between the two assemblies of contaminants in term of amassing by corals from the ecosystem could not be discovered (Yang *et al.*, 2019).

Samples obtained from an auction in the Lombok Island to examine the heavy metal concentration in commonly consumed marine biotas showed that concentrations differed among different heavy metals as well as species. The aggregation of metals in marine life forms was dependent on several abiotic and biotic factors. Abiotic factors relate to salinity, temperature, pH, metal types and their interaction with other metals. Biotic factors related to species and their individual physiological attributes that are connected to feeding behaviour, migration patterns and tropic level (Yi *et al.*, 2017; Suami *et al.*, 2018; Kepel, Salim & Heriati, 2019).

Coastal environments are regularly shifting multifaceted systems, a significant number of which are firmly affected by anthropogenic actions that influence coastline foraminifera that have the potential to be used as bio-indicators. Foraminifera exist, as planktonic and benthic species based on their life strategy, where planktonic float near the surface while benthic foraminifera live at depth. Exposing foraminifera to a range of heavy metal concentrations showed that foraminifera react adversely to Cd, Zn and Pb as reflected in its profusion, variety, and uniformity, aside from reactions fluctuating by type of foraminifera and metal. This could be used as an indicator to predict how pelagic and benthic organisms could be affected. It was further apparent that Zn produced distinct abnormal morphologies while Pb had the most severe consequence on total abundance, species richness and evenness (Brouillette Price, Kabengi & Goldstein, 2019).

Although seaweeds are a source of essential minerals, vitamins and antioxidants, they have a high absorption capability and may accumulate toxic metals. The major toxic metals detected were Al, Cd and Pb in Asian algae while the maximum levels of Hg were found in European algae. In both cases, the high levels were due to high levels of industrial pressure. While the consumption of 5 g per day of dehydrated Asian wakame algae would not pose a significant health risk, the mean Cd levels contribute 22.7% of the 2.5 mg/kg body weight per week acceptable limit (Paz *et al.*, 2019). In endeavours to explain the impact of HM perils and salinity distress on the ailment vulnerability of grouper fry to infectious pancreatic disease, heavy metals zinc, cadmium and copper were utilized to remedy groupers afore and subsequent to virus infection. Total mortalities in the enquiry were 96–100% inside 42 days when fry is presented to both HM and infection exposure while just 5–15% mortalities were seen when introduction was constrained to either HM or disease alone. This advocated that even an infection with a low pathogenicity may cause high mortality when joined with natural pressure like heavy metal exposure. Truth be told, scholars have perceived that pressures by way of precipitous temperature changes, contact by handling, overcrowding and dwindling water quality unfavourably influence fish wellbeing and escalates defencelessness to ailment (Chou *et al.*, 1999).

Advantages in Fish Diet:

The various medical advantages offered by fish intake may well be undermined by the occurrence of harmful metals and metalloids, for example, lead, cadmium, arsenic and mercury, which can adversely impinge on the human body when consumed in unsafe extents. The observation of metal intensity in fish meat is imperative to guarantee accordance with regulatory guidelines and ensuing consumer safety. The connection and impacts of individual metals are not constantly free of one another. One such relationship is the size–age impact on the degree of metal exposure where some metal fixations increase as fish size/age increases. This is particularly valid in predatory fish, though this pattern is not clear in all metals with a few including Cr, Cu, Fe, Cd, Ni, As and Pb which indicated negative relationships with fish size/age in various fish species. Research on trophic level variations can help in the comprehension of metal aggregation along the food web, while spatial scale research deliberating between and within species furnish the connection between ecological contamination, fish toxicity and customer wellbeing (Bosch *et al.*, 2016a). Albeit, a few inauspicious impacts of HM have been known for quite a while, exposure to HM continues and is in any event, expanding in certain parts of the world. Since there is a hazard to the embryo of pregnant ladies, a high consumption of several fish from contaminated waters ought to be avoided. Youngsters are additionally defenceless to Pb ingestion because of excessive gastrointestinal take-up and the penetrable blood–cerebrum divide. Blood Pb levels in kids ought to be decreased beneath the levels considered benign since it might cause neurotoxic impacts even at low levels of exposure intensities (Järup, 2003).

2.2 Heavy Metal Contamination in Water and Sediments

According to Department of Environmental Affairs (DEA, 2018), coastal waters in South Africa have lower levels of contamination as compared to international standards although there were several (67) discharging points contributing approximately 1.3 million m^3/ day of wastewater into the ocean. However, the rise of population might increase the anthropogenic disturbances and may lead to the continuous discharge of pollutants into to the ocean. This may increase the level of contamination from lower to higher levels in the ocean water, which is a great concern for the marine environment. Fauziah & Choesin (2014) measured the buildup of heavy metals in seawater, sediment, seagrass root and leaves in Indonesia. Sampling of these heavy metal containing indicators (water, sediment, and biota) was conducted at two stations. The first was located closer to the coastline while the second was offshore. The results showed both spatial and temporal variation which are most probably associated to the distance from the pollution source and physical conditions of the surroundings.

Jayaprakash *et al.* (2015) investigated the accumulation of heavy metals such as Fe, Mn, Cr, Cu, Ni, Co, Pb, Zn, Cd in water, sediment and six fish species of diverse feeding habits in Chennai, India. Species-explicit diverse relationships of tissue metal afflictions were evident with the overall enrichment factor indicating that metals are taken up by various organs. The bioaccumulation factors indicated that accumulation of metals was from the water to tissues. As illustrated in Figure 1, Trace metals conveyed to marine ecosystems by natural or external inputs are transformed, carried and often precipitated in aquatic environments where they are frequently deposited or adsorb onto finer sediment particles (Jayaprakash *et al.*, 2015). These metals can return into the water column in reduced oxygen deficient conditions and penetrate the fish through their gills and alimentary tract. Enrichment factors advocated that the higher values were attributed to the remobilization of metals in reduced conditions while biota sediment accumulation factors determined the net bioaccumulation due to absorption from the ecological sources (Jayaprakash *et al.*, 2015). This could be used for ecological risk assessment with species having high sediment accumulation factors being potential bio-indicators.

Abadi *et al.* (2019) demonstrated that the Pollution Load Index, which indicates the factor of instances by which the metal intensity in the residue surpasses that of the water, affirmed that the metals Ni, Co, Zn, Pb, Cu, Cd, Fe, and Mn had all through the southern-edge of the Caspian Sea suggested huge spatial dynamics within the system. Furthermore, the authors highlighted that the Hakanson Potential Ecological Risk Index, which is used as a quick and practical tool for environmental assessment, indicated that aquatic zones are at considerable biological danger and require intervention.

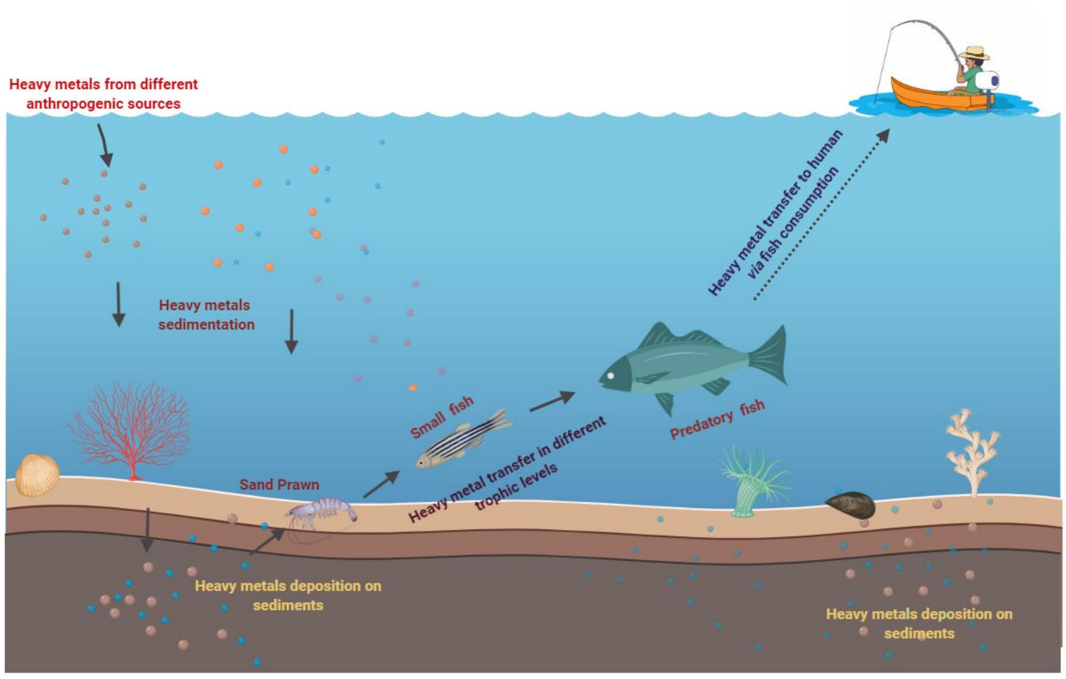

Figure 1. The transfer of toxic heavy metal along the food chain in marine ecosystem.

Sediments in marine systems are responsible for providing nutrients to aquatic plants and vegetation, with marine ecosystems profiting both directly and indirectly from sediment transport and deposition. When considering aquatic life, sediments are known as a significant influence for heavy metal buildup, and is the instigating reservoir of toxins for the lowermost dwelling life forms (Farag *et al.*, 1998). Furthermore, an excessive suspension of sediments can disrupt natural aquatic migrations, as well as damage gills and other organs (Sea *et al.*, 2006). Metals in water and silts represent a danger to sea-going creatures living in marine environments. Metalloids broken down in water could be assimilated onto particulates in sediment where they are more likely to be a biological hazard than in water. Furthermore, accumulation may also occur through the food web. Samples collected for trace metal analysis showed that the bioaccumulation pattern and trophic transfer was more in plankton with exception of Zn and Cu which were elevated in shrimp owing to metabolic prerequisites (Griboff *et al.*, 2018). A declining pattern was detected for Cr, Pb, As, Cd and Hg with growing feeding levels. The interface of rivers and sea plays a chief role in aquatic heavy metal contamination. The chemical metal balances showed that metal concentration in these zones were reliant and impacted by factors such as salinity, dissolved oxygen, pH, flocculation, dissolved organic carbon and sodium hypochlorite concentration at the interface of the mixing of river and ocean. These metals when accumulated in aquatic animals causes irreversible harm (Hesami, Salimi & Ghaderian, 2018) and could undesirably impact the entire coastal ecosystem (Lin *et al.*, 2018). On the flip side, this zone affords micronutrients which are crucial since they perform a major function in the electron transference process concomitant to photosynthesis, respiration, nitrogen fixation, and the reduction of nitrate and nitrite to ammonium (Heidari, 2019). Scrutiny of a recreational sandy seashore exposed considerable and irregular intermittent variations in metal concentration that was formidably affected by an estuary positioned nearby which was influenced by humans. It is alleged that the levels of metals found in the particulate fraction are linked to this human influence. Moreover, the concentrations of metals fluctuated appreciably and dynamically having a momentous aftereffect on the aquatic food web. Furthermore, heavy metal contamination and pollution judgments is not assessed merely by the metal levels but by paired method amalgamating enhancement and geo-accumulation to deliver a truthful judgement of the outcome and transportation of metals (Fernández-Severini *et al.*, 2019).

2.3 Heavy Metals in Fish and Shrimp

Khansari, Ghazi-Khansari & Abdollahi (2005) determined the levels of some toxic elements such as Hg, As, Cd, Pb and Sn in a canned tuna caught from the Persian Gulf for commercial purposes. The author's hypothesis was the level of concentrations of these metals in canned tuna from the Persian Gulf to be similar to the concentrations in the Mediterranean of Austrian and North Indian samples exhibiting elevated amounts. However, the Persian Gulf samples exhibited very low levels compared to Austrian and North Indian samples, suggesting that Persian Gulf was exposed to a minimal amount of contamination than the industrialized countries.

In Portugal da Silva *et al.* (2009) observed high level of Pb, Zn and Cd on the first 2.5 km of the flow path of river sediment trials in an abandoned mine. This contamination gradient was used to evaluate the diversity of benthic diatoms of this stressed environment. Results bordering the mining area showed higher contaminants level with changes in taxanomic composition, structure and morphological changes of benthic diatoms; however, there was a slight improvement from the sites located 2 km downstream. Notably, the samples collected at, 6 km downstream presented an intensification in species richness and diversity while the relative percentage of valve teratology's was lower suggesting that teratologies can be used as pollution indicator for toxic heavy metals.

Concentrations of heavy metals were ascertained in diverse tissue categories of *Clarias gariepinus* in Vaal Dam and Vaal River Barrage, South Africa (Crafford & Avenant-Oldewage, 2010). Sources of these metals incorporate wastewater arising out of informal settlements, leachates from landfill sites, mining activities and discarding of industrial effluents. It was uncovered that the uppermost concentrations were noted in gills trailed by muscle, skin and liver with no noteworthy variance amid locations. In addition, lesions instigated by lower then needed levels of essential metals might result in operational shits thus hindering essential processes in the organisms. Other pollution effects include gross pathologies like scale deformation, liver degeneration, the disruption of metabolic processes and spawning activities (Crafford & Avenant-Oldewage, 2010). From the findings it was surmised that species at the higher trophic levels tends to buildup extensive quantities of metals in their tissues presenting a risk to consumers. In addition, the risks to these top predators themselves include alterations in the procreative processes by intervening with hormonal activities due to high concentrations of chemical contaminants especially cadmium (Damiano, Papetti & Menesatti, 2011).

Fish and shellfish furnish all the quintessential elements vital for life and therefore form a key segment of human food. Shrimp and five common fish from India (Subarnarekha River) were examined for the presence of heavy metals. The mean target hazard quotient (THQ) for Cu, Ni, and Cr were high in some samples although their averages were below one, except for two fish species, shrimp values exceeded one demonstrating bioaccumulation of these metals. Based on the THQ, the level of heavy metals in shrimp and two fishes surpass safe consumption levels and consumption may lead to chronic disorders (Giri & Singh, 2013). However, the estimated daily intake (EDI) of fish was 15 g of fish per day translated to exposure values below the World Health Organization limit making them safe for consumption. Abdolahpur *et al.* (2013) measured the heavy metal concentrations in shrimp, fish and sediment from the mouth of the Arvand River, Meleh estuary and Musa estuary in the north east Persian Gulf. A total of 60 fish, 50 shrimp and 15 sediment samples were collected, analysed and found that high levels of metals were found in both benthic and pelagic species with respect to the sampling sites. Further, the authors also observed the higher levels of Ni, Cd, Cu, Pb and Zn in the hepatopancreas than muscle tissues in collected shrimp samples compared to fish samples.

Dadar, Peyghan & Memari (2014) studied and documented the levels of metals in *Litopenaeus vannamei* and submitted a dispersal pattern and accumulation of heavy metals in the Persian Gulf, an area in which petrochemical and refinery endeavors instigated an escalation in heavy metal wastes. The results revealed the manifestation of excessive Pb concentrations in areas of dense urbanization and industrialization as the principal hazard to human and marine health. This was evidenced in the lowest Pb levels observed in Deylam, an isolated area with less industrial activity. It was further found that the level of Cu was higher in shrimp.

Fauziah & Choesin (2014) measured heavy metal accumulation in seawater, sediment, leaves and roots of seagrass in Indonesia . These heavy metal encompassing indicators were sampled at two stations, the first was posted neighboring the coastline while the second was offshore. Outcomes exhibited spatial and temporal deviations which are in all probability produced by varying distance from the pollution source together with physical environmetal conditions such as water current.

The levels of Cu, Zn, Pb, Cd, Fe and Mn were appraised in the benthic and pelagic marketable fish species from the Red Sea. Gills with an exceptionally enormous surface area is the core route for ion exchange and percipitously absorb heavy metals from the water owing to diffusion. Pelagic filter feeders amassed high levels of all metals with Pb in muscles and Mn in all organs. In dissimilarity, benthic fish had greater metal concentrations because they were in unswerving interaction with sediments. Even though fish are ordinarily migratory, metal buildup in their organs promotes verification of exposure to contamination that may well be employed to assess their collection areas. El-Moselhy *et al.* (2014) and Ahmad et al. (2015) carried out a study downstream of a river in Nowshera city to evaluate the heavy metal concentrations in muscles and liver of commonly consumed fish. Findings demonstrated that concentrations of Cr, Ni, Cu, Zn and Pb were excessive in muscles and liver, whereas the concentration of Cd was low in comparison to other heavy metals. However, Cd concentration exceeded the given recommended dietary allowance of USA parameters and may result in consumer health complications. Gárriz *et al.* (2019) and Salam *et al.* (2019) reconfirmed that when studying heavy metal accumulation in fish, the gill tissue should be selected because it is considered the organ most exposed to dissolved and suspended heavy metals while the liver should be chosen since it is believed to be the organ of storage within the fish body while muscle tissue ought to be picked as it is the most popular edible part and hence the main route of heavy metal exposure to humans (Salam *et al.*, 2019). Every heavy metal has its potential effects on both environment and human hence, the need to examine the effects of selected heavy metals in this study.

2.4 Effects of Heavy Metals on Aquatic organisms and Humans

Gu *et al.* (2015) revealed that toxic heavy metals could be detrimental to human health when consumed over prolonged periods. Similarly, vital metals can also prove to be toxic with excessive intake. Fish have been found to accumulate heavy metals in both high and low concentration, which are potentially transferred to humans who consume them and to other organisms in the next trophic level of the food web pathway. Selected heavy metals and their environmental and human health impacts have been examined under subheadings below with a summary of the effect of different metals on human health given in Table 1.

2.4.1 Copper

Copper mostly mined as a chalcopyrite ($CuFeS_2$). It is a good conductor of both heat and electricity but has a low chemical reactivity. Copper is mainly used for electrical equipment, construction, industrial machinery and alloys such as bronze and brass. It's a common substance that occurs naturally and spreads through the environment (DWAF, 1996). However, as copper production continues to rise, increasing amounts end up in the environment. Copper also deposits as sludge on riverbanks due to mining activities and other human anthropogenic activities. Copper does not disintegrate in the soil and can thus accumulate in organisms interacting with the soil. Settled copper can interpose the actions in sediments by negatively influencing microorganism activity. Due to its affinity to particulate matter, iron, manganese and organics, copper tends to accumulate in sediments thus increasing exposure to benthic organisms (CCME, 2002)**.** The presence of copper in aquatic ecosystems is intricate and affected by pH and dissolved oxygen (WHO, 1993).Although copper is an important trace element essential for life, it can be toxic to plants at concentrations greater than 20 mg/kg, and toxic to microorganisms above 0.1 mg/L. The levels of copper in sediments associated with adverse biological effects is 197 mg/kg in freshwater sediment and 108 mg/kg in marine sediment (CCME, 2002). The target dissolved copper concentration in freshwater sources ranges from 0.0003 to 0.0014 mg/L while the target in South African coastal zones is 0.005 mg/L (DWAF, 1996). Copper originating from petroleum refining activities together with the manufacture of antifouling chemicals adversely stresses bacteria, plants, fish and benthic invertebrates (Couet *et al.*, 2018) thus causing a difficulty in marine ecosystem management (Qu *et al.*, 2016). In humans, long-term exposure may result in declined intelligence among adolescents while chronic exposure may result in Wilson's Disease, hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea. Copper is not the only metal that causes discomfort of the human stomach, chromium is another metal with this tendency.

2.4.2 Chromium

Chromium is a silver-gray lustrous, brittle and hard metal. Among the different isotopes of chromium that exists, chromium (lll) and (Vl) are more common in the environment. Chromium (III) and (VI) oxidation states depend on redox potential, pH and the presence of oxidizing and reducing compounds. In soil, it occurs mainly due to human actions and varies considerably with a mean value ranging from 14 – 70 mg/kg while the mean concentration in seawater is 0.00004 to 0.0005 mg/L, and 0.0005 to 0.002 mg/L in surface waters (Pedley and Pond, 2003).

Chromium (III) is a vital element for organisms and if daily dose is, too low it can upset sugar absorption and cause heart complications. Chromium (VI) is mainly lethal to organisms and could change genetic materials and even result in cancer. The accumulation of chromium is not known to occur in fish although high levels may damage their gills. In plants, excess chromium severely affects their biological functioning and alter the food chain because they are primary producers (Jaishankar *et al.*, 2014). Benthic organisms are exposed to dissolved and particulate chromium with levels in sediment associated with adverse biological effects ranging from 90 mg/kg in freshwater sediment and 160 mg/kg in marine sediment.

Table 1.The effect of different minerals and metals on human health.

Heavy metals	Positive effects	Negative effects
Copper (Cu)	Is crucial for life supporting biological progressions (de Romaña *et al.*, 2011).	In immoderation is toxic affecting habitual liver impairments and may give rise to Wilson disease. Grave deficit of copper may well lead to Menkes syndrome (de Romaña *et al.*, 2011).
Chromium (Cr)	Chromium is an imperative nutrient in the metabolism of sugar and fat (Anderson, 1997).	Hexavalent chromium is associated with the following: dermatitis, allergic and eczematous skin reactions, skin and mucous membrane ulcerations, perforation of the nasal septum, allergic asthmatic reactions, bronchial carcinomas, gastro-enteritis, hepatocellular deficiency, and renal oligo anuric deficiency (Baruthio, 1992). Cr scarcity may possibly lead to symptoms mimicking diabetes and cardiovascular disorders (Anderson, 1997).
Cadmium (Cd)	Cadmium has no physiological purpose within the human body (Godt *et al.*, 2006).	Cadmium tainted foods may perhaps trigger vomiting and diarrhoea. While persistent contact may well bring about kidney damage. Moreover effecting the ovarian steroidogenic pathway or bring about cancer (Godt *et al.*, 2006).
Manganese (Mn)	Is indispensable because: (i) it acts as an activator for gluconeogenic enzymes (ii) is vital for mitochondrial membrane security (iii) it initiates glycosyl transferase for glycosaminoglycans production (Zlotkin, Atkinson & Lockitch, 1995).	Neurotoxic at certain intensities of exposure (Santamaria, 2008).
Lead (Pb)	Is precarious at whichever concentration of exposure (Barbosa *et al.*, 2005).	Children may be subjected to hematological and neurological impacts. Furthermore, incumbering the production of red blood cells and chemical compounds. While enduring exposure gives rise to anemia, cancer, reproductive harm in males, hormonal imbalance and reduced intelligence (Mudgal *et al.*, 2010).
Zinc (Zn)	Has three foremost biological responsibilities: 1. Performs as catalyst. 2. Functions as a basic ion,	Studies bring forth that free ionic zinc is a compelling killer of neurons, glia and other cell types. Zinc levels in the brain are conserved within a confined span and deviances significantly

	3. Behaves as a regulatory ion. Zinc-binding motifs are uncovered in proteins encoded by the human genome physiologically, while free zinc is controlled by single cells and engage in homeostasis, immune functions, oxidative stresses, apoptosis and aging (Chasapis *et al.*, 2012).	beyond or lower being proconvulsive and cytolethal correspondingly and free zinc ions may be considerably more lethal biologically than assumed (Nriagu, 2011).
Calcium (Ca)	Calcium is the utmost copious mineral in the human body and is indispensable in several physiological and pathological progressions (Pu, Chen & Xue, 2016).	Disproportionate intake of calcium escalates the probabilities for kidney stone, myocardial infarction and stroke (Pu, Chen & Xue, 2016).
Magnesium (Mg)	Magnesium is a cofactor in processes that include, protein synthesis, cellular energy production and storage, reproduction, DNA and RNA synthesis, and stabilizing mitochondrial membranes. Correspondingly playing a vital function in nerve transmission, cardiac excitability, neuromuscular conduction, muscular contraction, vasomotor tone, blood pressure regulation, and glucose and insulin metabolism. It further participates in disease inhibition and general human health (Volpe, 2013).	Subdued levels of magnesium are supplementary to enduring diseases that comprise migraine headaches, Alzheimer's disease, stroke, hypertension, cardiovascular disease, and type 2 diabetes mellitus (Volpe, 2013).
Sodium (Na)	Sodium is a critical electrolyte vital for the body to perform routinely and to maintain fluid and blood levels in the body (Edelman & Leibman, 1959).	High sodium intake increases blood pressure and hence the danger of cardiovascular disease (Mozaffarian *et al.*, 2014), in addition to renal abnormalities (Kaplan, 2000).
Potassium (K)	Potassium is also an important electrolyte needed for normal body functioning and to maintain fluid and blood volumes (Edelman & Leibman, 1959). High-potassium diets lower blood pressure in individuals with raised blood pressure, reduces cardiovascular disease mortality, slows the progression of renal disease and lowers urinary calcium excretion. Potassium also plays an important role in the management of hypercalciuria and kidney stones and is likely to decrease the risk of osteoporosis (He & MacGregor, 2008).	High potassium intake increases blood pressure, a risk factor for cardiovascular disease and renal abnormalities (Kovesdy *et al.*, 2017). Reduced serum potassium increases the risk of lethal ventricular arrhythmias in patients with ischaemic heart disease, heart failure and left ventricular hypertrophy (He & MacGregor, 2008).

Selenium (Se)	• Is a trace mineral constituent of selenoproteins that participate in structural and enzymic roles. It is necessary for the production of active thyroid hormones, in sperm maturation and motility, and may reduce miscarriages, It also reduces the risk of cancer (Rayman, 2019).	low Se intake is associated to neurodegenerative diseases, cardiovascular diseases (Brenneisen, Steinbrenner and Sies, 2005), and adverse mood swings (Rayman, 2019).
Arsenic (As)	No known benefit.	Arsenic is linked to gastroenteritis, neurological manifestations, vascular changes, diabetes and cancers of the bladder, lung, liver, kidney and prostate (Abernathy, Thomas & Calderon, 2003).
Aluminium (Al)	Aluminium has no essential function (Pérez-Granados & Vaquero, 2002).	Neurotoxicity from long term exposure, associated with Alzheimer's disease, brain aging and Parkinson's disease (Antoine, Fung & Grant, 2017)
Vanadium (V)	Required as a building material for bones and teeth, used in the management of diabetes (Badmaev, Prakash & Majeed, 1999).	Adverse effects may include, reproductive toxicity, developmental toxicant, reduce fertility, embryolethality, fetotoxicity, and teratogenicity (Domingo, 1996).
Nickel (Ni)	Nickel is essential for normal growth and reproduction (Bhupander & P, 2011)	Is haematotoxic, immunotoxic, neurotoxic, genotoxic, reproductive toxic, pulmonary toxic, nephrotoxic , hepatotoxic and carcinogenic agent (Das, Das & Dhundasi, 2008).
Iron (Fe)	Participates in metabolic processes including oxygen transport, deoxyribonucleic acid (DNA) synthesis, and electron transport (Abbaspour *et al.*, 2014).	In excess can lead to tissue damage. Disorders range from anaemia to iron overload, and possibly neurodegenerative diseases (Abbaspour *et al.*, 2014).

The water quality standards for chromium for the security of aquatic life are 0.0089 mg/L and 0.056 mg/L for chromium (III) in freshwater and marine environments respectively; and 0.001 mg/L and 0.0015 mg/L for chromium (VI) in freshwater and marine environments respectively (CCME, 2002). In humans, shortage of chromium (lll) can cause adverse health conditions like diabetes whereas chromium (lV) causes a variety of diseases such as skin rashes, ulcers and change genetic materials. Chromium is not the only the heavy metal of importance that has the tendency to cause alteration in the genetic constituent of organisms exposed to it. Cadmium is another heavy metal of interest that possess similar trends of damaging effects on the genetic constituent of organisms (Oruko *et al.*, 2020).

2.4.3 Cadmium

Cadmium is used in Ni-Cd batteries, pigments, coatings, plating, and a stabilizer for plastics. It also has the specialized use in electroplating steel where a film of cadmium provides protection against marine environments. Naturally, cadmium is found in rocks and released into rivers through the weathering of these rocks. Other sources include human activities such as manures, pesticides and fertilizer production. In addition, combustion and burning of fossil fuels also release cadmium into the air. Cadmium present in manures, pesticides and fertilizers applied on farmlands end up in soils and surface waters and are transported great distances. This metal remains in soils and sediments for long periods, plants have the ability to absorb it to levels that it can be transferred to humans (Jaishankar *et al.*, 2014) . Cadmium has high bioavailability and hence tends to bioaccumulate.

Cadmium induces oxidative stress and nutritional insufficiency in plants**.** Once cadmium is absorbed into an organism's body, it builds up and remains in the organism for a long period. Acidic environments promote absorption of the metal by plants, which can be transferred to other organisms that depend on them. In aquatic ecosystems, the metal can bio-accumulate in mussels, oysters, shrimps, lobsters and fish but the vulnerability to cadmium can vary greatly among organisms. The consumption of these aquatic organisms by human and other animals can lead to high blood-pressure, liver disease and nerve or brain damage (Jaishankar *et al.*, 2014).

2.4.4 Manganese

Manganese, although does not occur naturally in its pure form, is an abundant metal in soil occurring primarily as pyrolusite (MnO_2) and rhodochrosite ($MnCO_3$). It is a chemically active element that is easily oxidized and essential in steel, stainless steel and fertilizer production (Ziemacki *et al.*, 1989). It has variable forms of occurrence in surface waters (WHO, 1993). Manganese compounds exist as solids in soil, water and air. Human actions such as mining, alloy production, goods processing, iron-manganese operations, welding, agrochemical production and other anthropogenic activities result in increased manganese pollution in the environment. Despite its negative impact, it also plays an essential role in organisms by playing a vital role for mitochondrial membrane security, acts as an activator for gluconeogenic enzymes and initiates glycosyl transferase for glycosaminoglycan's (Zlotkin, Atkinson & Lockitch, 1995)

Manganese is a vital element for carbohydrate, protein, and fat metabolism in many organisms. Fish and mammals may absorb 5 ppm and 3 ppm manganese, respectively. Little consumption of this metal by fish and mammals may meddle with normal growth processes while consuming too much manganese is lethal even at quite low dosage. Manganese can be adsorbed in soil and bioaccumulate in organisms such as mollusks and fish before being transferred to humans when they are eaten (WHO, 1993). Hence, the need to maintain its level within the acceptable standard that is non- threatening for human consumption. Lead is also other heavy metals of interest that needs to be maintained within acceptable limits because of its similar health impacts.

2.4.5 Lead

Lead (Pb) is usually found in ores with zinc, silver and copper. It is a major constituent of the lead-acid batteries (Jaishankar *et al.*, 2014). Lead typically takes the form of four naturally occurring isotopes in the environment depending on surrounding mineral sources and is poorly soluble in water. Lead is a growing poisonous metal that finds its way into marine ecosystems through runoff, industrial effluents and sewage waste streams (Bastami and Esmailian, 2012; Kohzadi *et al.*, 2019). The accumulated lead in the water bodies and sediment cause adverse health effects to organisms due to lead poisoning. Additionally, the presence of lead in water bodies may affect the metabolic activities of phytoplankton that releases oxygen in seas. Many larger sea creatures consume plankton making it particularly dangerous due to accumulation in individual organisms and the whole food chain. The target concentration of dissolved lead in freshwater environments range from 0.0002 to 0.0012 mg/L while that of the South African coastal zone is 0.012 mg/L (DWAF, 1995) while the level of lead in sediment associated with adverse biological effects is 91.3 and 112 mg/kg in fresh and marine sediment respectively. In human, lead causes anemia, rise in blood pressure, brain damage, kidney damage and many other diseases (Jaishankar *et al.*, 2014). Unlike lead, zinc has a more beneficial role in humans and its deficiency can be detrimental.

2.4.6 Zinc

Zinc occurs naturally in trivial quantities in virtually every igneous rock, with the natural content of zinc in soils ranging from 1 – 300 mg/kg (WHO, 2003). It is a mobile metal in soil with solubility increasing especially as pH falls below 6 (Fellenberg, 2000; Raoult *et al.*, 2018) and it is significantly affected by water chemistry, depth and silica levels in marine environments and are rising unnaturally, due to anthropogenic addition. Industrial activities comprise the most influential sources of zinc in natural environment (DWAF, 1995). Organisms present in the natural environment like fish in water bodies tends to accrue this metal. Humans are quite resilient to zinc. The toxic effects of zinc in plants begin at 200 mg/kg (Fellenberg, 2000). The target water quality range for dissolved zinc in freshwater sources is 0.002 mg/L while the value of total zinc in the South African coastal zone is 0.025 mg/L (DWAF, 1995) with the probable effects in sediment associated with frequent adverse biological effects being 315 mg/kg in freshwater sediment and 271 mg/kg in marine/estuarine sediments (CCME, 2002). Zinc is an essential element involved in most metabolic progressions in humans. However, too much zinc can still cause stomach cramps, skin irritations, vomiting, nausea and anemia. Other metals such as calcium, magnesium, arsenic, vanadium, nickel, sodium, selenium and iron are of great economic importance. Hence, the need to understand their impact to human and other organisms.

2.3.7 Other metals

Calcium (Ca) occurs naturally in the Earth's crust with an oxidation state of +2 and is an essential component of all organisms because it is required for shell development in most invertebrates and bones of all vertebrates. Calcium occurs in most suspended and sedimentary material and becomes mobile in the water column under acidic conditions. Calcium has the ability to transfer and concentrate up the food chain resulting in toxic effects at higher levels due to bioaccumulation. Anthropogenic sources that increase the levels of naturally occurring calcium include industrial and wastewater treatment processes, the typical concentration of calcium in freshwater is less than 15 mg/L (Chapman, 1991).

Magnesium (Mg) is an essential macronutrient and is naturally leached from ferromagnesian and carbonate rocks. Magnesium together with calcium is responsible for hardness in water. Being a macronutrient, it is essential for living organisms at a natural concentration of 1 to 100 mg/L. Deficiency of magnesium negatively impacts photosynthesis, increases skeletal deformities and reduces reproductive capabilities. However, levitated concentrations are toxic and adversely affect metabolism and the central nervous system. Toxic sources of magnesium include various steels, fertilizers and chemical industries (Chapman, 1991; DWAF, 1996; Sawyer, 2003).

Sodium (Na) is the most nontoxic metal found in natural waters and is abundant in the Earth's crust. Sodium salts are highly soluble and occur in large concentrations in surface waters emanating from industrial effluents and sewage. Elevated concentrations of sodium can be hazardous if ingested by people suffering from cardiac or kidney ailments, in addition this can deteriorate the physical condition of soil affecting plant growth (Chapman, 1991). Hence, the continuous monitoring of sodium levels in both aquatic and terrestrial ecosystem is warranted.

Potassium (K) containing rocks are relatively resistant to weathering causing minute levels of potassium found in water bodies. Potassium salts are highly soluble and form an essential nutritional element which can be easily absorbed by aquatic biota. Potassium salts are extensively used in industry and fertilizers, and consequently enter waterways through industrial discharge or run-off (Chapman, 1991).

Selenium (Se) occurs in the Earth's crust as elemental selenium, ferric selenite and calcium selenite with the SeO_3^{+2} ion being the most stable in water. Increased concentrations of selenium in water bodies can be directly attributed to industrial activities, thus increasing its toxicity to fish species with toxicity being directly related to water temperature. Selenium is essential in the diet of both humans and animals but is toxic at high concentrations. Normal selenium concentration is below 0.001 mg/L in natural water but can range between 0.05 – 0.3 mg/L. Elevated selenium concentrations are toxic to aquatic organisms causing immobilization, reduced survival, reduced reproduction and ultimately death. Selenium may accumulate in the liver of mammals and fish and subsequently bioaccumulated up the food chain, posing a more serious threat to predators. The target water quality range for total selenium in freshwater is 0.002 mg/L while the target coastal zone value is 0.41 mg/L (DWAF, 1995, 1996; Sawyer, 2003; Boyd, 2010).

Arsenic (As) occurs naturally within the Earth's crust as arsenate (AsO_4^{-3}) and at low concentrations in the environment due to its poor solubility. It occurs in several oxidation states depending on the pH and redox potential of the water. Arsenic enters aquatic systems through mining operations, arsenical insecticides and combustion of fossil fuels. Arsenic may be bio-concentrated in aquatic organisms since it has an affinity for organic substances, leading to declined development and reproduction in fish and invertebrates. Arsenic contamination may also change behavioral and migration patterns in fish. Humans are more sensitive to arsenic than aquatic organisms and therefore consumption of contaminated organisms or water may pose a great health risk. Biological effects associated with elevated arsenic in sediments include decreased invertebrate abundance, increased mortality and behavioral changes. The target concentration for arsenic in freshwater is 0.01 mg/L while the marine target for total arsenic in South African coasts is 0.012 mg/L and the levels of arsenic in sediment associated with frequent adverse biological effects is 17 mg/kg in fresh water aquatic systems and 41.6 mg/kg in marine sediment (DWAF, 1995, 1996; CCME, 2002; Sawyer, 2003; Boyd, 2010).

Aluminum (Al) is an element that constitute 8% of the Earth's crust and is released in the surroundings primarily via natural processes. The solubility of aluminum in surface waters is strongly dependent on pH, whereby elevated concentrations may exist under acidic conditions. Anthropogenic sources commonly include acid mine drainage upsurges dissolved Al content in natural waters. Dissolved Al at neutral pH range from 0.001 to 0.05 mg/L but rise to 0.5 to 1 mg/L in organic rich aquatic environments (DWAF, 1996; WHO, 2003).

Vanadium (V) exist all over the Earth's crust at a mean concentration of 150 mg/kg with soil concentrations of up to 310 mg/kg. Vanadium occurs in different oxidation states that is most soluble and mobile in aquatic environments. Vanadium is an essential element for the growth of green algae, and plants that have the ability to catabolize by producing vanadium bromoperoxidase enzyme and also provides supplement to some nitrogen-fixing micro-organisms, such as *Azotobacter*. The concentration of vanadium in water is region specific and generally ranges from 0.0002 – 0.1 mg/L in freshwaters which is governed by geography, with the range in freshwater being higher than that of seawater which has a target of 0.1 mg/L. Anthropogenic sources of vanadium include metallurgic works, and activities involving the processing of residual oil and coal (Ziemacki *et al.*, 1989; DWAF, 1995; CCME, 2002).

Nickel (Ni) occurs predominantly in iron and magnesium ores and is released naturally through weathering and erosion with anthropogenic sources including mining, smelting and refining activities. Nickel concentrations in the Earth's crust range from 58 – 94 mg/kg, with much lower levels in natural water bodies. Nickel is strongly attracted to negatively charged particles and is rapidly removed from solution depending on pH and accumulate in aquatic sediments which acts as a temporary nickel sink. The target nickel concentration in South African coastal zones is 0.025 mg/L. Although there are no available guidelines on specific concentrations of nickel that are considered safe for aquatic life, DWAF suggests that concentrations exceeding 0.2mg/L are unsuitable for irrigation (DWAF, 1995; CCME, 2002; WHO, 2003).

Iron (Fe) accounts for approximately 5% of the earth's crust and is rarely found in nature in its elemental form as ions. The two common states of iron in water are reduced Fe^{2+} (ferrous) and oxidized Fe^{3+} (ferric) states. Iron is released naturally by the weathering of sulphide ores, igneous, sedimentary and metamorphic rocks and is anthropologically released by burning of coal, acid mine drainage, metal processing and from the corrosion of iron and steel. The median iron concentration in river water is reported to be 0.7 mg/L. The iron concentration in freshwater ecosystems should not be allowed to vary by more than 10% of the dissolved background concentration and the European Economic Community international target for coastal zones is 1 mg/L (DWAF, 1995; WHO, 2003). In summary, these heavy metals at toxic levels affect the aquatic animals in water bodies in South Africa and could impede fish production in the country.

2.5 Durban Coast and the Associated Pollution Sources

The KZN shoreline of South Africa has experienced rapid development over a relatively short period of time. Moreover, the development is uneven and is largely concentrated in the southern section of the coast. The nearness of the ports and modern centres in the area favours tremendous demographic growth along the coastal cities leading to several anthropogenic pressures over the coastal environments. Metal concentrations along the coastal beaches of KZN suggest that these concentrations is mainly attributed to the natural source rock composition, however these coastal regions are recently affected by the external inputs like sewage outfalls, industrial effluents and other anthropogenic disturbances. Despite the fact that beach development is inevitable and beneficial from a financial view point, it must be effectively regulated and managed (Vetrimurugan *et al.*, 2018). Durban being eThekwini region's lead city is the third biggest city in South Africa, with a populace of 3.6 million, with enormous communities living in dense informal settlements that need essential amenities like the conveyance of clean water and sanitation (eThekwini Municipality, 2016). This region set on the Indian Ocean shoreline of South Africa is profoundly modern with the second biggest production hub in the nation enveloping a bustling harbour that encompasses 66% of the nation's freight traffic (eThekwini Municipality, 2014). Anthropogenic exercises in the zone incorporate a variety of businesses, petrochemical processing, pulp and paper production and vehicular traffic bringing about the aggregation of toxins in sediments which act as an extended toxin sink (Masood *et al.*, 2016; Zhu *et al.*, 2017). These chemical toxins may come to be bioavailable due to remobilisation occasions, for example, floods, dredging or bioturbation which may well bring about its introduction to benthic and related organisms and ultimately antagonistically influencing human and natural exposure (Vogt *et al.*, 2019).

Historically, for an anti-apartheid environmentalist, the development of ecological strategy in Durban alongside authentic endeavours to save and expand the wild was met with opposition of all classes had almost no enthusiasm for what we currently call green issues. At first there was no general ecological strategy even at the degree of conceptualization, not to mention any kind of extensive all-encompassing vision, be that as it may, the cleanliness of ocean water was checked to advance the ascent of the shoreline travel industry. Politically-sanctioned racial segregation was integrated with more extensive policies that redistributed, frequently mercilessly, to separate living districts by race, particularly under the aegis of the Group Areas Act to advance business interests that gave rise to polluting industries such as timber and chemical businesses during the 1980s. In 1993, the AECI at the southern fringe of the zone, spilled chlorine gas. Umlazi Waste-Tech site, which took care of the most contaminating and possibly perilous wastage in the metropolitan zone of Durban, started to spill leachate contaminating soil and groundwater while discharging toxic smells toward a nearby school. Thereafter, came the production of the petrochemical cluster, the predominance of an industrial zone and the extension of the port are some of developments of the Durban South Basin. These developments require a regulated industrial path requiring the promotion of environmental controls that are expensive, difficult to monitor and proves to be unrealistic because the private sector provides both capital and initiative (Freund, 2001).

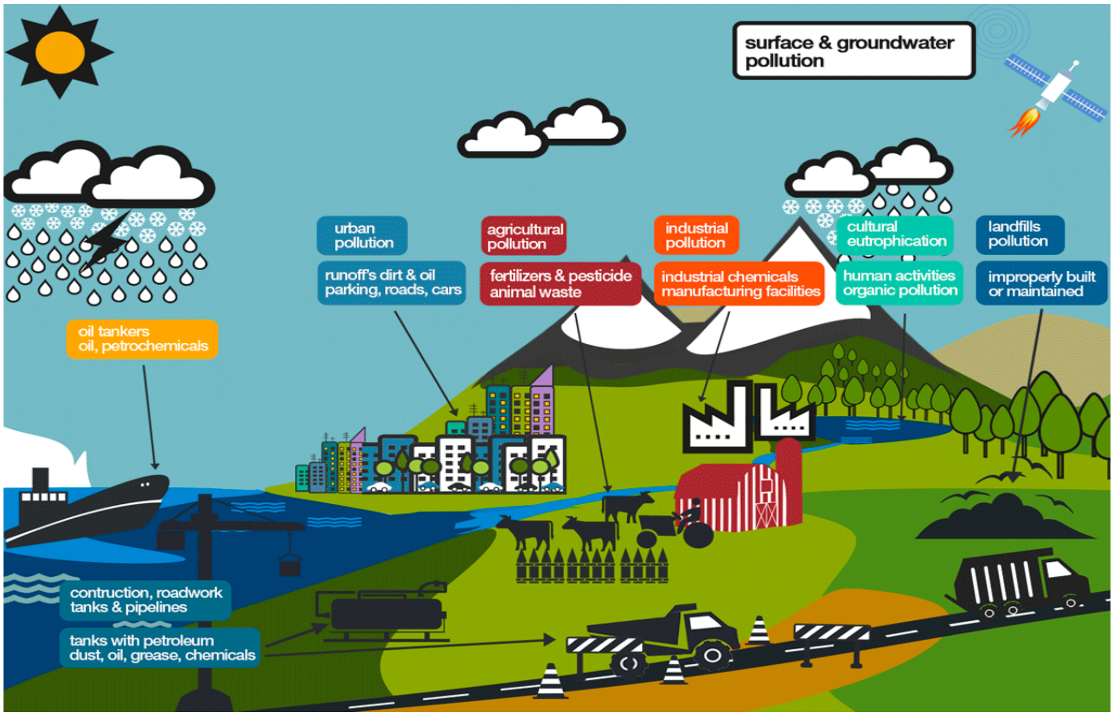

Figure 2. The typical anthropogenic activities contributing to the pollution of marine ecosystem. (Source: Buddha Jeans)

Monitoring timeous changes or a lack thereof forms an integral part of a pollution orientated programme. In the 70's and 80's pollution monitoring was primarily of a chemical nature measuring the total concentrations of various chemical compounds with reduced significance placed on biological indicators. Upon marine discharge, most materials undergo changes that may include precipitation, degradation, or decomposition. Since availability to organisms and toxicity are dependent on chemical form, an understanding of the processes of change is important. In the 80's, work was done to determine the 'availability' of a number of toxic metals in sediments and populating a method of assessing the relative 'pollution status' of marine environments. Much of the work relating to pollution comprised of assessing the effects after the fact and monitoring would only reach a full potential when predictive capabilities existed (Lord, Anderson & Basson, 1984). In view of satisfactory results from outfall monitoring programs, the Minister of Water Affairs granted permission to the Durban City Council to increase and alter discharge composition although monitoring continued at less frequent intervals. This increase in anthropogenic stress together with the decreased monitoring was risky and would fail to provide an early indication of possible degradation to the receiving marine environment. However, since the promulgation of the National Physical Development Plan coastal development awareness of the marine disposal of effluents increased to ensure that developments would have minimal effect and remain within the design dilution limits, however success resulted in an attitude shift of the authorities who readily accepted the disposal of a wider range of discharges (McGlashan & Macleod, 1986).

Common to large coastal cities globally, significant proportions of both domestic and industrial wastewater are discharged into marine environments through deep water outfalls (Figure 2). Durban Basin is not an exception and discharges via outfall wastewater treatment facilities operated by eThekwini Municipality exits. These effluents are regarded as a leading source of anthropogenic contaminants of both biological and chemical nature having the potential to prejudice the receiving water and compromise both the ecosystem and human health. Nevertheless, properly managed discharges of wastewater into marine environments are recognized as an acceptable disposal option (McClurg *et al.*, 2006). Changes in South African's marine environments have been seen with the fundamental burdens including changing sea temperatures, ocean currents, stratification and nutriment accessibility, marine acidification, contamination, natural surrounding modifications or obliteration, beach front eutrophication, spread of intrusive species and harvesting of fish is consistent with global trends. Contamination stresses may correlate with developing human populaces, expanded urbanization and industrialization. Marine pollution origins at both point and diffuse sources with point sources including the harbors, wastewater submarine pipelines, stormwater channels, waterways and streams while diffuse sources incorporate land–ocean interfaces, ships and precipitation form the atmosphere. The effects of these sources are predominately localized and experience rapid dilution by currents. In the Durban Basin it is believed that deleterious trace elements and compounds associated with the sewage outfalls are confined to point sources along the Durban coastline. In addition, elevated levels of certain toxins have been recorded in discharges from the Huntsman-Trioxide pipeline off Amanzimtoti and metal concentration in sediments from the Thukela Bank exceeded acceptable threshold levels (Reopanichkul *et al.*, 2009). In the Durban harbor, high levels of tributyltin contamination from antifouling paints was observed and although it was believed that the dilution and dispersion of these toxins would have a minimal effect, biological monitoring of mussels indicated an increased accumulation of these toxins which are also responsible for algal blooms (Moloney *et al.*, 2013).

2.6 Major Industries Contributing to Marine Pollution in Durban

2.6.1 Sugar industry

As early as December 1852 it was believed that in Durban "sugar is probably destined to constitute the first basis of our advancement and prosperity" following Edwin Morewood's production of the first sugar. Since then interest in sugar steadily increased and within a decade a line of sugar estates had sprung up and to date remain. Tongaat Hulett Sugar Refinery located in Rossburgh was established in 1910 and commissioned to refine raw brown sugar to white sugar. Hulett Sugar is a resident of the heavily industrialised Durban South Basin, which includes and is surrounded by dense communities. The twenty first century has witnessed rapid legislation changes and aggressive public environmental awareness resulting in the sugar refinery being under severe environmental stress. The industry contributes to environmental impacts through process operation that incorporate a waste filter cake from carbonation and a chemical effluent emanating from ion exchange which is disposed via the sea outfall while other effluents leave through the municipal sewer which also find its way to the marine environment (Padayachee 2010; Anon 2018).

2.6.2 Shipping industry

The prominent vessel transportation industry in the region may possibly affect oceanic biological variability through ballast discharge and other debris that diminish the quality of ocean water resulting in it being less apposite for aquatic existence (RSA, 2002). For instance, in the year 2007 about 22 million tons of stabilizer water was released in South African ports (RSA, 2012). The Marine Environmental Protection Committee of the International Maritime Organization embraced voluntary guidelines to prevent introducing undesirable sea-going life forms and pathogens from stabilizer water and residue releases. However, before the year 2000, South Africa did not implement any guidelines.

In addition, although some countries banned the cleaning of ship hulls at sea, South Africa did not subscribe to this. However, encouragingly, post 2000, South Africa implemented the Global Ballast Water Management Programme to systematically monitor the country's ports (Atkinson, 2008)**.**

2.6.3 Central work outfall

The Central Works outfall carries predominantly sanitary wastewater and extends 3200m from the shoreline. It is a 1.32 m diameter pipe with 18 diffusers discharging about 135 mega liters per day at a depth of between 43-53m (McClurg *et al.*, 2006). Despite, the fact that the concentration of chemical discharges measured might be utilized as a gauge of harmfulness. This by itself is inadequate to regulate discharges since some toxic chemicals have obscure additive substances, adversarial or synergistic harmful impacts when amalgamated. The Central Works embraced the ocean urchin fertilization test as a measure of discharge effluent toxicity. The test determines the modicum tolerable toxicant intensity which is the smallest number of attenuations in seawater that is expected to neutralize the emission lethality to ocean urchin gametes. The smallest adequate toxicant intensity together with the hypothetical minimum number of dilutions in seawater, makes it conceivable to predict a region where harmful effects may be expected around the outfalls. The results of these tests demonstrated that there was limited danger of poisonous qualities past the zone of primary dilution. Tests of the Central works demonstrated that the quantity of weakening required to have a non-lethal impact to ocean urchin gametes surpassed the speculative iota of dilution of the submarine pipeline showing that when there is no water movement organisms beyond the zone of initial dilution may encounter adverse impacts. Water tests gathered from the midpoint and sea floor of the water section denoted levels that complied to the South African Water Quality Guidelines for Coastal Marine Waters. Albeit a vast array of toxins which are ordinarily sparingly soluble and upon discharge are quickly adsorb onto suspended sediments and 'foraged' from the water segment through flocculation, coagulation and sedimentation which could unfavorably influence benthic networks. Sediment examinations which is a progressively moderate, spatially and timely coordinated unified appraisal of pollution issues are completed since the major focus in the region's outfall monitoring programme is on the benthic environments. A study in 2011 gave proof that outfall releases have degraded sediment quality around the diffuser areas of the Central Works, it is additionally recommended that examination of the benthic macrofaunal populations is a key biomarker to gauge the environmental effect of the outfalls (CSIR, 2012).

2.6.4 Offshore dumping ground

The offshore dumping of dredged materials is governed by the Dumping at Sea Control Act No. 73 of 1980 and the international London Convention of 1972. In 2007, on average, only 10 permits were issued annually allowing dumping at specified locations except that these locations were mostly near harbours including the Durban harbour. To this end the pollution sub-directorate was responsible for issuing permits, establishing dump sites, implementing environmental monitoring programmes and monitoring the dumped waste's nature since it threatens biodiversity via oppressing influences, sediment toxicity and increasing water turbidity (Atkinson, 2008). The Umgeni River flows through this region with its mouth at Blue Lagoon. The point sources of pollution associated with this river as with many other South African rivers are industries and sewage purification plants located alongside the river. These sources contain oxidizable material that include detergents, nutrients and metals which bioaccumulate in a variety of tissues and organs of fish (Coetzee, Preez & Vuren, 2006).

2.6.5 South Durban industrial zone

The South Durban industrial zone arose in the mid twentieth century. It was crafted by the regional government with a dominant commercial interest perspective and by 1938, the South Durban Basin had become the most profitable zone of the city. The Group Areas Act proclaimed in 1950 intentionally regimented a progression of residential localities around this profitable industrial hub to furnish workers. The American-held Standard Vacuum positioned its petrochemical plant in Wentworth during the 1950s providing South Africa with its primarily home-produced fuel. During the 1960s, Shell Oil established the second oil refinery at Isipingo in the South Durban Basin despite the fact that the white dominated authorities at the time knew this will result in large scale pollution and significant health risk to the local population (Cloete and Oliff, 1975). Since the 1960s, the South Durban Industrial Basin has continued to draw in different industrial groups including paper manufacture, brewing, fabric, plastics, and automotive industries notwithstanding the already existing refineries. This industrialized nucleus was additionally fortified with the development of an immense ocean-going transport terminal followed by investment around the chemical industry (Wepener and Degger, 2012). The progression of industrial extension in the region coerced the residents to form the South Durban Community Environmental Alliance, despite the fact that to date inhabitants are nonetheless imperilled to enduring environmental perils, for example, effluence and, on occasion, intense ecological threats like industrial disasters. At the point when youngsters from communities in the southern industrialized zone were compared with those of a comparative socio-economic profile living in the northern region, results show that increased adverse health effects were suffered about the southern locale (Mentz *et al*., 2018; Brooks *et al.*, 2010).

2.6.6 Southern work outfall

Unlike the Central Works, the Southern outfall conveys both sewer and industrial wastewater and extends 4200m from the shoreline with a 1.37 m diameter pipe, 34 diffusers and discharges about 230 mega litres per day at a depth of between 54-64m. Seawater samples obtained through the water column also signified concentration levels that complied with the South African Water Quality Guidelines for Coastal Marine Waters. A survey in 2011 provided evidence that the outfall discharges has degraded sediment quality around the diffusers of the Southern outfall, in addition it experienced more frequent and greater spatial contamination with increased severity (CSIR, 2012).

2.6.7 Mondi Manufacturing Company (Mondi Paper)

Mondi was commissioned in 1969, located in Merebank adjacent to the old Durban International Airport, South African Petroleum Refineries, and surrounded by several residential suburbs. In Mondi, there has been a longstanding focus on community health issues specifically the effects of emissions; to this end, a vibrant environmental activist network monitors these effects. Mondi produces a range of paper products that are supplied to the South African and regional African markets and since 2001 has replaced over 90% of its freshwater requirement with second class wastewater resulting in input reductions of 24% from 2010 to 2014. However, this second class water is obtained from treated sewage and industrial waste and after reuse by Mondi is treated in clarifiers and disposed of via the Southern sea outfall (Mondi, 2015).

2.6.8 Single Buoy Mooring (SBM)

The Durban harbor is South Africa's busiest port, but because the working depth at the entrance was only 11.6m, confining crude carriers to 50000 tons resulting in oil companies being unable to take advantage of lower freightage using 200000 tons super tankers. Since deepening the harbor was not an economic proposition, the alternative was an offshore single buoy mooring. Globally, there are nineteen other single buoy moorings in the world, but the one in Reunion, Durban remains the largest. The buoy has a fixed position 2.4 km offshore at a depth of 45 m; it is a large floating chamber approximately 9 m in diameter and about 4.5 m high and anchored to the seabed. The Buoy connects hoses to the submarine pipeline, which runs back to the seashore into the crude oil tank farm enabling possible discharge into the ocean. Although pumping is carried out at sea the valves in the systems are operated from the shore enabling discharge of 80% of entire crude oil imports to South Africa with discharging taking about 42 hours (Holtz, 1971). Knowledge of cumulative impacts of oil activities in concert with fisheries is needed. The petroleum sector motivates that protection of fish may benefit biodiversity and contends that petroleum infrastructures serve as artificial reefs and increase biodiversity by providing a protected habitat for fish and coral colonies (Hall, 2001; Love & Schroeder, 2005).

2.7 Marine protected areas in South Africa

There are 23 Marine Protected Areas in South Africa, which are vitally important for sustainable line fish management since they provide safety for both juvenile fishes as well as spawning stocks of reef-associated species. It has been proven that these marine protected areas are positively benefitting both line fish species as well as anglers alike (Mann, 2013). Marine Protected Areas were declared under Section 22A of the National Environmental Management Protected Areas Act (Act No. 57 of 2003) (South Africa, 2003). This section of the act stipulates that no fishing in certain zones, construction work, pollution, or any form of disturbance be permitted in the area. The iSimangaliso Wetland Park that includes the St Lucia and Maputaland marine protected areas is one such area. St Lucia Marine Protected Area extends from the north of Ngoboseleni Stream to the south of Cape Vidal in which no fishing is allowed in a Sanctuary Zone. The area also includes a Restricted Zones which lie to the north of Red Cliffs and to the south of Leven Point in which shore angling is allowed while offshore anglers and spear fishermen are restricted to catching pelagic fish only (DAFF, 2017).

2.8 Common (popular) fishes and shrimp in Durban Coast

The South African Marine Living Resources Act of 1998 governs the exploitation of marine resource and divides fisheries into commercial, recreational and subsistence fishing. Within these divisions is the charter boat fisheries that catch approximately 79 different fish species. The fisheries recorded that *Chrysoblephus puniceus* (slinger) made up 34%, while *Cheimerius nufar* (solider) made up 14% of the total catches (Pradervand & Van Der Elst, 2008) while *Pachymetopon grande* (copper bream) was the most caught species in the shore angling fishery along the Transkei coast and accounted for 26% of total catches (Mann *et al.*, 2003). Below is a list of common South African species captured by recreational, commercial and subsistence anglers (Table 2).

Table 2. Summary of common South African species captured by recreational, commercial and subsistence fishermen (Marine Recreational Activity Information Brochure 2017 / 2018).

Common Name	Scientific Name	Minimum Size/ Mass	Bag Limits
Anchovies	*Family Engraulidae*	None	none
Baardman (bellman, tasselfish)	*Umbrina* spp.	40 cm	5
Banded galjoen	*Dichistius multifasciatus*	None	5
Bank streenbras	*Chirodactylus grandis*	None	5
Billfishes (marlin, sailfish)	*Family Istiophoridae*	None	5
Blacktail (dassie)	*Diplodus sargus capensis*	20 cm	5
Blue hottentot	*Pachymetopon aeneum*	None	5
Bronze bream (bluefish)	*Pachymetopon grande*	30 cm	2
Cape knifejaw	*Oplegnathus conwayi*	None	5
Cape stumpnose	*Rhabdosargus holubi*	20 cm	5
Carpenter (silverfish)	*Argyrozona argyrozona*	35 cm	4
Catface rockcod	*Epinephelus andersoni*	50 cm	5
Chub mackerel	*Scomber japonicus*	None	none
Cutlassfish (walla walla)	*Trichiurus lepturus*	None	none
Dageraad	*Chrysoblephus cristiceps*	40 cm	1
Dane	*Porcostoma dentata*	None	5
Elf (shad)	*Pomatomus saltatrix*	30 cm	4
Englishman	*Chrysoblephus anglicus*	40 cm	1
Fransmadam (Karel groot oog)	*Boopsoidea inornata*	None	10
Galjoen	*Dichistius capensis*	35 cm	2
Garfishes	*Family Belonidae*	None	none
Garrick (leervis)	*Lichia amia*	70 cm	2
Geelbek (Cape salmon)	*Atractoscion aequidens*	60 cm	2
Glassies	*Family Ambassidae*	None	none
Hake (stockfish)	*Merluccius* spp.	none	5
Halfbeaks	*Family Hemiramphidae*	none	none
Horse mackerel / maasbanker	*Trachurus trachurus capensis*	none	none
Hottentot	*Pachymetopon blochii*	22 cm	10
John Brown	*Gymnocrotaphus curvidens*	none	5
Kingfishes	*Caranx* spp. & *Carangoides* spp.	none	5
Kingklip	*Genypterus capensis*	none	1
King mackerel	*Scomberomorus commerson*	none	10
Kob [Cape Agulhas to Umtamvuna River]	*Argyrosomus* spp.	50 cm	5
Kob caught from a boat at sea [KwaZulu-Natal]	*Argyrosomus* spp.	40 cm	1
Kob [East of Cape Agulhas only]	*Argyrosomus* spp.	60 cm	1
Kob [West of Cape Agulhas only]	*Argyrosomus* spp.	50 cm	5
Large-spot pompano (wave garrick)	*Trachinotus botla*	none	5
Leopard cat shark	*Poroderma pantherinum*	none	1
Mullets / harders	*Family Mugilidae*	none	50

Common Name	Scientific Name	Minimum Size/ Mass	Bag Limits
Natal knifejaw (cuckoo bass)	*Oplegnathus robinsoni*	none	5
Natal stumpnose (yellowfin bream)	*Rhabdosargus sarba*	25 cm	5
Pinky (piggy)	*Pomadasys olivaceum*	7.5 cm	10
Poenskop (black steenbras or musselcracker)	*Cymatoceps nasutus*	50 cm	1
Queen mackerel	*Scomberomorus plurilineatus*	none	10
Ragged tooth shark	*Carcharias taurus*	none	1
Red steenbras	*Petrus rupestris*	60 cm	1
Red stumpnose (Miss Lucy)	*Chrysoblephus gibbiceps*	30 cm	1
River bream (perch)	*Acanthopagrus perda* spp.	25 cm	5
River snapper (rock salmon)	*Lutjanus argentimaculatus*	40 cm	5
Roman	*Chrysoblephus laticeps*	30 cm	2
Santer (soldier)	*Cheimerius nufar*	30 cm	5
Sardines (pilchard & red-eye)	*Family Clupeidae*	none	none
Sauries	*Family Scomberesocidae*	none	none
Scads	*Decapterus* spp.	none	none
Scotsman	*Polysteganus praeorbitalis*	40 cm	1
Slinger	*Chrysoblephus puniceus*	25 cm	5
Snoek (Cape snoek)	*Thyrsites atun*	60 cm	10
Southern pompano	*Trachinotus africanus*	none	5
Spotted grunter (tiger)	*Pomadasys commersonnii*	40 cm	5
Spotted gulley shark	*Triakis megalopterus*	none	1
Springer (ten pounder)	*Elops machnata*	none	5
Steentjie	*Spondyliosoma emarginatum*	none	10
Stonebream	*Neoscorpis lithophilus*	none	5
Strepie (karanteen)	*Sarpa salpa*	15 cm	10
Striped cat shark	*Poroderma africanum*	none	1
Swordfish (broadbill)	*Xiphias gladius*	25 kg	5
Squid (Chokka)	*Loligo vulgarus reynaudii*	none	20
Tunas (tunny)	*Thunnus* spp.	none	10
Albacore / longfin tuna	*Thunnus alalunga*	none	10
Bigeye tuna	*Thunnus obesus*	3.2 kg	10
Bluefin tuna	*Thunnus maccoyii*	6.4 kg	10
Yellowfin tuna	*Thunnus albacares*	3.2 kg	10
West coast steenbras	*Lithognathus aureti*	60 cm	1
White edged (Captain Fine) rockcod	*Epinephelus albomarginatus*	40 cm	5
White musselcracker (brusher, cracker)	*Sparodon durbanensis*	60 cm	2
White steenbras (pignose grunter)	*Lithognathus lithognathus*	60 cm	1
White stumpnose	*Rhabdosargus globicebs*	25 cm	10
Wolfherring	*Chirocentrus dorab*	none	none
Yellowbelly rockcod	*Epinephelus marginatus*	60 cm	1
Yellowtail	*Seriola lalandi*	none	10
Zebra (wildeperd)	*Diplodus cervinus hottentotus*	30 cm	5

2.8.1 Cracker Shrimp (*Callianassa kraussii*)

Plate 1. Cracker shrimp (*Callianassa kraussii*) / common sand prawn.

Cracker shrimp otherwise called sand prawns are one of the primary life forms utilized as an enticement for the capture of fish (Plate 1). Shockingly, it is one of the most prolific large scale benthic spineless creature of considerable abundance in most of South Africa's estuaries. The distribution of sand prawn reaches out from Lamberts Bay on the west coast and stretches as far as Maputo in Mozambique. The bounds on its dissemination is by all accounts characterized by water temperature resilience. Be that as it may, they are just located in estuaries that are either perpetually open to the ocean or are unrestricted for the dominant part, for the reason that the sand prawn's complex life cycle incorporates a commit marine larval growth stage that requires ocean access. Sand prawns are abundant on sandy flats, sand banks, and sheltered marine environments in which they may be capable of tunneling in the sediments to depths of about 1m. They are pink, delicate and translucent with one pincer that is a lot bigger than the other which is utilized predominantly for defense and excavating. Sand prawns are detritivores, filtering silts and consuming bits of decaying biota. They can grow to a length of 6 cm at which length they become sexually mature and can subsist for approximately 24 months. They reproduce from May to August and again November to January with females carrying eggs underneath their stomach region. It was noted that juveniles don't leave their paternal burrows but subsequently tunnel modest side chambers, however after a quarter of their first year they tunnel a separable opening to the surface therefore isolating themselves from the parental burrow (SAIAB, 2004; Maree *et al.*, 2016). They are excellent hyper osmo-regulators and can survive in extremely low salinities. Another key deciding variable related with distribution and plenitude is sediment type. Sand prawns are a crucial food source for many birds and fishes. Fishes like the spotted grunter, white Steenbras, ocean catfish and cape moony all depend to differing extents on the organism for nourishment. Sand prawns are tunneling species that filter feed and are low on their habitat food web. The unsettling influence or misuse of stocks may have a domino effect on different segments of marine and estuarine environments and therefore scrutinizing the heavy metal intensities in sand prawn from South African coastal regions are required (Simon *et al.*, 2019).

2.8.2 Grunter (*Pomadasys commersonnii*)

Spotted grunter is a silver-brownish fish with plenty little dark spots on their body and usually occur in estuaries and shallow beaches from False Bay, South Africa and extend beyond the Mozambiqian coast (Plate 2). The basic name "grunter" is given to the species for the reason, that the fish when expelled from the water makes a snorting sound. Other regular names incorporate tiger, spotty, gespikkelde knorder and knorhaan. The spotted grunter is both an estuary-residing and coastal species inhabiting the Indian Ocean eastwards from Cape Point, South Africa up and down the African and Asian coastlines to India (Muir *et al.*, 1999; Smith & Heemstra, 2003).The species spawn in the ocean and estuary mouths, diminutive fish stay in estuaries for at least two years and when they reach sexual maturity at around 40 cm they occupy the sea. Other than spawning, adults are genuinely occupants of estuary mouths and can grow to nearly 85 cm, which corresponds to a fish of roughly 9 kg and may live for 15 years eating mostly sand prawns which they are seen blowing from holes on the shallow sandbanks (SAIAB, 2004).

Spotted grunter albeit far less predominant in shore-based angling (Bennett, 1989; Coetzee, Baird & Tregoning, 1989; Brouwer *et al.*, 2011) is one of the most significant line fishery species among the South African estuaries predominantly in the Eastern Cape and KwaZulu-Natal (Pradervand *et al.*, 2003). Expanded angling strain laid on estuaries (Lamberth and Turpie, 2003) together with the estuarine reliant character of spotted grunter leave them susceptible to over capture during both their adolescent and post-breeding live stages. Thus, a comprehension of the level of estuarine use and the elements affecting estuarine use is indispensable for species management planning. Spotted grunters may live to 15 years with an extreme immensity of roughly 10 kg (SAIAB, 2004). Spotted grunters could be both pelagic and benthic feeders contingent upon their life stage and zone in which they are found (Whitfield, 2000).

Plate 2. Spotted grunter (*Pomadasys commersonni*) / Tiger / Spikkel knorder /Knorhaan /Inkolokolo / Spotty. (Source: SAIAB, South Africa)

Long-term roaming patterns of the species and their sand prawn prey were studied in the East Kleinemonde Estuary, South Africa. In the examination nine adult spotted grunters of various sizes were affixed with acoustic transmitters and their whereabouts logged. Movement patterns recorded a 95% use of the lower 33% of the estuary with no impact on seasons, day by day cycles or fish length. It was also ascertained that the dissemination of their sand prawn prey was related to wonderings of the affixed fish proposing that the scatter of prey is the influential component regarding distribution of the grunter inside estuaries. Since estuaries are significant as they work as both a nursery and a sheltered feeding habitat for these fish, long haul perceptions demonstrate that the movement of spotted grunter remained comparative over extended periods and showed resident behavior (Maree *et al.*, 2016).

2.8.3 Maasbanker / Horse Mackeral (*Trachurus trachurus*)

Maasbanker is round with body shading running from olive-green to grey above and white underneath with a distinct black spot on the gills and darker vertical bars occasionally present on either side of the body (Plate 3). The Maasbanker has a wide distribution and inclined towards cooler marine waters up to a profundity of 400 m. Being of an important food source for humans, makes the species an important commercial fish that is thought to be under exploited (SASSI, 2018). Maasbanker is a pelagic, oceanodromous fish that exists in enormous shoals on coastlines with sandy substrates and devours small fish, crustacea and cephalopods. This species may reach a maximum length of 60 cm with the norm being 30 cm. It is split into the West Sea stock and North Sea stock. The West stock reproduces in a belt from Biscay to Ireland in the beginning of spring, then relocates north and eastwards to southern Norway and the northern North Sea. The North Sea stock reproduces in the southern region all summer before moving to the central North Sea. Female Maasbankers are adept for laying around 140,000 eggs which produce 5 mm long hatchlings (Hecht, 1990). This species can live for 24 years in South Africa and 40 years in the Northeast Atlantic. Longevity under exploitation is estimated to be eight years, although it is crucial to mention that age and development dissimilarity are contemporary in their wide dispersal and fluctuating harvest levels affect these rates (Mangel, Quinn & Deriso, 2000). The species displays a high migratory and aggregating behavior with patchy distribution problems with reports demonstrating that they lean toward environments with temperatures extending from 18 – 21^{o}C and can endure dissolved oxygen concentrations ranging from 0.13 to 6.35 ml/l (Geist *et al.*, 2014).

Maasbankers are also found in the eastern Atlantic Ocean, from Norway to South Africa, around the coast to Maputo and the Mediterranean and Marmara Seas. In these regions it is commonly found to profundities of 200m, amid records stretching out the profundity range to more than 1,000m. In certain pieces of the Mediterranean the species is over fished with augmented extents of juveniles being the rationale for concern. In the North Atlantic, the western stock is encountering above target angling pressure with subjective assessments proposing a declining with more youthful angling mortality ages arriving at record highs. The Saharo-Mauritanian stock and catches is assessed to have declined by over 90% in the course of the last 30 years. In this bit of its range, landings have deteriorated from a normal of 15,000-20,000 metric tons in the mid 1980's to only 20 metric tons per year. Worldwide accounts on harvesting of this species have remained moderately steady or expanding in the course of the last 30-35 years, with a mean of more than 55,000,000 metric tons in the mid-1980s to a norm of 68,000,000 tons by 2014 (FAO FishStat, 2015).

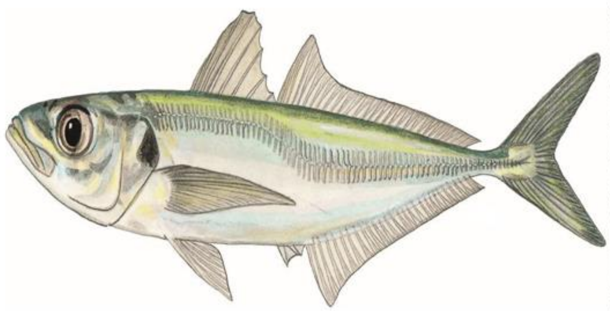

Plate 3. Cape horse mackerel (*Trachurus trachurus*) / maasbanker / slimy mackerel. (Source: SAIAB, South Africa)

2.8.4 Atlantic chub Mackerel (*Scomber japonicas*)

This species is a pelagic fish, and to a lesser degree epipelagic to mesopelagic over the continental shelf. Mackerel is a foraging fish since it is a little, low trophic level fish that exhibits schooling behaviour with a high variation in recruitment. Investigations of this species demonstrated that there was no distinction in mean length-at-age between genders (Plate 4). Atlantic Chub Mackerel is a commercially exploited fish with the mean length-at-maturity for females fluctuated from 19.9 cm in the Canary Islands to 29.0 cm in the Bay of Biscay while the mean length-at-maturity for males extended from 19.8 cm to 30.8 cm. The species additionally displays extreme variations in spawning periods with relation to location (Daley, 2018). They feed on little pelagic fish fry that includes, anchovy, pilchard, sardinella, sprat, silversides, as well as pelagic invertebrates. In Mauritania, it was stated that they dwell close to the sea floor during daylight and move up the water column after dark where they feed on copepods, crustaceans, fish and squids. They may live to a maximum of 13 years (Keč & Zorica, 2013). Atlantic Chub Mackerel is prevalent and profuse across its range and is actively pursued primarily in the eastern Atlantic segment of its distribution. It is quick developing, reaches adulthood at 2–3 years, and may live ordinarily to 8 to 10 years. The biggest harvests are announced from the eastern central Atlantic where captures have vacillated, even though an appraisal indicated that stocks are fully exploited with there being no proof of extended tenure decay and is thus recorded as Least Concern. Nevertheless, landings indicated that yields comprised of essentially fish of 1-2 years of age with a length of between 20 and 24 cm. This species is additionally common all through the Mediterranean with worldwide landings peaking at about 40,000 mt. toward the south of Cape Blanc, landings and reached around 100,000 tons. Commercial landings of this species indicated a striking increment since 2013 as can be seen from data obtained from dealers in New England with an average of 62,293 pounds and a peak of 5.25 million pounds from 2013 to 2017 (Martins *et al.*, 2013; Cape May and City, 2018).

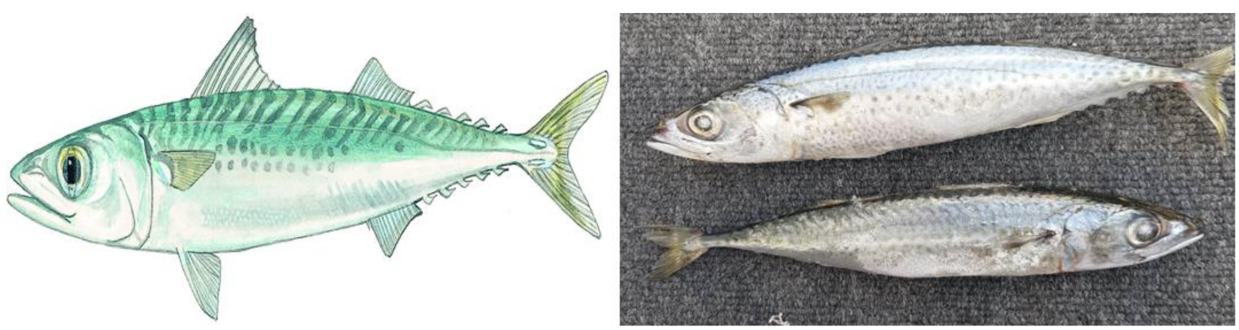

Plate 4. Atlantic Chub Mackerel (*Scomber japonicus*) / Pacific chub mackerel/ Chub / Chub mackerel. (Source: SAIAB, South Africa)

Atlantic chub mackerel are a schooling pelagic fish found to depths of 250-300 meters while some trawler and recreational catch studies recommend that the chub mackerel can likewise be found inshore. Investigations of the species from various regions of their dissemination showed a dependence on morphology, spawning, and size at maturity recommending that the species is certainly not a solitary stock animal and exists as sub-stocks (Cerna and Plaza, 2014; Yasuda, Yukami and Ohshimo, 2014). Although identified to be genetically uniform across wide ranges the sub-stock theory was confirmed since significant genetic differences of the species were established from mackerels taken from the western and eastern Atlantic. Juveniles and sub-adults tend to inhabit the inshore regions and grow rapidly up to 40% of its maximum length during the first year of life (Daley, 2018) while adults prefer deeper waters with a temperature range of 15-20°C. These fish may spawn several times throughout the year during favourable oceanographic conditions and if sufficient food is available (Hernández-Almaraz *et al.*, 2014; Crone *et al.*, 2019). As of late, because of the expanding apprehension over their damaging effects, plastics and microplastics have become the subject of extreme examinations. Microplastics can be effortlessly ingested by various marine life forms due to their minute size (< 5 mm) and have been found in the digestive tract of 78.3 % of the Atlantic chub mackerels examined. Microplastic in the digestive tract of these fish need to be further studied since this species is a filter feeder and are excellent candidates to be an indicator of microplastic contamination within their capture region (Herrera *et al.*, 2019).

2.8.5 Slinger (*Chrysoblephus puniceus*)

Slinger is a seabream of the family Sparidae (Plate 5) and is commercially harvested in South Africa and Mozambique, the genetic connectivity between localities was investigated using the mitochondrial control and found to be insignificant and failed to reject slinger as a single stock. The transboundary nature of the slinger together with temporal and spatial distribution of the species makes them resilient to over exploitation. However there is concern since management strategies for the species is not aligned within its distribution even though the species is harvested throughout its distribution (Duncan *et al.*, 2015). Slingers mainstay dispersion rangers from Mozambique to Coffee Bay in the Eastern Cape and registers profundities of around 130 m. These fish exhibit intrinsic characteristics that include hermaphroditism, late maturation, and resident behaviour making them more vulnerable to over-exploitation as they are a significant part of the mercantile line fishery in KwaZulu-Natal and southern Mozambique.

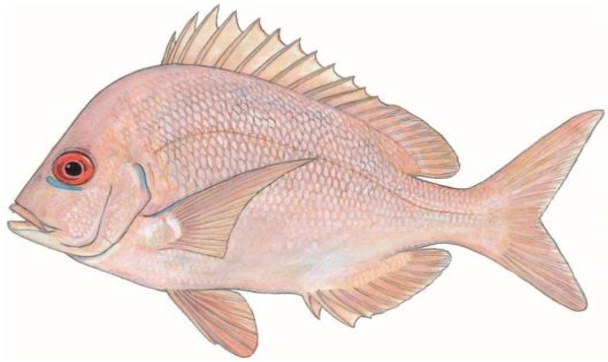 

Plate 5. Slinger (*Chrysoblephus puniceus*) / slinger seabream. (Source: SAIAB, South Africa)

The species enjoys some protection through fishing regulation and the establishment of a few no-take marine protected regions. Slingers have been vigorously overexploited in KwaZulu-Natal and southern Mozambique, however in later years, capture bag information shows that catch rates have been balanced out and improved. Furthermore, the species is also making a moderate recovery on account of the reduced limit available to be purchased with angling effort (Diop, Scheren and Machiwa, 2016). Slinger is additionally a significant part in the recreational off-shore fishery in KwaZulu-Natal and southern Mozambique with the species being the principal food fish in the region (Dunlop, Mann & Van der Elst, 2013).

The generative biology evaluated through gonad somatic index, infinitesimal and visible appraisal demonstrated that propagation happens from August to November and that slingers are protogynous hermaphrodites that experience slow growth and long life. The length-weight relationships indicating distinct differences in size between males and females with males restricted to the larger size classes. The Von Bertalanffy growth parameters suggest relatively slow growth, with 2 to 18 otolith rings found while reproducibility was estimated at 22% with analysis of age-at-50% maturity suggesting that Slingers matured at 1.5 years at a fork length of about 240mm (Lichucha, 2001). Stock evaluations uncovered that the fishery is modestly overfished, with the reproducing biomass at 35 to 36 % of the unexploited level. The lower age class of this species is not more than 3 years and comprises entirely of females, it is along these lines accepted that a portion of these females change sex at each age from that point. Slinger hatchlings ride the Agulhas current from Mozambique in the north to Transkei on the south, with fish moving from south to north. Microsatellite information gave additional proof that this species exists as a solitary stock all through its dissemination because of an absence of hereditary separation. Albeit constrained identification examinations demonstrated that adult slingers are somewhat permanent residents of rocky reefs from 20m to 130m deep thus suggesting that juvenile fish migrate northwards. The increased dependency of recruitment of this fish into the fishery through MPAs like the St Lucia Marine Reserve protect spawning adults and are becoming increasingly important (Duncan *et al.*, 2015). Spawning tapers off towards the south along the East Coast where no reproductively active adults occur which strengthens the notation that eggs and larvae that are spawned in the northern region are disperse southwards (Maggs *et al*., 2013).

2.8.6 Copper Bream (*Pachymetopon grande*)

Plate 6. Bronze Bream (*Pachymetopon grande*) / Copper bream / Bruin hottentot / Pens-en-derms. (Source: SAIAB, South Africa)

Bronze bream (*Pachymetopon grande*) (Plate 6) otherwise called copper bream, hottentot, bluefish, janbruin, JB and pensenderm at various areas is an inshore reef related species endemic to southern Africa in spite of the fact that there have been unsubstantiated reports of this species in Madagascar (Heemstra & Heemstra 2004). Assessments have not recorded this species further north than Richards Bay, KwaZulu-Natal, and showed that the southern range is as far south as Cape Agulhas (Mann *et al.*, 2016). The species are essentially herbivorous eating predominately red and green reef growth. They are longwinded growing up to 50 cm and reaching an upper mass limit of 5 kg with an average 30-year life expectancy. Bronze bream arrive at sexual maturity after around 6 years at a length of 30 cm (DAFF, 2012). Results from a tag and discharge study uncovered that a vast portion of the released fish were retrieved inside the assigned research territory. Despite the uncommon fish that moved widely ostensibly suggesting that the species are extremely localised inhabitant for significant lengths of time (Cowley, Brouwer & Tilney, 2011). Exploring the science of the species affirmed that they are laborious developing, long living species in surplus of 40 years. Comprehensive histological assessments of gonadal change revealed that these fish are essentially hermaphrodites with maturity occurring after a non-performing intersexual stage, while reproduction through group spawning resulted in pelagic eggs (Buxton & Clarke, 2015).

The bronze seabream dwells in shallow intertidal rock-strewn shorelines and offshore reefs to a depth of 25m. This species shows life history qualities that heightens its helplessness to overexploitation, including sluggish development, delayed reproductive development, increased life span, limited roaming, and restricted habitations. Bronze bream is actively pursued by leisure and subsistence anglers however is precluded from commercial piscators as this is a “not for sale” species. It is given some shelter from angling by the founding of Marine Protected Area (MPA) which has demonstrated to be exceptionally compelling in the preservation of this species (UNEP-WCMC, 2019). Autonomous fishery review information for the species in the Eastern Cape showed a decay of practically 30% in seven years. Catch per unit effort from 1998 to 2005 swayed in the Tsitsikamma National Park MPA with a 55.5% decay recorded. While a 29% decrease was seen in Port Elizabeth dropping from 12.6 g/person/hour in 1989 (Clarke & Buxton, 1989) to 9 g/individual/hour in 1996 (Brouwer *et al.*, 2011) while the National Marine Line fish System in KwaZulu-Natal demonstrated a slender decay from 0.003 to

0.002 fish/fisherman/day from 1985 to 2008. Bronze bream stayed one of the commonest species caught by anglers and in 2010 a catch component of 9.6% was accounted for with 99.6% being adult fish perhaps representing the diminishing in catch per unit effort (Dicken, Smale & Booth, 2012). This species has encountered stock decays of about 30% inside three life spans and is now boarding the vulnerable limit under standard A2bd and might be further stressed since they are dependent upon natural surroundings that may be tainted and it is therefore listed as near threatened (Heemstra and Heemstra, 2004; Mann *et al.*, 2016). In metropolitan territories, bronze bream are defenceless against territory debasement from both contamination and deposition. As to ensure copper bream stocks, fisheries management of this species incorporated a bare minimum capture size of 30 cm with a day by day capture limit of two fish per angler (DAFF, 2012; Maggs, Mann & Cowley, 2013b; IUCN, 2019).

2.8.7 Rock Cod (*Epinephelus andersoni*)

Plate 7. Catface rockcod (*Epinephelus andersoni*) / Brown spotted rockcod / Bruinkol klipkabeljou. (Source: SAIAB, South Africa)

The Catface Rockcod (Plate 7), occasionally referred to as Rockcod is the most widely recognized Rockcod species that populates South Africa's coastline. The Catface Rockcod is a belligerent voracious saltwater fish that is common in several marine habitation of various profundities. The Catface Rockcod can be captured in the surf zone, offshore, river mouths or in estuaries. This species being intently connected with shallow rocky reefs are frequently among the main species to arrive on recently made non-natural reefs or wrecks (Maggs, Mann & Cowley, 2013b). Nurseries are predominately shallow reefed surf-zones with fish moving to more deep seaward reefs with expanding size and age (Mann, Cowley and Fennessy, 2015). Findings of tagging studies revealed that the species exhibited a high degree of site devotion although some adolescent fish undertake movements in excess of 400 km (Mann, Cowley & Fennessy, 2015; Mann *et al.*, 2016). Based on the Oceanographic Research Institute tagging program of the 2,320-tagged catface rockcod studied over a period of 30 years, 22% have been recaptured and recorded a movement on average of only 5 km. The size and age at primary maturity are slightly greater for females at 49 cm or about 3.9 years while males mature at 43 cm or 2.7 years old. The species can live for about 11 years and obtain a length of approximately 90 cm. Surveillance of this species has uncovered that there is a more prominent plenitude of this species in the contiguous exploited regions when contrasted with the iSimangaliso MPA because of the denizen conduct of the species. South African guidelines that apply, incorporate a base size confinement of 50 cm complete length and a daily threshold of five fish apiece (Coppinger *et al.*, 2019; IUCN, 2019). The species is moderately widespread in South African waters especially in the region of KwaZulu-Natal with the populace thought to be a similar stock in both South Africa and Mozambique. Its range is confined to rocky living spaces from the Eastern Cape coastline to southern Mozambique with the most noteworthy expanse occurring on the KwaZulu Natal coastline, however spawning only occurs from the north of Durban to southern Mozambique representing less than half of its distribution. Despite the catface rockcod being regularly a minor segment of the reef fish fishery it constitutes up to 60% of the complete grouper catches of the commercial ski-boat fishery in KwaZulu-Natal. The populace in KwaZulu Natal is bigger since the vast majority of the coral Mozambican reefs are unsuitable since the species is more inclined toward shallow rocky reefs (Coppinger *et al.*, 2019).

Spawning does not happen far south and not all fish spawn each year (Fennessy, 2000) with proof that there are spawning related conglomerations during summer from January to March. Rockcods are laborious developers, diandric protogynous hermaphrodites where a few males are acquired from performing females while others are created from the adolescent stage to guarantee that the sex proportion isn't female prejudiced as in monandric protogynous sex changers (Fennessy, 2000). Size and age from the start of sexual development for both genders are comparable (Fennessy, 2000). In KwaZulu-Natal the shore-based recreational fishery experienced a decline in catch per unit effort of 67% compared to a decline of approximately 50% in the ski-boat fisheries from 1994 to 2009 and in southern Mozambique the semi-industrial line fishery declined by approximately 75% between 2009 to 2014. The aggregating behavior during spawning makes the catface rockcod susceptible to high fishing pressure resulting in population declines of nearly 30% over the past three generation from 1993 to 2016. Some of the conservation measures implemented to reduce fishing efforts for this species included a bag limit, a size limit and limiting the number of commercial fishing licenses issued in South Africa but monitoring compliance in this regard has been difficult thus resulting in a decline in compliance to these regulations. This species enjoys protection in at least two large, relatively well-managed offshore marine protected areas in KwaZulu-Natal and southern Mozambique; however this may not be enough to allow the recovery of this near threatened species that nearly meets the threshold for Vulnerable A2bd. Standardized catch per unit effort for groupers of which catface rockcod is dominant was 8 kg/boat/day by 2013 (Attwood *et al*., 2013).

Stomach content investigations of catface rockcod uncovered a diet of 50.8% fish, which constituted their main nutrition while Brachyura or crabs at 15.6% were additionally significant. Catface rockcods are mostly seen on the rocky sea floor normally hiding in crevices or openings where it lies unwearyingly waiting for clueless prey (Joubert and Hanekom, 2015). The species is a range-confined significant commercial and recreational line fish that makes up about 10% of catches and is at present viewed as ideally utilized in spite of the fact that there are indications of reduction inside its habitat range because of its intricate life history of diandric protogyny and locale loyalty. It is however proposed that populaces are dependent upon a phenomenon known as chaotic genetic patchiness which suggested that a conservative management approach be adopted by regarding the species as a solitary stock on the grounds that spawning has only been accounted for inside northern KZN (Coppinger *et al.*, 2019).

2.7.8 Soldier (*Cheimerius nufar*)

Plate 8 Santer (*Cheimerius nufar*) / Santa / Basterman / Soldier / Soldaat. (Source: SAIAB, South Africa)

The soldier is distributed across East Africa, Madagascar, the western Mascarenes, the Red Sea, Persian Gulf and South Africa (Heemstra and Heemstra, 2004). Although soldiers don't seem to assume extensive migrations they appear to roam between reef complexes with movements into shallower regions during storms or shadowing cold water upsurges (Mann, 2000). Soldiers are carnivorous, feeding on fish and squid (First 2013) and is fundamentally a hermaphrodite having just one distinct sex in any individual, but early spawning gonadal development propose the likelihood of protogynous sex change with some females changing to males permanently (McIlwain *et al.*, 2006). In South Africa, commercial catch per unit effort remained stable from 1985 to 2000, with a notable increase following management intervention. Soldiers exhibit life history characteristics such as longevity, large body size and slow growth that increase its vulnerability to overfishing.

Soldiers heightened and now remain an important commercial line fish in KwaZulu-Natal (South Africa) as other larger species were fished out with the mean capture size in the region ranging from 30 to 32cm (Penney *et al.*, 1999). Surveys conducted in the Southern Cape showed increases in commercial catches of soldier from 6% to 21% (Griffiths, 2000). The total commercial catch for soldiers in South Africa is estimated to be between

60–120 tonnes per year from 1985 to 2007 with the catch per unit effort increasing significantly from 0.05 kg/man hr to 0.15 kg/man hr (Bq. Mann, 2013; Dunlop, Mann and Van der Elst, 2013). Soldiers are slow growing and may reach a maximum age of 22 years in South Africa and 25 years in the Gulf of Aden. The first conservation actions was implemented in 1984, where Sea Fisheries Act No. 58 of 1973 (Republic of South Africa, 1973) adopted a minimum size limit of 25 cm total length with a daily limit of 10 fish per person for recreational anglers, which was later modified in 1992. The new minimum size increased to 30 cm total length in Sea Fisheries Act No. 12 of 1988 (Republic of South Africa, 1988) with further restrictions of five fish per day per angler limit in 2005 (Republic of South Africa, 1998). Other measures to protect the stock included the reduction in the number of commercial line fishing vessels in 2006. Although these measures have undoubtedly reduced commercial line fishing effort in South Africa no known species specific measures have been implemented in the rest of the distributional range (Seabream & Russell, 2015).

2.9 Human health risk assessments

From a nutritional point of view, metals can be divided into essentials and non-essential. Essential metals such as copper (Cu), selenium (Se), iron (Fe), chromium (Cr), manganese (Mn), and zinc (Zn), are all crucial for the right metabolism in the human body in trace levels. Non-essential metals, such as mercury (Hg), lead (Pb), and cadmium (Cd), lack an essential role in the human body and may cause damage at high concentrations (Rahmani *et al.*, 2018). Therefore, it is necessary to assess the risk involved in fish intake. Consumption of fish contaminated with hazardous heavy metals is a source of exposure to toxic metals and therefore poses a potential risk to human health (Fakhri *et al.*, 2018). For instance, the relationship between habitual fish intake and the danger of hip fractures was established through case-control studies done in Guangdong Province, China where findings showed that a greater intake of fish and shellfish with high bioavailable protein reduces the risk of hip fractures. This is due to the richness of nutrients that support bone health through improved calcium absorption, increased insulin growth, and improved lean body mass (Fan *et al.*, 2013). The potential hazards to human health from transfer of heavy metals depend on the amount of fish consumed by a person and it was confirmed that a higher intake of seafood was significantly and independently associated with a lower risk of hip fracture especially in the elderly (Fan *et al.*, 2013)**.** The health benefits associated with the consumption of fish may be compromised by the presence of toxic metals which may have a harmful effect on the human body if consumed in toxic quantities (Bosch *et al.*, 2016). Evaluation of heavy metal buildup in fish have generally been done in food safety and the effects of some metals are as follows:

- Cadmium accumulation may cause kidney dysfunction, skeletal damage, and reproductive deficiencies.
- Lead poisoning can reduce cognitive development and intellectual performance in children and increased blood pressure and cardiovascular disease in adults.
- Chromium although an essential trace element in glucose metabolism, insulin, and blood lipids, suboptimal dietary intake may be associated to diabetes mellitus and cardiovascular disease.
- Copper if taken in high concentrations can cause liver and kidney damage.
- Zinc is involved in metabolic path ways in humans and a deficiency results in loss of appetite, inhibition of growth, skin changes, and immunological abnormalities (Gu *et al.*, 2015).

Risk assessment is one of fastest method which is need to evaluate the impact of the hazards on human health and also need to determine the level of treatment which are tend to solve the environmental problem that occur in daily life (Amirah *et al.*, 2013).

2.9.1 Estimation of potential health risks from fish consumption

Appraisal of the prospective health threats related to the consumption of fish primarily requires the tolerable daily intake of toxic metals and determining the estimated daily intake (Song *et al.*, 2009). The target hazard quotient propositioned by the US Environmental Protection Agency (USEPA, 2011) is used as a well-known sensible guide (Hough *et al.*, 2004; Sridhara & Raj, 2008). If the target hazard quotient value exceeds one, then the likelihood of experiencing harmful health effects are higher. For a risk assessment of several heavy metals, a total hazard index is used by adding the individual target hazard quotients (Sarkar *et al.*, 2016). The risk to human health from consumption of contaminated fish is usually quantified by calculating certain established or proposed indices. Some of these indices include Estimated Daily Intake (EDI), target hazard quotient (THQ), Target Carcinogenic Risk (TR). Another quantitative term, bioaccumulation factor (BAF), is used to assess the degree of accumulation or enrichment of the heavy metals in the fish (Ali and Khan, 2018).

2.9.2 Estimated Daily Intake (EDI)

Despite fish being a decent wellspring of protein for individuals since it contains Omega-3 which has unsaturated fats that give a low-cholesterol salubrious wellspring of proteins and different supplements, in this manner utilization is suggested a few times each week. However, tragically fish can bioaccumulate heavy metals which might be harmful to human wellbeing and along these lines should be assessed for safe utilization (Al-Ghanim *et al.*, 2015). The temporary endurable day by day ingestion suggested by US-EPA (US-EPA, 2000) shows that the safe tolerable levels are utilized to assess the aggregate sum of contaminants ingested over a lifetime without considerable peril. The EDI of heavy metals relying upon both the metal fixations in the fish tissue and the totality of fish devoured. The EDI is determined by calculating the normal metal fixation in fish tissue, the normal day by day utilization of fish by an adult quotients (Sarkar *et al.*, 2016), the normal mass of a full-grown African (Walpole *et al.*, 2012), and the admissible daily ingestion of the metal (US-EPA, 2000).

2.9.3 Target Hazard Quotient (THQ)

The target hazard quotient communicates the hazard related with the admission of heavy metals through ingestion. There are a few techniques that have been proposed to appraise the potential dangers of toxic heavy metals on human wellbeing for which the target hazard quotient (THQ) proposed by the US Environmental Protection Agency (US.EPA, 2009) has been perceived as a sensible indication (Hough *et al.*, 2004; Sridhara & Raj, 2008). The THQ is a gauge of the non-cancer-causing danger associated with contaminate exposure. For a risk valuation of numerous heavy metals, a total hazard index (HI) was commissioned by adding the individually calculated THQi. However, there are certain notions taken into while calculating the THQ for human health risk assessments, these include:

(a) Consumed quantity of contaminant is equal to the absorbed dose (EPA, 1989).
(b) Cooking has no effect on pollutants (Forti *et al.*, 2011).

2.9.4 Target Carcinogenic Risk (TR)

Target cancer risk is used to indicate the carcinogenic risk. It is dimensionless. The technique which is used to evaluate TR is provided in USEPA Region III Risk-Based Concentration Table (U.S.EPA, 2011). When calculating the target cancer risk, only elements that are known carcinogens must be considered, for example, Pb is a carcinogen since experimental studies have indicated that it is potentially carcinogenic since it induced renal tumors in rats and mice and is therefore considered by the IARC as a probable human carcinogen (Tchounwou *et al.*, 2013). Excessive consumption over a long time period might cause carcinogenic effect as the TR values become higher than the acceptable guideline value of 10^{-6} (U.S.EPA, 2011).

2.9.5 Bioaccumulation factor (BAF)

Bioaccumulation factors, represented by the ratio of heavy metal concentration in the soft tissues and the heavy metal concentrations in the sediment or water, for the buildup of heavy metals cadmium, lead, chromium, nickel and copper in water, sediment and living tissues of marine species from different trophic levels of the Romanian Black Sea were determined (Jitar *et al.*, 2015). For the sediments, significant differences were observed between sampling sites with the highest concentrations being registered in the southern sector where anthropogenic pollution sources are represented by a harbour and wastewater treatment plants. Bioaccumulation factors showed that algae are good accumulators for Cu > Pb > Ni > Cr > Cd which could be used in assessing marine ecosystems (Qiu, 2015). Mollusks had high bioaccumulation factors for Cu and Cd, also organisms that had an exoskeleton or shell showed higher Pb uptake since Pb follows a similar biochemical model as calcium (Mendoza-Carranza *et al.*, 2016). Sediment pollution plays a huge role in pollutant transfer to the biota and represents the first step in a complete human exposure pathway, however it was found that sediments had high bio-concentration factors for Cu and Ni (Topcuoğlu, Kirbaşoğlu and Güngör, 2001). Fish had high bio-concentration factors for Pb, Cu and Ni accumulation depending on the degree of environmental contamination and species feeding habits. It was further identified that sub-lethal concentrations often pose as serious a threat as compared to the lethal dosages accepted in toxicological studies and that more than 90% of the heavy metal load in the aquatic ecosystems has been found to be associated with suspended particulate matter and sediments (Jitar *et al.*, 2015).

2.10 Fish management

Marine fisheries although important for food security and providing a livelihood for many South Africans is plagued by transnational fisheries crimes that exist at the interface between low-level poaching and organized crime in the sector. The relationship between fisheries-crime law enforcement and a management approach needs to be looked at (Isaacs and Witbooi, 2019). The commercial, recreational and subsistence fishery sectors targets over 200 of the approximate 2 200 known South African fish species. As a management intervention, when line fishery rights were allocated for both medium and long term, the total allowable effort was significantly reduced to effectively reduce total catches by approximately 70% thus allowing for the recovery of line fish stock (DAFF, 2014).

The growing interest in creating market-based incentives for sustainable fisheries and understanding the factors driving demand are recognized as key in developing sustainable long-term solutions. WWF-SA via its Southern African Sustainable Seafood Initiative (SASSI) has through The Wildlife Trade Monitoring Network looked at the trade dynamics of seafood on the South African market (Attwood *et al.*, 2013b). South African fisheries is certified by an independent agency for their compliance with the Marine Stewardship Council’s main principles stating that commercial fishing is conducted in a manner that does not lead to overfishing or impacts on the health of marine ecosystems and that it is managed and regulated in a responsible manner. The alliance formed by WWF South Africa, Birdlife South Africa, Oceana, I&J, Pioneer Fishing, Sea Harvest and Viking Fishing to ensure that the seafood industry in South Africa is supported by a healthy marine ecosystems are working together on projects that relate to ecosystem-based management to effectively appreciate and alleviate the influences of detrimental fishing habits. “Although no large scale health on fish consumption research was not performed, it is envisage that the SA health department may initiate a project after the current study is published”. In addition, the following commitments for “going sustainable” from market, leaders were pledged as follows:

• Woolworths has accepted to ensure that all its wild-caught seafood will be sourced from fisheries that are undertaking credible, time-bound improvement projects, will be Sassi Green-listed, or be caught from MSC (Marine Stewardship Council) or equivalent certified fisheries.
• Pick n Pay has committed to transforming its fresh, frozen and canned seafood operations to ensure that it only sells seafood products that are certified as sustainable by the MSC, or fish from Sassi green list.
• I&J has committed to only selling certified fish, fish from the Green-list, or fish from fisheries with time-bound improvement project (Haggard, 2015)**.**

The fishing sector in Africa is plagued with policy failures, and illegal activities that results in over-exploitation and begs for increased policy interventions. Long-term policy interventions should focus on international long-term policy changes aimed at creating a culture shift while short-term interventions should be the basis for longer-term policy measures with efforts focusing on collaboration with existing stakeholders, which include the scientific community, governments, non-governmental organizations, communities and anglers. Immediate efforts should focus on creating a sustainable monitoring framework and increasing fines against both illegal fishing and under-reporting of catches (Belhabib, Sumaila &Le Billon, 2019). Due to increasing pressure and policy changes to maintain healthy fisheries, growth in the fishing industry will be slow and result in a declining per capita fish consumption. This creates an opportunity to grow the potentially important African aquaculture industry to address food security. Fish, owing to its infamy in the African sustenance basket necessitates policies that stimulate maintainable fish farming, shrink harvest deficits, and enable fish transact (Belhabib, Sumaila & Le Billon, 2019).

CHAPTER 3:
MATERIALS AND METHODS

3.1 Description of the study area

3.1.1 Durban basin

The Durban basin area is one of South Africa's most important industrialized hotspot known for different manufacturing and refining industries. It is home to two of the biggest oil refineries for the petrochemical industries in the country that refines approximately 60 percent of South Africa's petroleum. Apart from being overwhelmed with petrochemical companies, the Durban industrial basin is also home to wastewater treatment works, numerous toxic waste landfill sites, a paper manufacturing plant and a multitude of chemical process industries. In total, the basin has over 120 industries that are constant of large quantities of wastes. The ocean has been for many years the ultimate recipient and sink for both treated and untreated industrial, agricultural and sewage waste in the basin.

The present study was undertaken in the Durban basin spanning from Umdloti, situated at the mouth of the Mdloti River north of Durban to Isipingo, at the mouth of the iSiphingo River on the south. Between Isipingo on the south and the central coastal region (herein referred to as "South") lies the Durban Industrial basin that characterized by presence of petrochemical, pulp and paper, beverages, textiles, plastics, and motor vehicle industries, including domestic sewerage. The south basin has canals (Plate 8) and two outfall pipelines (Plate 9) that discharges sewerage and industrial waste directly into the Indian Ocean. These outfall pipelines carry a range of contaminants that have the potential to impact the ecological functioning of the receiving water and compromise human health (CSIR, 2010). A Single Buoy Mooring (SBM) (Plate 10) *via* which crude oil is pumped from oil tankers to two petroleum refineries is also situated on the southern basin. The "Central" region has Durban harbor that is characterized by prominent shipping industry (Plate 11). An outfall pipeline discharging 135 million liters per day of sanitary wastewater into the ocean also services the region. The northern coastline of Durban basin (herein denoted to as “North”) have Umdloti and Umgeni rivers that are recipient of partially treated sewage wastes from adjacent wastewater treatment plants before discharging into the ocean.

Plate 8. Storm water canals carrying discharges from South Durban industrial basin draining into the ocean that are popular for shore-based line fishing.

Plate 9. Pumping station for sewerage and industrial wastewater outfall pipelines in the South Durban basin.

Plate 10. Single Buoy Mooring (SBM) located in the South Durban basin for pumping crude oil from super tankers to the inland petrochemical refineries.

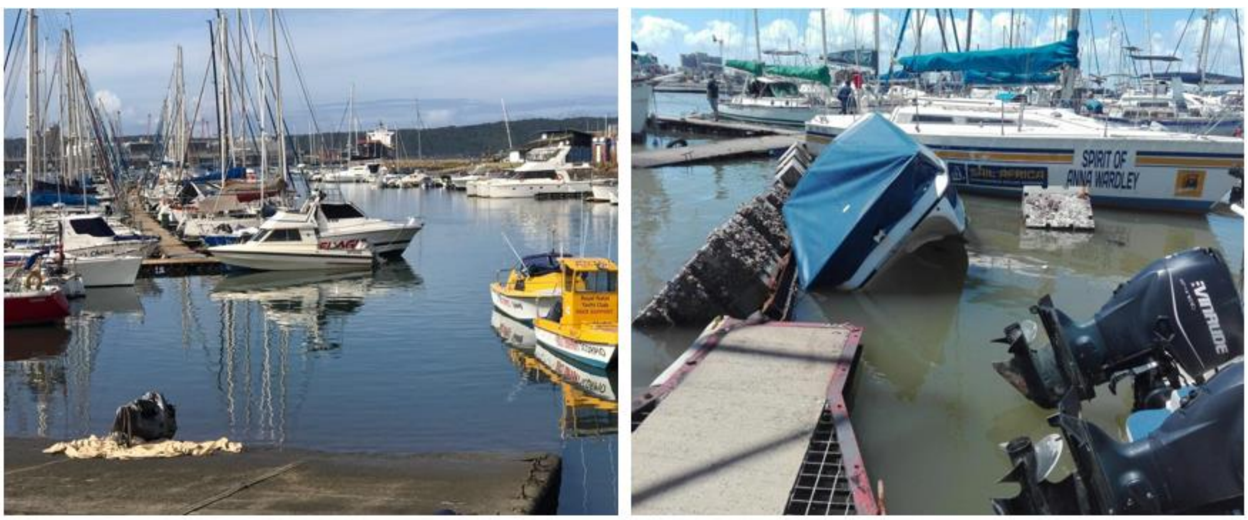

Plate 11. Durban harbour showing mooring of vessels fishing vessels.

Within the study areas, random sampling points were selected using a fish finder within a geographic location. The sampling codes together with GPS Co-ordinates and the location of sampling points are given in Table 3 and shown on the map (Figure 3).

Table 3. GPS co-ordinates of all sampling points in the Durban Basin

Location	Sampling site	Latitude/longitude	
South	**S1**	S 30° 00.810’	E 30° 56.696’
	S2	S 30° 01.471’	E 30° 58.506’
	S3	S 29° 59.249’	E 30° 58.485’
	S4	S 29° 57.285’	E 30° 59.825’
	S5	S 29° 59.666’	E 31° 02.369’
Central	**C1**	S 29° 57.797’	E 31° 02.452’
	C2	S 29° 53.826’	E 31° 03.008’
	C3	S 29° 51.019’	E 31° 05.831’
	C4	S 29° 51.409’	E 31° 06.921’
	C5	S 29° 49.947’	E 31° 08.763’
North	**N1**	S 29° 46.839’	E 31° 10.188’
	N2	S 29° 44.758’	E 31° 10.182’
	N3	S 29° 42.095’	E 31° 13.567’
	N4	S 29° 39.217’	E 31° 08.198’
	N5	S 29° 44.620’	E 31° 05.738’

3.1.2. Pristine coastline (Cape Vidal)

To compare the heavy metal accumulation in fishes from the Durban Basin against those of a pristine coastal system, the ISimangaliso Wetland Park, a recognised and protected World Heritage Site, was selected. This national reserve is an important area for threatened species, turtles and linefish, and provides protection against benthic fishing with appropriate zoning, while in some zones pelagic fishing is not permitted within 20 nm of the coastline (Figure 4a). The Marine Protected Area extends from beacon N3 north of Ngoboseleni Stream to beacon N4 south of Cape Vidal extending three nautical miles seawards from the high-water mark. The area consist of a Sanctuary Zone between beacon N5 at Red Cliffs and beacon N6 at Leven Point in which no fishing is allowed and a Restricted Zone between Red Cliffs and Leven Point in which pelagic fish may only be captured.

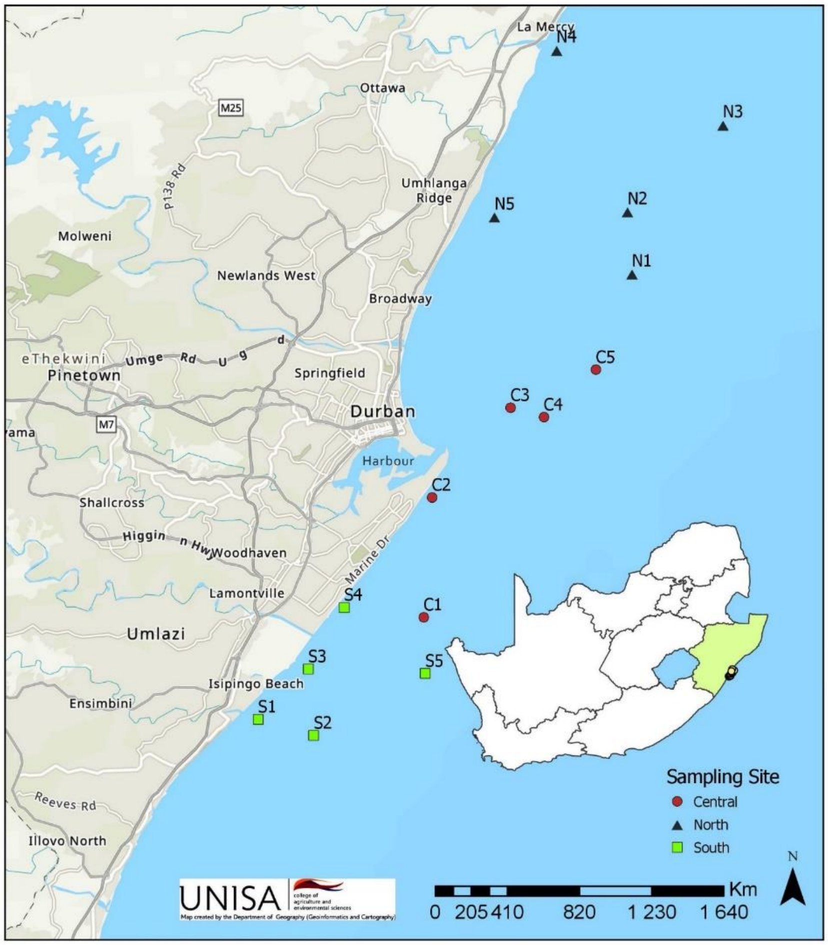

Figure 3. Map of the entire Durban basin showing the location of sampling points.

In this study, an approval was obtained from both the Department of Environmental Affairs and iSimangaliso Wetland and Marine Park, to collect samples of Maasbanker and slinger from two locations (P1 and P2) within the Cape Vidal Controlled Zone (CVCZ) (Figure 4b). Sampling point P1 is situated approximately 4.5 km north of Cape Vidal and 2.5km north of the Cape Vidal Lighthouse. The second sampling point (P2) was located within Cape Vidal Controlled Catch and Release Zone (CVCCRZ). This Controlled Catch and Release Zone is situated approximately 2.5km south of the Cape Vidal Lighthouse (Figure 4b).

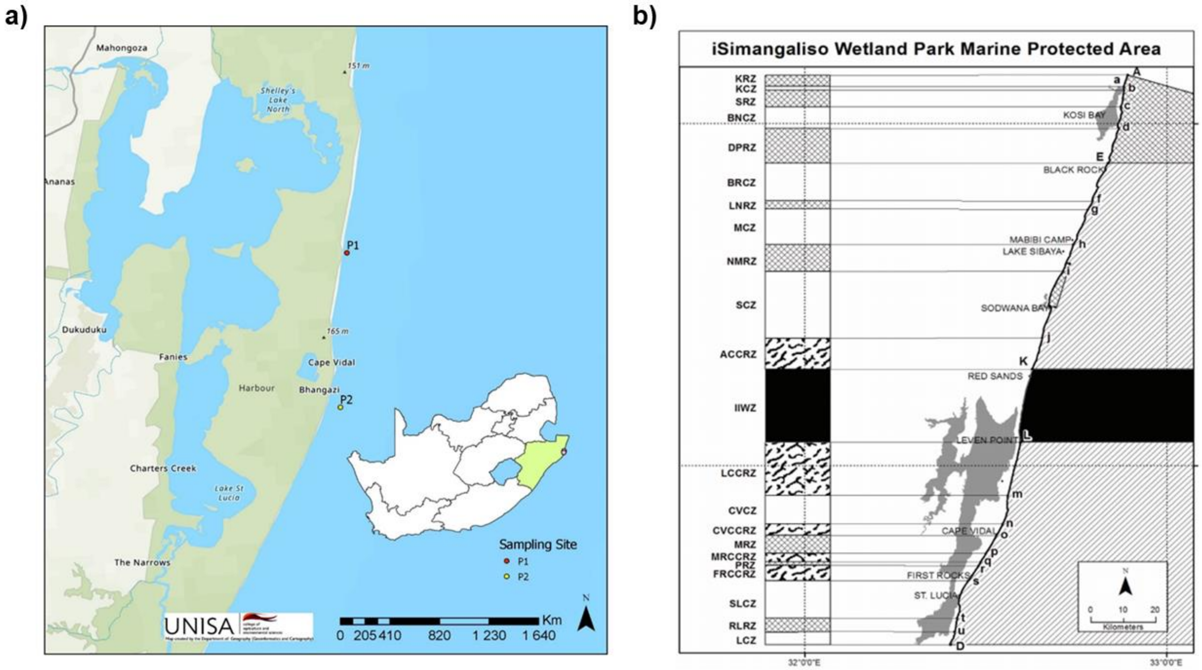

Figure 4. Map showing exact location of the sampling points within the selected zones at iSimangaliso Wetland Park Marine Protected area (a) and the iSimangaliso Wetland Park area showing the marine protected areas (b).

3.2 Sample collection and processing

A total of 231 fishes consisting of four commonly consumed species and two bait species were sampled simultaneously from five sampling points each in the three sampling regions in the Durban basin between April 2016 and February 2019. In addition, shrimp samples were collected from the local fisherman and a total of 12 fish samples – 6 slinger (common fish) and six Maasbanker (bait fish) – was collected from pristine Cape Vidal marine environment for comparative analysis of pollution levels with those from Durban basin. All the samples were collected using spearfishing and rod and/or reel with baited hooks in areas that were too deep for spearfishing. In most cases, spearfishing was used as there was no control of what species could take a baited hook, and thus was used as a strategy to prevent unnecessary capture and release of fish that did not meet sampling criteria. Under circumstances where baited hooks were used, fish which did not meet sampling criteria was safely released back into the ocean (Plate 12). In addition, to understand the heavy metals accumulation based on fish feeding habits, all the fishes were carefully caught in their natural habitat. Fishes caught in habitats, to which they do not belong, was omitted from this study. At all times, sampling adhered to the protocol prescribed by the Royal Society for the Prevention to Cruelty to Animals (RSPCA) for the humane killing of fish intended for eating (RSPCA, 2012) All fish that were caught were handled carefully to reduce stress, and those that were sampled were humanely killed quickly driving a sharp spike into the brain after capture in accordance to UNISA ethics Approval. This produced immediate unconsciousness (Lines and Spence, 2014).

Plate 12. Safe release of protected fish species caught with baited hooks during sampling.

The fish caught were initially chilled on ice before different samples (fleshy tissue, gills and liver for edible fish species and fleshy tissue, frame and gut for bait species) were collected into separate sample bottles. The remaining fish parts were discarded back into the ocean to serve as a food source for other fish. The fish samples for metal analysis were transported to the laboratory at 4 °C in a cooler box with ice.

3.3 Heavy metal analysis

3.3.1 Chemicals and materials

Analytical grade acids such as nitric acid (CAS No. 7696-37-2 : Purity-32%) and hydrochloric acid (CAS No. 7647-01-0 : Purity-55%) and sodium peroxide (CAS No. 1313-60-6, Purity – 99%) was purchased from Glass world & Chemical Suppliers CC (Johannesburg, South Africa) and Merck Chemicals (Pty) Ltd. (Johannesburg, South Africa) and used for the designed experiments. Multi-Element Stock Solution (Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Se, Sr, V, Zn) was bought from De Bruyn Spectroscopic Solutions (Pty) Ltd. (Johannesburg, South Africa), whereas indium standard was sourced from Industrial Analytical (Pty) Ltd, South Africa. A Milli-QRO4 system (Millipore, Bedford, MA, USA) was used to prepare deionized water.

3.3.2 Reagents and calibration standards preparation

An in-house method was used to digest and measure the heavy metal concentrations from fish samples. Indium was prepared by digesting 40.0 g of Indium metal with 150 ml of nitric acid in 500 mL beaker on hotplate until all the metal completely dissolved and used as internal standard for inductively coupled plasma optical emission spectrometry (**ICP**-OES). The resultant solution after digestion was made up to 1 L volume with analytical grade double distilled water to make 40g/L stock solution. Indium stock solution (400 ppm) was prepared by mixing 20 mL of 40g/L stock solution with 50 mL of nitric acid, followed by analytical grade double distilled water was used to make up 2L volume of solution. Prior to each ICP-OES analysis of samples, a calibration blank was prepared by pipetting 100ml from the 400-ppm Indium standard and adding 90 mL HCl and 30 mL HNO_3 before diluting to 1L with distilled water.

To prepare the multi element standards, 32% hydrochloric acid, 55% nitric acid, 400 ppm of Indium solution, 500ppm Multi-element stock solution 1 and 500ppm Multi-element stock solution 2 were used. Initially, a 100ppm intermediate standard was prepared by pipetting 50 ml of the 500ppm multi-element stock solution 1 into a 250ml volumetric flask containing 7.5 ml HNO_3 and 22.5 ml HCl and filled to the mark with distilled water. Similarly, a second 100-ppm intermediate standard was prepared using multi-element stock solution 2. For dilution purposes, a 10-ppm intermediate was also prepared by pipetting 10ml of the 100-ppm solution into a 100 ml volumetric flask containing 3 mL HNO_3 and 9 mL HCl and filled to the mark with distilled water. These stock solutions were used to prepare calibration standards as illustrated in Table 4.

Table 4. Preparation of multi-element calibration standards.

Volume (ml)	**Standards**							
	1 (250)	**2 (500)**	**3 (100)**	**4 (500)**	**5 (250)**	**6 (500)**	**7 (100)**	**8 (500)**
Target Concentration (ppm)	0.20	2	10	20	0.20	2	10	20
10 ppm stock solution 1 (ml)	5							
10 ppm stock solution 2 (ml)					5			
100ppm stock solution 1 (ml)		10	50	100				
100ppm stock solution 2 (ml)						10	50	100

Generally, three or four calibration standards are used to evaluate the linear range of ICP-OES method in order to evaluate the appropriate measurement uncertainty. While measurement uncertainty was evaluated based on the bottom-up approach. All the contributions were obtained from calibration certificates and from statistical analysis of repeated measurements. For instance, the measurement uncertainty is 2(SD)/1.716, where SD is the standard deviation. The 2 is referred to as the coverage factor and the 1.716 is the square root of 3 (for three measurements). Uncertainty of balances was calculated from data obtained from calibration certificates (declared uncertainty) and the repeatability of weighing.

3.3.3 Sample digestion

Determination of the total heavy metal concentrations (Al, As, Cr, Cu, Mn, Ni, Pb, and Zn) included fish sample preparation, i.e., initial drying of weighed samples in a porcelain crucible to constant mass 105 °C for 8 h. In the next step, dried samples were then ashed at 600 °C for 6 h produce an inorganic residue suitable for downstream analysis of the total amount of metals within the fish sample. As a quality control step to prevent the loss of metals, the ashing temperature was maintained at (600 °C) which below the boiling temperatures of the respective metals: Al (2056 °C), Cr (2200 °C), Cd (766.8 °C), Cu (1083 °C), Mn (1900 °C), Ni (2900 °C), Pb (1620 °C), As (613°C) and Zn (907 °C). The resultant ash was milled to fine particle size prior to digestion of 0.5 g with 30 ml of HCl and 10 ml of HNO_3 on a hot plate maintained at 100 °C until all sample was completely dissolved. The resultant solution samples were then evaporated to a volume of 5 - 10 ml followed by cooling to room temperature mixing with 2.5 ml of an internal indium standard. The digestions were performed in triplicate for each sample.

3.3.4 Measurement of heavy metals using ICP-OES

The total heavy metal concentrations were determined using inductively coupled plasma-optical emission spectrometry (Optima 8300® ICP-OES, Perkin Elmer Inc., Watham, MA, USA) according manufacturer instructions. The limit of detection (LOD) for the instrument was 10 µg/g and all analytical results were expressed as µg/g dry weight. Every ICP-OES measurement began with a calibration blank solution containing indium internal standard followed running the eight calibration standards, then samples and finally ending with the calibration blank. Sample analysis was only done when the calibration blank reading was below the instrument LOD. During the analysis, every element was analysed in triplicate. Standard instrumental parameters used during the measurement process are given in the Table 5.

Table 5. Typical instrumental parameters used during ICP-OES analysis.

Parameters	Values	Units
RF Forward power	1300	W
Plasma gas flow rate	15	L/min
Carrier gas flow rate	0.8	L/min
Auxiliary gas flow	0.2	L/min
Purge gas flow	normal	-
Spectral profiling	No	-
Resolution	Normal	-
Delay time	15	Sec
Replicates	3	-
Sample flow rate	1.5	ml/min
Flush time	10	Sec
Internal standard concentration	0.4	g/L

3.3.5 Sample analysis quality control

Metal analysis was done in Golden Pond Trading 97 (PTY) LTD (Co.Reg. No: 2004/007514/07), which is a South Africa National Accreditation System (SANAS) accredited laboratory for analytical services. The method set-up protocols included a minimum of four calibration standards covering a range of concentrations and analytes, internal QC samples, blanks, replicates, and reference materials. QC samples were read after calibration standards, periodically during sample analysis and at the end of the analysis. To ensure that the process was running correctly, the results for the QC samples were checked to see if they were within a pre-determined control limit before any samples were reported. In cases of failure, all samples after the last passed QC would be repeated and, if necessary, the instrument recalibrated. The QC samples were purchased from a different supplier than the calibration standards and came with a Certificate of Analysis. Sample blanks, method blanks and reagent blanks were used to assess responses other than those inherent to the blank material.

3.4 Heavy metal contamination and health risk assessment

3.4.1 Bioaccumulation factor (BAF)

The bioaccumulation factor (BAF) was adopted to gauge the bioaccumulation of trace metals as advocated by the U.S.EPA (1991) in the tissues of commonly consumed fish. BAF ratio is defined as the concentration of a pollutant accumulated in the tissue of an organism with respect to the concentration of that pollutant in the surrounding water body. The BAF was determined using the given formula as suggested by Lau et al. (Lau *et al.*, 1998):

$$\text{BAF}=\frac{T_c}{S_c}$$

where T_c is metal concentration in tissue (mg/g dry weight (d.w.)) and S_c is the metal concentration in sediment (mg/g d.w.) (Abdolahpur Monikh *et al.*, 2013).

3.4.2 Estimation of potential health risks from fish consumption

To estimate the potential health risks associated with the consumption of fish exposed to toxic metals, the tolerable daily intake (TDI) of toxic metals and estimated daily intake (EDI) were first determined.

3.4.2.1 Tolerable daily intake (TDI) of toxic metals

The provisional tolerable daily intake (TDI), recommended by US-EPA (2000) (US-EPA, 2000), indicates the applicable safe exposure levels and is used to evaluate the amount of contaminants ingested over a lifetime without appreciable risk.

3.4.2.2 Estimated Daily Intake (EDI)

The EDI of heavy metals was calculated depending on both the metal concentrations in fish and the amount of fish consumed. The EDI was calculated by factoring in the average metal concentration in fish tissue, the average daily consumption of fish by an adult person (Elnabris, Muzyed & El-Ashgar, 2013), the average weight of an adult African (Walpole *et al.*, 2012) with the permissible tolerable daily intake of heavy metals

(U.S.EPA, 1993). The EDI value for an adult was calculated using Equation (1) according to Song et al. (2009) (Song *et al.*, 2009).

$$\text{EDI} = \frac{\text{C} \times \text{D}}{\text{Aw}}$$

The EDI represents the intake of heavy metals through the consumption of fish by an adult (mg kg^{-1}), C is the average concentration of heavy metals in fish (mg kg^{-1}), *D fish* represents the daily consumption of fish (g^{-1}), and Aw is the average body weight of an adult (in kilograms).

3.4.2.3 Risk from the intake of heavy metals through ingestion (target hazard quotient, THQ)

Several methods have been proposed to estimate the potential risks of toxic metals on human health, in which the target hazard quotient (THQ) proposed by the US Environmental Protection Agency (US.EPA, 2009) has been recognized as a reasonable index for the evaluation associated with the intake of heavy metals by consuming contaminated foods (Hough *et al.*, 2004; Sridhara & Raj, 2008). The THQ is an estimate of the non-carcinogenic risk level due to pollutant exposure and calculated by the following equation:

$$\text{THQ} = \frac{\text{M}_\text{c} \times \text{IR} \times 10^{-3} \times \text{EF} \times \text{ED}}{\text{R}_\text{f}\text{D} \times \text{BW} \times \text{AT}_\text{n}}$$

where THQ is the non-carcinogenic risk and is dimensionless. EF is the exposure frequency (365 days/year). *ED* is the exposure duration (64.2 years) (since in South Africa the average life expectancy for males is 61.1 years (approx.) and for females is 67.3 years (approx.), therefore an average of two have been taken). RfD is the reference dose of the individual metal (mg/kg/day) (U.S.EPA, 2012). AT_n is the averaging time for non-carcinogens (365 days/year x ED) (U.S.EPA, 2011). If the value of THQ is above one (i.e., THQ > 1), it means that the exposed population is likely to experience adverse health effects. The higher the THQ value, the higher the probability of a hazardous risk on the human body. For a risk assessment of multiple heavy metals contained in fish, a total hazard index (HI) was employed by summing all the calculated THQi values of heavy metals as described in Equation (3):

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{THQ}\, i$$

THQi is the target hazard quotient of an individual element of heavy metal; HI is the total hazard index for all 8 metals in the present study, thus n equals 8.

3.4.2.4 Target cancer risk (TR)

Target cancer risk (TR) is used to indicate the carcinogenic risk and is dimensionless. The method which is used to estimate TR is provided in USEPA Region III Risk-Based Concentration Table (U.S.EPA, 2011). TR was calculated by the following equation:

$$\mathrm{TR} = \frac{\mathrm{M_c} \times \mathrm{IR} \times 10^{-3} \times \mathrm{CPS_o} \times \mathrm{EF} \times \mathrm{ED}}{\mathrm{BW} \times \mathrm{AT_c}}$$

where M_C, *IR*, *EF*, *ED*, *BW* are already explained above. CPS_o is the carcinogenic potency slope, oral (mg/kg bw-day^{-1}). AT_c is the averaging time for carcinogens (365 days/year × 64.2 years), since in South Africa the average life expectancy for males is 61.1 years (approx.) and for females is 67.3 years (approx.), therefore an average of two extremes have been taken for carcinogenic averaging time (https://www.statssa.gov.za/publications/P0302/P03022018.pdf). Heavy metals including Cu, Cr, Zn, As, Al, Mn and Pb do not cause any carcinogenic effects as their CPS_o have yet not been established (USEPA 2012), only the *TR* value for fee toxic metals intake (As, Ni and Pb) was calculated to show the carcinogenic risk. Its slope factor CPS_o was calculated from slope as stipulated by (USEPA 2012).

The potential carcinogenic effects of metals (As, Ni and Pb) was further characterized by calculating the maximum allowable daily fish consumption limit (TR_{lim}). TR_{lim} was determined by following equation:

$$TR_{lim} = \frac{(\mathrm{ARL\ x\ BW})}{(\mathrm{C\ x\ }CPS_o)}$$

where, *ARL* is maximum acceptable risk level (10^{-5}, unitless); *BW* is average adult body in kg (60.7kg for South African population); *C* is mean metal concentration in the different fish species; and CPS_o is the cancer slope factor (1.5, 1.7 and 0.009 mg/kg/day for As, Ni and Pb, respectively) (USEPA, 2000).

In addition, the allowable number of fish meals of a specified meal size that may be consumed over a given time period (TR_{mm})was also calculated using the following equation according USEPA (2000):

$$TR_{mm} = \frac{(TR_{lim}\ \mathrm{x}\ T_{ap})}{\mathrm{MS}}$$

where, TR_{mm} is maximum allowable fish consumption rate (meals/month); T_{ap} is time averaging period (365.25 days/12 months = 30.44 days per month), *MS* is meal size (0.227 kg fish/meal for adults person (USEPA, 2000)).

3.5 Statistical analysis

Descriptive statistical analysis were used to calculate the statistical parameters of different sites and fish heavy metal concentrations to evaluate the data distribution. To examine the normality of the probability distributions of heavy metal concentrations in different fish species, the Kolmogorov-Smirnov (K-S) test, Shapiro-Wilk test for marginal normality test, Bartlett's test for homogeneity of variance-covariance matrix assumption check were used. Normal Q-Q plots were also generated to check normality. Assumptions of homogeneity and normality of data were assessed through examination of residual plots and data were appropriately transformed when assumptions of homogeneity were not met (transformations are identified where applied). For example, where variables did not obey the normality test at the 0.05 significance level, the data was initially normalized by either logarithmic transformation or Box-Cox transformation before analysis.

Multivariate analysis of variance (MANOVA) was used to test for inter-species differences, intra-species differences between different body parts, and site differences in heavy metal levels followed by post hoc Tukey's least significant difference test ($p < 0.05$). In all cases the type III sums of squares were used to test the null hypothesis due to the unbalanced nature of experimental design in most cases. To assess differences between pairs of species and differences in concentration of the heavy metals in their tissues, and between-site differences, paired t-tests were performed. Kendall's tau correlation analysis was used to investigate the relationship between the selected metals concentration of different sampling sites with heavy metal contamination and identify potential sources of heavy metals. All statistical analyses were performed using various packages in R software (R Development Core Team, 2008) at a 0.05 significance level.

CHAPTER 4:
RESULTS

4.1 Heavy metal concentration in seawater, sediments and characteristics of fish sampled.

In this study, heavy metal concentration was analysed in the seawater, sediments and fish samples from 5 different sampling sites (North, Central, South and Harbour of the Durban basin and Cape Vidal). In general, the results of recovery of digestion method and analytical technique used in the present investigation were between 90.5 to 97%. A summary of the average values of heavy metal concentrations in the seawater and sediments of different sampling sites is provided in Table 6. Among the eight elements analyzed, the most abundant were Al and Zn, with higher levels detected in Durban South (2634 mg/kg in sediments) and Durban North (42.4 mg/L in seawater). The metal concentrations in the sediments were in elevated orders of magnitude above the concentrations recorded in water samples. In seawater, the metal contents ranged between 0.3-47.1 mg/L, with a magnitude in the order of Al > Zn >> As > Cu > Mn > Pb > Cr > Ni, whereas in sediment samples the metals concentrations were in the order of Al >> Mn > Cr > Zn > As > Cu > Ni > Pb. Comparatively, samples from Durban South reported higher values of Al, As, Mn, Cr, Cu and Ni than other sites. Heavy metal concentration values reported in other sites in the eastern seaboard of South Africa has been provided in Table 6 for comparison.

In total, the study used 313 fish samples including two baitfish species and five common edible fish species from Durban basin and Cape Vidal. The common edible fish species included copper bream (*n*=57), catface rockcod (*n*=46), slinger seabream (*n*=62), santer seabream (*n*=71) and grunter (*n*=25). Whereas the baitfish species were massbanker (*n*=18) and Atlantic chub mackerel (*n*=34). Additional information relating to samples, average depth they were caught (m), their mean length (mm) and weight (g), lifestyle and trophic level of the fish species, is given in Table 7.

Table 6. Summary of heavy metal concentrations in seawater and corresponding values in sediment samples from the Durban Basin and Cape Vidal compared with metal concentrations in ocean and other estuaries along the eastern seaboard of South Africa.

Location	Metal concentration (mg/L)[†]								Reference
	Al	As	Cr	Cu	Mn	Ni	Pb	Zn	
Durban North	32.6 (508)	3.9 (2.94)	1.4 (2.8)	3.6 (0.43)	2.9 (20.9)	1.1 (0.78)	2.4 (0.93)	42.4 (2.39)	this study
Durban South	47.1 (2634)	4.1 (6.34)	1.3 (12.8)	2.6 (4.46)	3.1 (92.0)	0.8 (4.99)	1.2 (2.04)	10.3 (8.88)	this study
Durban Central	33.0 (1389)	4.0 (6.10)	1.4 (11.8)	2.0 (2.08)	1.3 (68.1)	0.5 (3.35)	1.6 (2.89)	5.0 (8.00)	this study
Durban Harbour	41.6 (1218)	3.7 (2.36)	1.5 (9.00)	3.1 (5.52)	1.4 (24.8)	0.9 (2.36)	3.0 (5.00)	9.8 (26.7)	this study
Cape Vidal	34.1 (1338)	3.6 (4.83)	1.1 (6.85)	1.3 (1.44)	1.0 (77.7)	0.3 (2.96)	0.4 (0.98)	1.2 (3.22)	this study
Mhlathuze[‡]	990.0 (18677.4)	-	48.0 (64.4)	39.1 (12.2)	48.2 (13.5)	-	130.2 (45.6)	66.5 (45.6)	Mzimela et al. (2014)
Richard's Bay[‡]	504.4 (31323.4)	-	23.6 (388)	50.8 (57)	80.7 (117)	-	117 (287)	85.4 (287)	Wepener and Vermeulen (2005)
Durban[‡]	-	-	-	27 (183)	(549)	-	117 (332)	287 (332)	Fatoki and Mathabatha (2001)
Durban	-	1.14	<1	<1	-	<2	<1	4.81	CSIR (2010)

[†] Seawater heavy metal concentrations. The corresponding sediment metal concentrations (mg/kg dw) has been provided in brackets

[‡] Sediment and water samples collected from the estuaries along the eastern seaboard of South Africa

Table 7. The number of fish samples, average depth caught, their length and weight, lifestyle and trophic level of the species used in the study.

Fish Species (Scientific name)	N	Depth (m)	Length (mm)	Weight (g ww)	Lifestyle	Trophic level
Catface RockCod (*Epinephelus andersoni*)	46	32.4±19.5	570.2±67.8	2293.0±4.7	Demersal	Carnivore (feeds on crabs, other crustaceans and small fish)
Slinger-Seabream (*Chrysoblephus puniceus*)	62	40.3±15.2	303.9±47.0	722.0±3.7	Demersal	Carnivore (feeds on bivalve mollusks, crustaceans and small fish)
Santer-Seabream /Soldier (*Cheimerius nufar)*	71	54.9±8.8	366.3±61.3	937.5±9.5	Demersal	Carnivore (feeds on small fish, squid, and crustaceans)
Bronze/Copper-Seabream (*Pachymetopon grande*)	57	17.1±11.4	421.3±46.2	2171.9±2.6	Benthic	Omnivore (feeds on algae and small invertebrates)
Grunter (*Pomadasys commersonnii*)	25	9.7±1.7	654.4±113.7	2764.6±17.5	Benthic	Carnivore (feeds on crustaceans, shrimps, sand prawns and mollusks)
Maasbanker (*Trachurus trachurus*)	18	22.3±5.4	202.4±17.3	76.7±0.1	Benthic/ Pelagic	Carnivore (feeds on zooplanktons, crustaceans such as copepods, amphipods and euphasiids)
Atlantic Chub Mackerel *(Scomber japonicas)*	34	16.6±5.0	249.9±36.0	166.6±0.3	Pelagic	Carnivore (feeds on small fish, squids, prawns, and shrimp species)

4.2 Accumulation, biomagnification and potential trophic transfer of heavy metals along simple food chain in Durban harbour

To monitor the contamination and potential bioaccumulation of heavy metals in different trophic levels within the polluted Durban Harbour, the metal concentrations were analysed in the seawater, sediments, cracker shrimp (*C. kraussi*) and grunter (*P. commersonni),* and the enrichment values in the trophic levels calculated. Table 8 shows the concentrations of heavy metals in sediment, cracker shrimp and different tissues in grunter (mg/kg (dw)) and seawater (mg/L) and the corresponding enrichment (biomagnification factor) values. In seawater, the accumulation pattern of the heavy metals was Al >>> Zn >> As > Cu > Cr > Mn > Ni > Pb. A similar trend, albeit with small differences, was reported for sediment samples.

Overall, heavy metal and metalloids concentrations in cracker shrimp (2.77±1.1 to 318.00±137 mg/kg (dw)) were relatively higher than grunter tissues (1.4±0.97 to 23.8±9.86 mg/kg (dw)), the level of variability being dependent on the metal. In cracker shrimp, the accumulation pattern was Al > Cu >> Mn > Zn > Pb > As > Cr > Ni (Table 8). In contrast, the grunter bioaccumulation pattern was dependent on the metal/metalloid and tissue/body parts analysed. Irrespective of tissue/body parts, the average accumulation pattern was Al >Zn >> Cu> Pb > Mn > Cr > As > Ni, with gills and liver samples having comparatively higher metals/metalloid levels than tissues samples of grunter. The only exception was Cu and Pb whose concentrations was not significantly different (at p <0.05) between the different fish parts/organs. Interestingly, higher accumulation patterns (>2-fold) were observed for As, Cu and Mn in the gills than in other fish parts/organs. In terms of biomagnification, there was overall significant (2-50-fold) enrichment of the heavy metals in the sediments from water, with exception of As that had lower concentration level in the sediment than seawater. Regarding the sediment-cracker shrimp trophic level, significant biomagnification of four metallic elements was evidenced: Cu (41.5±19.1), Mn (5.1±1.40), Pb (4.3±6.51) and Zn (2.35±0.73). However, no enrichment values higher than 1.0 were found in the trophic level cracker shrimp-grunter relationship.

Table 8. Average values (±SD) of heavy metals concentration detected in seawater, sediments, cracker shrimp (*C. kraussi*) and grunter (*P. commersonni*), and their enrichment values in trophic levels in the Durban harbour.

Metal	Concentration						Enrichment (biomagnification factor)		
	Water (mg/L)	Sediment (mg/kg dw)	Cracker shrimp (mg/kg dw)	Grunter* (mg/kg dw)			Water - sediment	Sediment – Cracker	Cracker - Grunter
				Tissue	Gills	Liver			
Al	41.6	1218	318.00±137	23.8±19.1[a]	19.5±15.9[a]	38.8±28.8[b]	29.3	0.26±0.11	0.08±0.06
As	3.7	2.36	4.02±2.7	1.5±1.47[a]	3.3±1.88[b]	1.1±1.84[a]	0.7	1.70±1.13	0.37±0.36
Cr	1.5	9.00	4.02±2.9	1.6±1.42[a]	3.9±2.62[b]	1.1±0.97[a]	6.0	0.45±0.32	0.40±0.35
Cu	3.1	5.52	229.07±105	3.8±2.46	4.1±2.64	4.0±2.62	1.8	41.50±19.1	0.02±0.01
Mn	1.4	24.8	126.29±35	1.9±1.97[a]	5.1±3.73[b]	1.9±2.68[a]	17.7	5.08±1.40	0.02±0.01
Ni	0.9	2.36	2.77±1.1	1.4±0.97[a]	2.3±0.86[b]	1.3±1.17[a]	2.6	1.17±0.47	0.51±0.23
Pb	0.4	5.00	21.61±32.5	2.4±0.90	2.8±1.81	3.8±2.47	12.5	4.32±6.51	0.11±0.04
Zn	9.8	26.7	62.68±19.4	23.8±9.86[a]	45.5±15.9[b]	55.5±29.5[b]	2.7	2.35±0.73	0.38±0.16

* Mean±SD for tissue, gills and liver samples for grunter have been given in the row, respectively. Mean values followed by different letters within a row are statistically different (ANOVA; Tukey's HSD test, $P < 0.05$).

Bioaccumulation factor of heavy metal in cracker shrimp and different fish parts/organs of grunter are show in Figure 5. The highest of BAF of heavy metal (Mn, Cu, Pb, Al, Zn, Ni, Cr, and As) in cracker shrimp were 90.0±6.89, 78.9±9.42, 54.0±22.6, 7.5±0.92, 6.4±0.55, 3.1±0.34, 2.7±0.20 and 1.1±0.92, respectively. As well as, the highest of BAF of heavy metal (Al, As, Cr, Cu Mn, Ni, Pb, and Zn) in grunter tissue samples were 0.57±0.09, 0.39±0.08, 1.07±0.19, 1.24±0.61, 1.35±0.29, 1.55±0.22, 5.9±0.46, and 2.4±0.21, respectively, a trend also observed for the gills and liver samples (Figure 5).

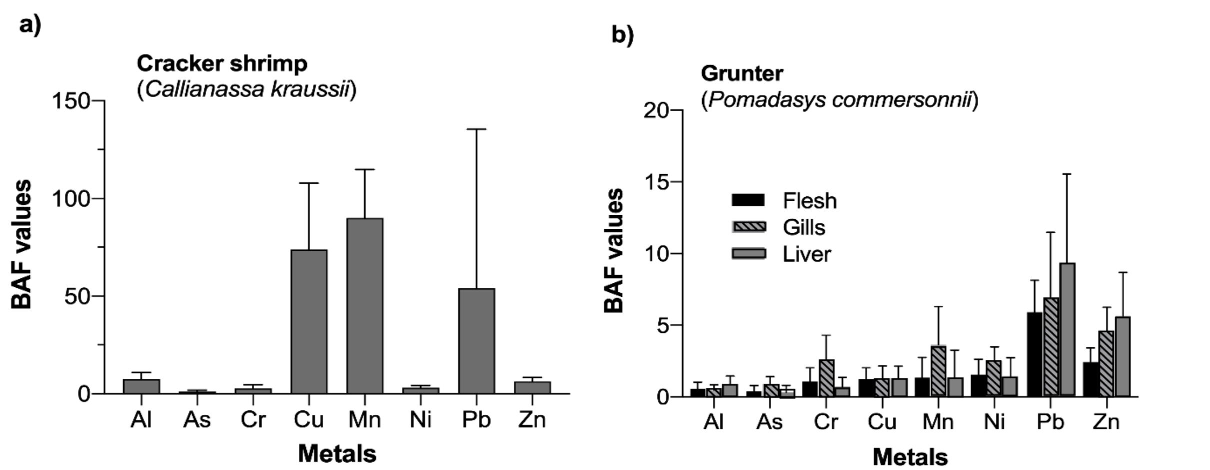

Figure 5. Bioaccumulation factor of different heavy metal in cracker shrimp (*Callianassa kraussii*) and different tissues of grunter (*Pomadasys commersonnii*).

Pearson correlation analysis results among heavy metal concentrations between cracker shrimp and grunter indicated statistically significant relationships (Table 9). Al showed strong positive correlations with Cu (r=0.78,), and Mn (r=0.95) at p<0.001. Strong positive correlations were also observed between Cr and Ni (r=0.71, $p < 0.001$) and Cu and Mn (r=0.90, $p < 0.001$, while other metal combinations showed significant but weak to moderate correlation coefficients (Table 9).

Table 9. Two-tailed Pearson's correlation coefficients for heavy contents in the cracker shrimp and grunter fish samples§.

	Al	As	Cr	Cu	Mn	Ni	Pb	Zn
Al	1							
As	0.26*	1						
Cr	0.23*	0.57***	1					
Cu	**0.78***	0.43***	0.42***	1				
Mn	**0.95***	0.40***	0.31**	**0.90***	1			
Ni	0.33**	0.59***	**0.71***	0.44***	0.40***	1		
Pb	0.43***	0.46***	0.05	0.48***	0.56***	0.19	1	
Zn	0.32**	0.28**	0.28**	0.40***	0.35**	0.42***	0.27*	1

§ Correlations are defined as weak ($0 < |r| < 0.3$), moderate ($0.3 < |r| < 0.7$) or strong ($|r| > 0.7$). Significant correlations (at $p < 0.001$ '***', $p < 0.01$ '**', $p < 0.05$ '*') are bolded.

4.3 Heavy metal concentration of fish species in Durban Basin

4.3.1 Baitfishes - Maasbanker (*Trachurus trachurus*) and Atlantic Chub Mackerel (*Scomber japonicas*)

Impact of species, location, and fish body parts/organs

Table 10 and Figure 6 shows the mean concentrations of Al, As, Cr, Cu, Mn, Ni, Pb and Zn recorded in whole fish body of two bait species caught from all locations in the Durban basin, respectively. The mean heavy metal concentration in the two fish species ranged between 1.65 - 58.31mg/kg, with a magnitude in the order of Zn>>Al>>Cu>Pb>Mn>Cr>As>Ni. Two tailed two-sample Student's t-test, used to test the null hypothesis (H_o) - that there was no significant difference in heavy metal concentrations between the two baitfish at $p<0.05$, showed that there was only significant difference in the Al (t=4.25, $p<0.001$), As (t=-3.46, $p=0.001$), Cr (t=-3.21, $p=0.002$) and Mn (t=-4.03, $p<0.001$) levels in the two fish species (Table 10).

Table 10. Mean concentrations of heavy metal in two common baitfish (whole body) within the Durban basin, maasbanker (*Trachurus trachurus*) and Atlantic Chub Mackerel (*Scomber japonicas*).

Metal	Mean ± SE concentrations (mg/kg dw)†		t-statistic‡	*p*-Value
	Maasbanker	Chub mackerel		
Al	**29.70 ± 3.31 (3.43-93.24)**	15.08 ± 0.92 (2.29-38.88)	4.251	<0.001
As	1.66 ± 0.14 (0.75-7.04)	**2.40 ± 0.16 (0.2-7.76)**	-3.464	0.001
Cr	2.17 ± 0.16 (0.00-7.06)	**3.08 ± 0.23 (0.25-11.74)**	-3.206	0.002
Cu	4.71 ± 0.39 (0.98-11.80)	5.62 ± 0.31 (0.25-15.84)	-1.833	0.069
Mn	2.14 ± 0.17 (0.84-6.54)	**3.33 ± 0.24 (0.32-9.96)**	-4.033	<0.001
Ni	1.65 ± 0.10 (0.00-4.44)	1.81 ± 0.13 (0.36-9.41)	-0.969	0.334
Pb	4.06 ± 0.35 (0.77-9.74)	3.63 ± 0.24 (0.39-10.42)	1.016	0.312
Zn	58.31 ± 2.72 (27.64-115.54)	54.17 ± 2.06 (12.25-112.35)	1.213	0.227

† Results based on n=18 and n=34 for maasbanker and Atlantic chub mackerel, respectively.

‡ Two tailed two-sample Student's t-test was used to test the H_o at $p<0.05$ as described by Zheng et al. (2013)

To further determine whether species, location and body parts/organs had an effect on the heavy metal concentrations, the data was subjected to multivariate analysis of variance (MANOVA) after Box-Cox transformation to satisfy the assumption of normality and homogeneity of variance-covariance matrix of residuals (Pek, Wong & Wong, 2018). Summary of the MANOVA analysis for the heavy metal concentrations is given in Table 11. Overall, MANOVA results showed that there was a significant difference in the levels of toxic heavy metals within and between baitfish species caught in different locations, and their accumulation having different patterns in different fish parts/organs.

Table 11. MANOVA test for the effect of species, location and fish body parts/organs on the heavy metal concentrations.

Parameter	Al	As	Cr	Cu	Mn	Ni	Pb	Zn
Species								
Maasbanker	29.7±3.3^{a}	1.7±0.14^{a}	2.2±0.16^{a}	4.7±0.39	2.1±0.17^{a}	1.7±0.10	4.1±0.35	58.3±2.7
	(3.4-93.2)	(0.8-7.04)	(0.0-7.06)	(1.0-11.8)	(0.8-6.54)	(0.0-4.44)	(0.8-9.74)	(27.6-115.5)
Chub mackerel	15.1±0.9^{b}	2.4±0.16^{b}	3.1±0.23^{b}	5.6±0.31	3.3±0.24^{b}	1.8±0.13	3.63±0.2	54.2±2.1
	(2.3-38.8)	(0.2-7.76)	(0.3-11.7)	(0.3-15.8)	(0.3-9.96)	(0.4-9.41)	(0.4-10.4)	(12.3-112.4)
p-Value	***<0.001******	***0.001*****	***0.003******(9.44)*	*0.057*	***<0.001******	*0.381*	*0.295*	*0.148*
(df=1,150)	*(35.68)*	*(11.06)*		*(3.67)*	*(25.81)*	*(0.77)*	*(1.11)*	*(2.12)*
Body parts†								
Frame	17.5±1.3^{a}	2.6±0.23^{a}	2.7±0.19^{a}	3.8±0.29^{a}	2.8±0.16^{a}	2.0±0.12^{a}	3.6 ± 0.33	59.7 ± 2.2^{a}
	(3.4-38.9)	(0.7-7.76)	(0.0-6.98)	(1.0-10.7)	(0.7-5.58)	(0.6-6.81)	(0.8-10.4)	(22.0-83.0)
Tissue	13.6±1.8^{a}	1.3±0.13^{b}	1.8±0.18^{b}	5.5±0.35^{b}	1.1±0.06^{b}	1.2±0.11^{b}	3.7 ± 0.34	40.4 ± 2.2^{b}
	(2.3-68.1)	(0.3-5.36)	(0.3-5.05)	(0.3-11.0)	(0.3-2.46)	(0.4-4.44)	(0.7-9.3)	(12.3-84.7)
Gut	29.3±3.2^{b}	2.5±0.20^{a}	3.9±0.37^{c}	6.5±0.52^{b}	4.9±0.31^{c}	2.1±0.19^{a}	4.1 ± 0.36	66.8 ± 2.8^{a}
	(4.7-93.2)	(0.7-7.48)	(1.4-11.7)	(1.5-15.8)	(1.1-3.31)	(0.0-9.41)	(0.4-9.74)	(20.1-115.5)
p-Value	***<0.001******	***<0.001******	***<0.001***	***<0.001******	***<0.001******	***<0.001******	*0.439*	***<0.001******
(df=2,150)	*(16.46)*	*(16.88)*	*(18.61)*	*(12.10)*	*(100.97)*	*(10.03)*	*(0.83)*	*(33.99)*
Location†								
Central	27.9±4.3^{a}	1.9±0.19^{a}	3.6±0.50^{a}	6.0±0.63	2.5±0.37	2.0±0.27	4.3±0.50	57.6±3.8
	(2.3-93.2)	(0.6-7.03)	(1.0-11.7)	(1.6-13.5)	(0.8-9.96)	(0.5-9.41)	(0.9-10.4)	(18.5-113.5)
North	19.6±2.5^{ab}	1.7±0.15^{a}	2.6±0.32^{ab}	5.4±0.54	2.6±0.29	1.6±0.19	3.1±0.33	49.0 ± 3.5
	(4.6-85.0)	(0.7-4.67)	(0.6-8.87)	(1.0-15.8)	(0.6-6.46)	(0.6-6.81)	(0.6-8.59)	(12.3-112.3)
South	17.0±1.3^{b}	2.5±0.19^{b}	2.5±0.16^{b}	4.9±0.29	3.2±0.25	1.7±0.09	3.9±0.26	57.6 ± 2.1
	(2.5-68.1)	(0.3-7.76)	(0-9.83)	(0.3-11.7)	(0.3-8.98)	(0.0-4.59)	(0.4-9.75)	(15.7-115.5)
p-Value (df=2,150)	***0.031****	***0.049****	***<0.001*****(8.72)*	*0.054*	*0.321*	*0.202*	*0.070*	*0.124*
	(3.55)	*(3.07)*		*(3.67)*	*(1.15)*	*(1.62)*	*(2.70)*	*(4.52)*
Multivariate ANOVA analysis (interaction effect)								
Species x	***0.001*****	*0.430*	***<0.001*****	***0.005****	*0.051*	*0.077*	*0.113*	***0.002****
Location (df=2,148)	*(7.79)*	*(0.85)*	*(7.44)*	*(5.499)*	*(3.04)*	*(2.61)*	*(2.20)*	*(6.29)*

‡ p-Values rounded to three decimal places, with $F_{statistic}$ values given in brackets. Significant values have been bolded for clarity; *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$.

At species level, consistent with findings using two-tailed two-sample Student's t-test analysis (Table 11), MANOVA results also showed a significant effect on Al, As, Cr and Mn levels. Whereas Al levels were significantly higher ($F_{1,150}$=35.68, p < 0.001) in maasbanker (Table 11), Atlantic chub mackerel had higher accumulation of As ($F_{1,150}$=11.06, p=0.049), Cr ($F_{1,150}$=9.44, p=0.003) and Mn ($F_{1,150}$=3.55, p = 0.001) which was dependent on fish parts/organs and location. Comparatively, gut samples exhibited significantly higher mean concentration for all metals, followed by frame then tissues. However, no significant difference was observed for Pb ($F_{2,150}$=0.83, p<0.439) in all the different body parts, with mean values of 3.6 ± 0.33, 3.7 ± 0.34 and 4.1 ± 0.36 mg/kg Pb for frame, tissue and gut, respectively.

On the other hand, analysis of the location effect also revealed specific difference on heavy metal concentration in the baitfish irrespective of fish species. Overall, significant difference were only observed for Al ($F_{2,150}$=9.44, p=0.031), As ($F_{2,150}$=3.07, p=0.049) and Cr ($F_{1,150}$=8.72, p<0.001), whereas other metals did not show any significant (p>0.05) location differences. While baitfish caught in Central Durban basin had significant higher Al (27.9±4.3 mg/kg) and Cr (3.6±0.50 mg/kg) content than other locations at p<0.05, fish samples from Durban South had higher As (2.5±0.19 mg/kg). In contrast, Cu, Mn, Ni, Pb and Zn content showed only subtle differences related to location in the Durban basin. However, the differences were not significant at p<0.05. Further analysis was also done to check if there were significant differences between different fish species at different locations (interaction between species and location) in the Durban basin.

As shown in Table 11 and Figure 6, significant interaction effect was only observed for Al, Cr, Cu and Zn. Specifically, there was an observed significantly higher ($F_{2,148}$=6.29, p=0.002) level of Zn in maasbanker caught in the Durban South and Central (mean: 67.7±4.5 and 63.3±5.3 mg/kg, respectively) compared to Durban North (43.8±1.5 mg/kg). However, no significant difference was observed in Zn concentration in Atlantic chub mackerel from all the locations. In contrast, Cr levels in maasbanker did not exhibit location effect, whereas its level in Atlantic chub mackerel from Durban Central (5.0±1.2 mg/kg) was approximately two-fold higher than those from Durban South (2.59±0.98

mg/kg). Detailed comparison of the metal concentration in the two bait fishes from the three different locations in the Durban basins is illustrated in Figure 6.

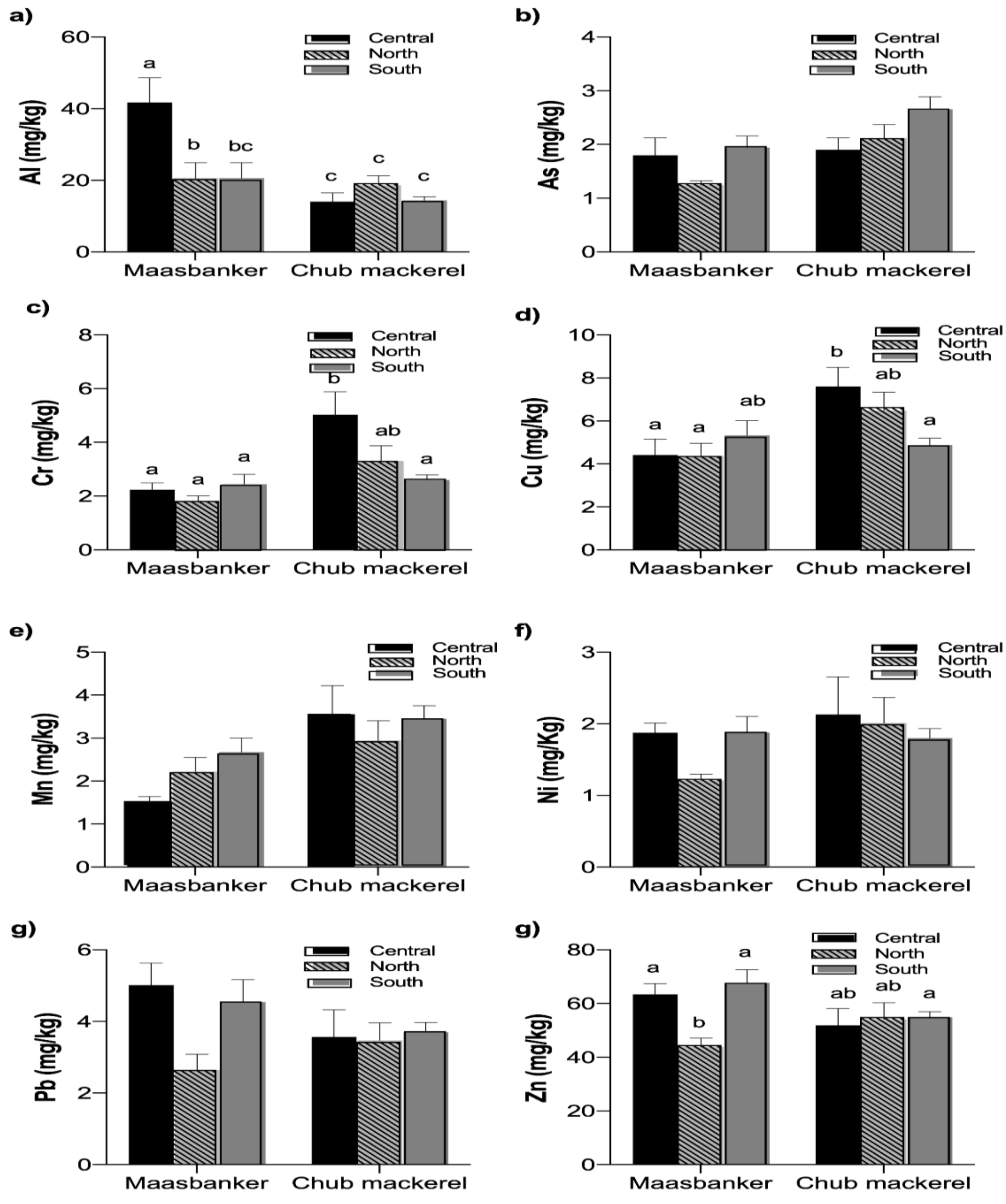

Figure 6. Average heavy metals concentrations comparison by baitfish species and location. *Mean values followed with different letters within each species are statistically different (ANOVA; Tukey's test, p > 0.05). p-values showing significant species versus location interactions effect are provided in Table 11.*

Correlation studies on heavy metal concentration in the two baitfishes

The correlation between element pairs in maasbanker and Atlantic chub mackerel are shown in Table 12. For maasbanker, the Kendall's coefficient (τ) showed that a significant positive moderate correlation between metals [As-Cu (τ=0.255, p < 0.01), As-Mn (τ=0.542, p < 0.001), As-Ni (τ=0.427, p < 0.001), As-Zn (τ=0.380, p < 0.001), Cr-Mn (τ=0.405, p < 0.001) and Cr-Ni (τ=0.380, p < 0.01)], except that between Cu-As that showed a significant but weak negative correlation (τ=-0.186, p < 0.05). Other significant but weak positive correlations were observed for Al vs Pb, Al vs Zn, Cu vs Pb and Ni vs Zn, whereas other metal pairs had insignificant correlations (Table 12). In Atlantic chub mackerel, significant positive correlation was observed for most metal pairs, with exception of Cu-Al, Cu-As, Cu-Ni, Cu-Zn, and Pb and all other metal pairs. Among the significant values, most metal pair had moderate positive correlation (0.3 < |τ| < 0.7) at p <0.001. Weak positive correlations were only observed between Cu-Cr (τ=0.175, p < 0.01) and Cu-Mn (τ=0.156, p < 0.05).

Table 12. Kendall's tau correlation coefficients (τ) for heavy metals in two baitfish species, maasbanker (bottom panel) and Atlantic chub mackerel (upper shaded panel) §.

	Al	As	Cr	Cu	Mn	Ni	Pb	Zn
Al		0.313***	0.348***	NS	0.356***	0.331***	NS	0.352***
As	NS		0.405***	NS	0.381***	0.400***	NS	0.343***
Cr	NS	0.341**		0.175**	0.419***	0.550***	NS	0.405***
Cu	NS	-0.186*	NS		0.156*	NS	NS	NS
Mn	NS	0.542***	0.405***	NS		0.444***	NS	0.501***
Ni	NS	0.427***	0.333**	NS	NS		NS	0.502***
Pb	0.255**	NS	NS	0.189*	NS	NS		NS
Zn	0.240*	0.380***	NS	NS	NS	0.286**	NS	

§ Correlations are defined as weak (0 < |τ| < 0.3), moderate (0.3 < |τ| < 0.7) or strong (|τ| > 0.7). Significant correlations (at *p < 0.001 '***', p < 0.01 '**', p < 0.05 '*'*) are indicated.

4.2.2 Common edible fishes - copperbream (*Pachymetopon grande*), catface rock cod (*Epinephelus andersoni*), slinger (*Chrysoblephus puniceus*) and soldier (*Cheimerius nufar*)

Heavy metal accumulation patterns in liver, gills and muscles (fleshy tissue)

Figure 7. shows heavy metals (Al, As, Cr, Cu Mn, Ni, Pb, and Zn) concentration in liver, gills and muscles of four common edible fishes in Durban basin. Based on the mean concentrations of studied metals in the different fish species, the highest levels of Al, Cr, Ni and Pb were found in slinger, while the highest levels of As and Cu were found in Catface rockcod. Similarly, the highest concentration of Mn and Zn was observed in copper bream. On the other hand, the lowest concentrations of Al, Cr Mn and Pb were detected in catface rock cod. Soldier showed the average lowest concentrations of Ni and Zn, while slinger recorded the lowest concentrations of As. Results on the species and location effect on the heavy metal accumulation patterns in the four fish species is elaborated in detail in the subsequent parts of this subsection.

Overall, the mean metal concentrations in the four fish species under study could be summarized in descending order as follows: liver>gills>muscles, however the subtle differences could be ascribed to fish species and metal under study. In copper bream, the highest Al (50.6 ± 3.06 mg/kg), Cu (6.05 ± 0.53 mg/kg), Ni (4.05 ± 0.4 mg/kg) and Zn (62.7 ± 3.58 mg/kg) were found in liver, As (3.42 ± 0.22 mg/kg), Cr (3.61 ± 0.16 mg/kg) and Mn (20.4 ± 2.00 mg/kg) was found in gills. Similar accumulation pattern of heavy metals was observed for catface rock cod and slinger, however, no significant differences ($p < 0.05$) in Cu and Cr accumulation was observed in liver, gills and muscles tissues of slinger. In soldier, however, highest level of As (4.64 ± 0.69 mg/kg) and Zn (62.4 ± 2.82 mg/kg) was recorded in gills, whereas Pb (62.4 ± 2.82 mg/kg) was highest in liver samples. In contrast, Pb levels were not significantly different ($p < 0.05$) in liver, gills and muscles tissues of copper bream, catface rock cod and slinger fish samples caught in the Durban basin.

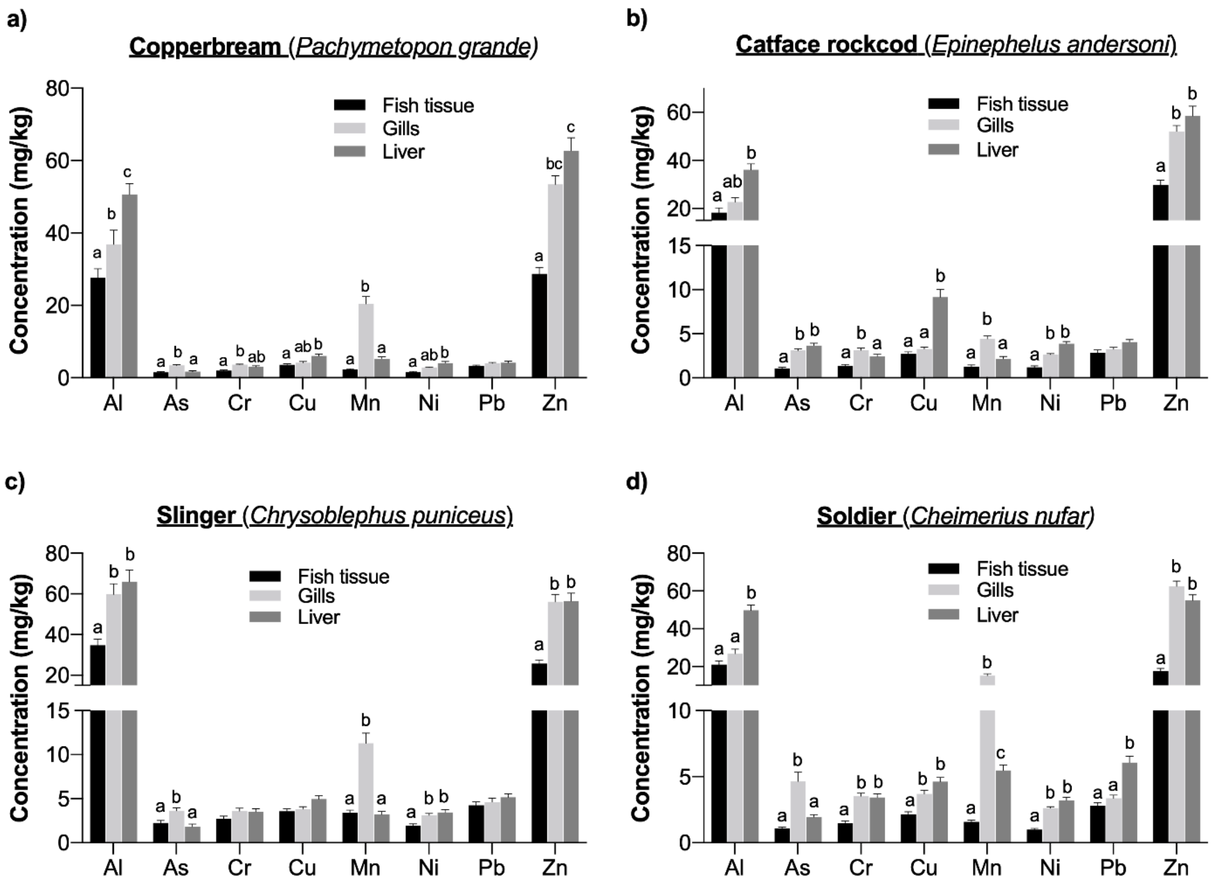

Figure 7. Heavy metals concentrations in the liver, gills and muscles in copperbream (*Pachymetopon grande*), catface rock cod (*Epinephelus andersoni*), slinger (*Chrysoblephus puniceus*) and soldier (*Cheimerius nufar*). *Mean values followed by different letters (a, b, c) within a metal grouping are statistically different (ANOVA; Tukey's test, $p < 0.05$).*

Influence of species and location on heavy metal accumulation

In this study, the main objective was to analyze the potential risk assessment of consumption of edible fish species on human health. To evaluate the contribution of species and location on the accumulation patterns of heavy metals, results have been limited to fish muscles tissues (edible part of fish) only. Initially, fish muscle metal concentration data were transformed using $\log_{10}(x)$ function, to meet the assumptions of normality and homogeneity of variance prior to analysis, before being subjected to two-way ANOVA test to analyze the effects of fish species and sampling location on heavy metal accumulation patterns.

Table 13. *F*-value and significance of two-way ANOVA results for effects of four fish species (S) and sampling location (L) on heavy metal (Al, As, Cr, Cu Mn, Ni, Pb, and Zn) concentrations in the muscles tissues of common edible fish species in Durban basin.

Metal (mg/kg)	Fish species (S)		Sampling location (L)		S x L	
	F	*P*	*F*	*P*	*F*	*P*
Al	9.93	**<0.001**	1.51	0.222	3.55	**0.002**
As	8.40	**<0.001**	0.4	0.668	1.51	0.069
Cr	8.17	**<0.001**	0.07	0.934	0.40	0.112
Cu	8.85	**<0.001**	0.23	0.795	0.07	0.068
Mn	17.0	**<0.001**	3.43	0.054	0.23	0.438
Ni	8.15	**<0.001**	1.48	0.231	3.43	0.201
Pb	4.97	**0.002**	0.53	0.589	1.48	0.259
Zn	10.7	**<0.001**	0.13	0.878	0.53	0.634

* Significant *P*-values are shown in bold.

As shown in Table 13, fish species had significant influence on all the heavy metal accumulation patterns, irrespective of sampling location. In contrast, sampling location did not affect the accumulation patterns of heavy metals in the four fish species. The interaction effect of fish species and sampling location had a significant effect only on Al concentration (Table 13). Only exception was catface rockcod that did not exhibit any significant difference ($p < 0.05$) in Al concentration affected by sampling location within the Durban basin. In copper bream, highest Al concentration was observed in Central (31.8 ± 4.20 mg/kg) and North (31.7 ± 4.45 mg/kg); however, these values were not significantly different from samples collected in the South Durban basin (29.8 ± 3.63 mg/kg) at $p < 0.05$. In contrast, soldier fish samples caught in South Durban basin had approximately two-fold higher Al levels (29.8 ± 3.63 mg/kg) than other sampling sites. For slinger, central Durban samples had the highest Al accumulation (47.2 ± 4.45 mg/kg), followed with Durban south (31.5 ± 3.36 mg/kg), with lowest values reported for the Durban north (29.1 ± 4.20 m/kg).

Table 14. One-way ANOVA analysis of heavy metal accumulation in the tissues of four edible fish species in Durban basin.

Metal	Metal concentrations in fish species (mg/kg dw)[∂]				F statistic
	Rock cod	Soldier	Copper bream	Slinger	($_{df=3,\ 224}$)
Al[#]	-	-	-	-	-
As	1.09 ± 0.221[a]	1.09 ± 0.175[a]	1.61 ± 0.198[ab]	2.24 ± 0.193[b]	8.40 ***
Cr	1.31 ± 0.254[a]	1.48 ± 0.202[a]	1.97 ± 0.228[ab]	2.65 ± 0.222[b]	8.17 ***
Cu	2.72 ± 0.274[ab]	2.17 ± 0.218[a]	3.54 ± 0.246[b]	3.56 ± 0.240[b]	8.85 ***
Mn	1.23 ± 0.266[a]	1.58 ± 0.212[ab]	2.29 ± 0.239[b]	3.25 ± 0.233[c]	17.0 ***
Ni	1.17 ± 0.180[ab]	0.99 ±0.143[a]	1.55 ± 0.161[bc]	1.96 ± 0.151[c]	8.15 ***
Pb	2.79 ± 0.353[a]	2.82 ± 0.280[a]	3.17 ±0.316[ab]	4.13 ± 0.308[b]	4.97 **
Zn	17.6 ± 1.59[a]	25.7 ± 1.75[b]	28.9 ± 1.79[b]	30.3 ± 2.00[b]	10.7***

[#] Means for Al is not provided, as the interaction effect was significant (making any interpretation on individual fish species irrelevant)

[∂] Means within a row denoted by different letter are significantly different from each other (ANOVA; Tukey's test, at *$p < 0.001$ '***', $p < 0.01$ '**', $p < 0.05$ '*')* are indicated.

Due to insignificant effect of sampling location on metal bioaccumulation in the different fish species, location was dropped from ANOVA analysis, and one-way ANOVA test performed with species as the only factor variable in the model. The results of fish species effect on As, Cr, Cu Mn, Ni, Pb, and Zn levels given in Table 14, showed that the average metal concentration in fish was biased towards certain fish species. Overall, all metal concentrations were significantly higher in slinger than other fish species. However, subtle differences in variability was observed in other fish species. For example, in copper bream As levels (1.61 ± 0.198 mg/kg dw) was significantly higher ($F_{3,24}$ =8.40, $p < 0.001$) than those reported in catface rockcod (1.09 ± 0.221 mg/kg dw) and soldier (1.09 ± 0.175 mg/kg dw); these values, however, were comparable to those reported in slinger. With respect to Mn, Cr, Ni and Pb, the fleshy tissues of slinger, catface rockcod, soldier and copper bream had comparable levels with no significant differences at $p < 0.05$. In contrast, significant higher values ($F_{3,24}$ = 10.7, $p < 0.001$) of Zn was reported in soldier (25.7 ± 1.75 mg/kg dw), copper bream (28.9 ± 1.79 mg/kg dw) and slinger (30.3 ± 2.00

mg/kg dw) than in catface rockcod (17.6 ± 1.59 mg/kg dw). For Cu, lower mean values were only reported in soldier compared to other fish species.

Table 15. Kendall's tau correlation coefficients (τ) for heavy metals in four common edible fish species.

	Copper bream	Rockcod	Slinger	Soldier
Al vs				
As	0.127*	NS	0.147**	NS
Cr	0.276***	0.120*	0.125*	0.374***
Cu	0.395***	NS	0.228***	0.430***
Mn	NS	0.193**	0.134**	0.128*
Ni	0.405***	0.322***	0.103*	0.461***
Pb	0.453***	NS	0.232***	0.412***
Zn	0.423***	NS	0.289***	0.376***
As vs				
Cr	0.282***	NS	0.245***	0.276***
Cu	NS	-0.237***	NS	NS
Mn	0.146*	-0.213***	0.243***	0.208***
Ni	NS	NS	0.316***	0.119*
Pb	NS	NS	0.100*	0.137*
Zn	NS	-0.151*	0.213***	0.105*
Cr vs				
Cu	0.268***	NS	NS	0.331***
Mn	0.249***	0.234**	0.234***	0.370***
Ni	0.297***	0.281***	0.409***	0.547***
Pb	0.276***	0.232**	0.181**	0.325***
Zn	0.300***	NS	0.218***	0.478***
Cu with				
Mn	NS	NS	NS	0.112*
Ni	0.466***	NS	NS	0.453***
Pb	0.461***	0.407***	0.220***	0.482***
Zn	0.510***	0.372***	0.181**	0.463***
Mn vs				
Ni	-0.174*	-0.295***	0.174***	0.125*
Pb	NS	NS	NS	NS
Zn	0.204**	0.200**	0.162*	0.431***
Ni vs				
Pb	0.522***	0.281***	0.130*	0.385***
Zn	0.322***	NS	0.250***	0.366***
Pb vs				
Zn	0.333***	0.144*	0.237***	0.275***

**$p \leq 0.05$ (correlation is significant); ***$p \leq 0.01$ (correlation is highly significant)

Correlation analysis of heavy metals in common edible fish species

Nonparametric Kendall tau test correlation was used to examine the relationships among the different metals in each fish species (Table 15). In general, the pair wise correlation showed varied correlations between metal concentrations. No strong correlations were observed between the studied heavy metals. The concentrations of Al, Cr, and Pb were positively correlated; exceptions were with Cu, Mn and Zn with As, and Ni with Zn in catface rockcod and Mn with Ni in Copper bream. Strong, significant ($p < 0.01$) and moderate correlations were observed in two common edible fishes as follows: Al-Ni (τ = 0.405), Al-Pb (τ = 0.453), Al-Zn (τ = 0.421), Cu-Ni (τ = 0.466), Cu-Pb (τ = 0.461) and Ni-Pb (τ = 0.522) in copper bream; Al-Cu (τ = 0.430), Al-Ni (τ = 0.461), Al-Pb (τ = 0.412), Cr-Ni (τ = 0.547), Cu-Ni (τ = 0.453), Cu-Pb (τ = 0.482), Cu-Zn (τ = 0.463) and Mn-Zn (τ = 0.431) in soldier. Similarly, strong, significant ($p < 0.01$) and moderate correlations was observed only with Cr-Ni (τ = 0.409) in slinger. On the other hand, the remaining relations were ranged from weak to very weak positive correlations ($\tau < 0.40$) between the different metals in the different fish species and with low levels of confidence ($p>0.05$). Despite the negative correlations that were found between As-Cu, As-Mn, As-Zn, Mn-Ni (catface rockcod) and Mn-Ni (copper bream), significance confidence was detected between them ($p \leq 0.05$).

4.3 Comparison of fishes from Cape Vidal (pristine habitat) and Durban basin (polluted ecosystem)

In an effort to test fish as bioindicators of heavy metal pollution from the two contrasting marine environments, the study pursued the comparison of trace element levels in two fish species - Massbanker **(***T. trachurus*)*,* a common baitfish in the two habitats, and slinger (*C. puniceus*), a popular edible fish species with a greater ability to bioaccumulate trace metals (see subsection 4.2.2). Element concentrations in fleshy tissues, gut and liver are presented in Table 16, and the comparison of the trace elements in fleshy tissues illustrated in Figure 8. The mean concentrations of heavy metals per kg fleshy tissue (muscles) and other parts of maasbanker and slinger indicated Al and Zn concentrations were the highest among the seven heavy metals. Generally, the metal concentrations were higher in the gills and liver of soldier, whereas the gut and the frame had higher trace metal contents in maasbanker, in the two habitats. With exception of Zn, slinger samples had higher levels of trace metals accumulation in their tissue. To compare the total metals accumulation level in various tissues of the two fish species under study as affected by location, metal pollution index (MPI) was also calculated. As shown in Table 4.9, the sequence of MPI in different organs was as follows: gut>frame> fleshy tissue in maasbanker, and gills>liver>fleshy tissue in slinger. In the different locations, Durban basin>Cape Vidal for both fish species, with flesh tissue of slinger reporting higher values compared with maasbanker samples.

In terms of individual metal and metalloid species, accumulation pattern of trace metals (mg/kg dw) in the fleshy tissue of maasbanker caught in Durban basin followed the rank order Zn (52.5) >> Al (24.7) >> Cu (5.60) > Pb (4.72) > Cr (1.80 > Ni (1.64) > Mn (1.23) > As (1.04) (Table 16). Similar pattern was observed for maasbanker caught in Cape Vidal; however, metal concentration values were lower than those reported in Durban basin. Statistically, two tailed two sample Student's t-test showed that the concentrations of Al (t=-4.823, $p < 0.001$), Cu (t=-3.016, $p < 0.01$), Ni (t=-2.581, $p < 0.001$), Pb (t=-3.748, $p < 0.001$), and Zn (t=4.189, $p<0.001$) were significantly higher in maasbanker samples caught in Durban basin than in Cape Vidal. Consistent with MPI results, the Durban basin maasbanker samples had comparable Al, Cu, Ni, Pb and Zn levels that were 4.6-, 1.8-, 2.2-, 2.2-, and 1.6-fold higher, respectively, than Cape Vidal samples. With respect to slinger, metal concentrations (mg/kg dw) occurred in the rank order Al (34.2) > Zn (25.7) > Pb (4.25) > Cu (3.57) > Mn (3.41 > Cr > (2.75) >As (2.25 >Ni (1.96). Except for Cu, Ni and Zn concentrations that were statistically similar, the concentration of the remaining metals in slinger fleshy tissue samples from Durban basin and Cape Vidal were significantly different at $p < 0.05$ (Table 16). Detailed comparison of the heavy metal concentrations in the fleshy tissue of slinger samples caught in Durban basin and Cape Vidal is illustrated in Figure 8.

Table 16. Mean (± SE) comparison of heavy metal concentration (mg/kg dw) and metal pollution index (MPI) value of the total metal accumulation level in different body parts of maasbanker and slinger in Cape Vidal and Durban basin.

Species/parts	Location	Al	As	Cr	Cu	Mn	Ni	Pb	Zn	MPI
Maasbanker										
Gut	Durban	50.7 ± 6.37	1.82 ± 0.21	2.69 ± 0.33	4.56 ± 0.74	2.84 ± 0.34	1.43 ± 0.11	4.96 ± 0.70	65.3 ± 6.04	7.62
	Cape Vidal	10.4 ± 0.91	1.44 ± 0.07	1.74 ± 0.07	4.38 ± 0.73	3.08 ± 0.18	1.17 ± 0.06	4.18 ± 0.78	43.0 ± 4.57	4.96
	t-value	-6.27***	-1.73	-2.85 *	-0.18	0.622	-2.022	-0.750	-2.938**	
Frame	Durban	13.7 ± 2.08	2.12 ± 0.31	2.02 ± 0.15	4.38 ± 0.73	2.37 ± 0.23	1.89 ± 0.16	2.51 ± 0.30	57.2 ± 4.28	5.57
	Cape Vidal	2.97 ± 0.52	1.64 ± 0.06	2.37 ± 0.07	3.96 ± 0.60	2.64 ± 0.14	1.64 ± 0.10	2.22 ± 0.29	44.9 ± 2.56	4.11
	t-value	-5.014***	-1.535	2.087*	-3.016**	1.013	-1.499	-0.693	-2.456*	
Fleshy tissue	Durban	24.7 ± 3.91	1.04 ± 0.03	1.80 ± 0.30	5.60 ± 0.64	1.23 ± 0.10	1.64 ± 0.22	4.72 ± 0.61	52.4 ± 3.05	5.37
	Cape Vidal	5.31 ± 0.88	0.82 ± 0.25	1.25 ± 0.45	3.19 ± 0.44	1.00 ± 0.34	0.74 ± 0.27	2.15 ± 0.32	32.4 ± 3.68	2.64
	t-value	-4.823***	-0.861	-1.028	-3.106**	-0.648	-2.581*	-3.748***	-4.189***	
Slinger										
Fleshy tissue	Durban	34.2 ± 2.85	2.25 ± 0.28	2.75 ± 0.27	3.57 ± 0.28	3.41 ± 0.31	1.96 ± 0.18	4.25 ± 0.38	25.7 ± 1.79	6.62
	Cape Vidal	12.7 ± 3.26	0.88 ± 0.11	1.78 ± 0.30	3.40 ± 0.74	1.29 ± 0.35	1.45 ± 0.29	1.81 ± 0.34	22.6 ± 4.25	3.40
	t-value	-4.975***	-4.536***	-2.414*	-0.221	-4.540***	-1.494	-4.765***	-0.687	
Gills	Durban	60.4 ± 5.18	3.64 ± 0.31	3.60 ± 0.32	3.82 ± 0.27	11.3 ± 1.15	3.12 ± 0.19	4.59 ± 0.48	56.1 ± 3.70	11.6
	Cape Vidal	31.8 ± 7.41	2.80 ± 0.28	4.51 ± 0.36	3.03 ± 0.26	2.47 ± 0.21	2.87 ± 0.21	2.79 ± 1.06	44.3 ± 4.20	7.27
	t-value	-3.163*	-2.008	1.886	-2.117*	-7.569***	-0.881	-1.548	-2.094	
Liver	Durban	66.2 ± 6.35	1.86 ± 0.31	3.56 ± 0.34	4.80 ± 0.38	3.24 ± 0.29	3.56 ± 0.35	5.12 ± 0.41	56.7 ± 4.31	9.52
	Cape Vidal	45.4 ± 6.49	0.59 ± 0.12	3.70 ± 0.89	5.38 ± 1.21	1.97 ± 0.42	2.09 ± 0.53	4.86 ± 1.29	66.9 ± 10.8	6.86
	t-value	-2.284*	-3.851***	0.149	0.456	-2.498*	-2.323*	-0.192	0.879	

[#] Two tailed two sample Student's t-test *($p < 0.001$ '***', $p < 0.01$ '**', $p < 0.05$ '*')*

[∂] MPI values were calculated using the equation by Usero et al., (1997): $MPI=(Cf_1 \times Cf_2 \times \cdots \times Cf_n)^{1/n}$, where Cf_n is the contents for the metal *n* in the sample.

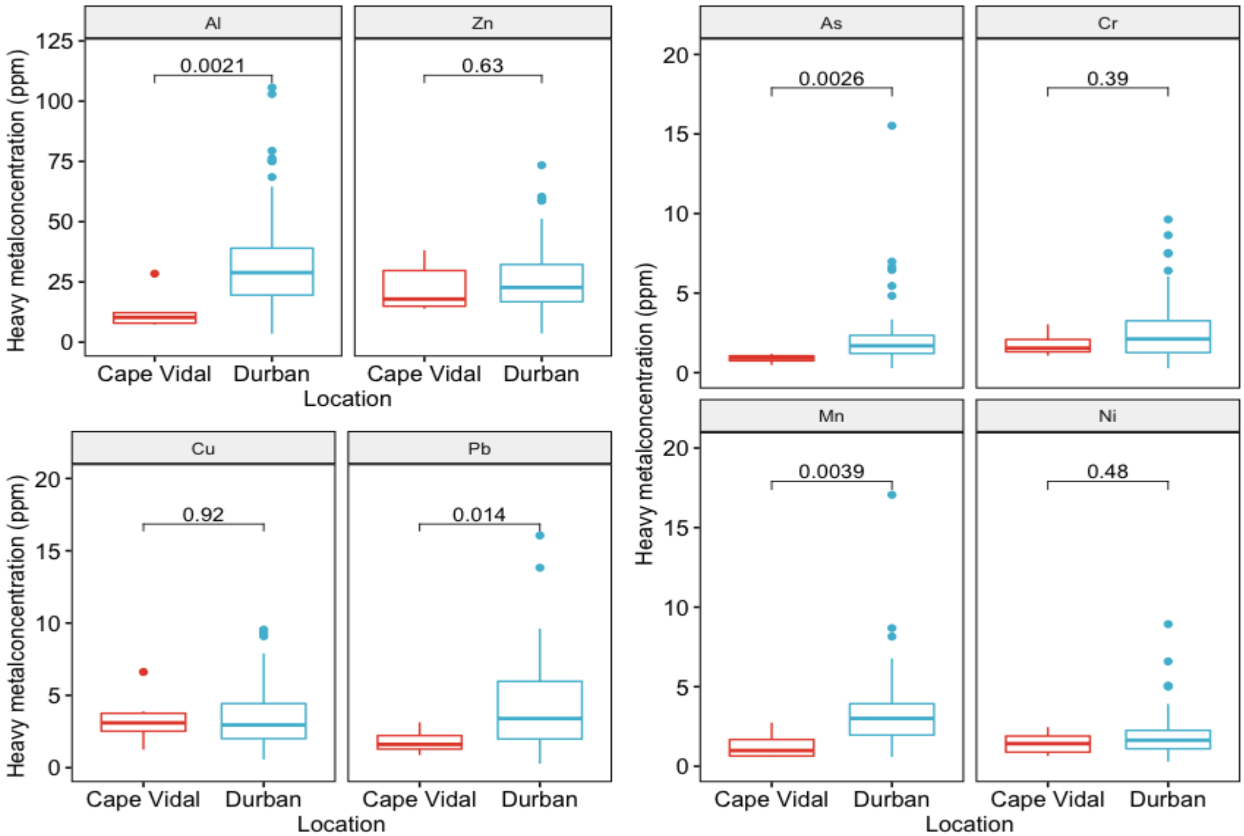

Figure 8. Comparison of the heavy metal accumulation pattern in slinger (*C. puniceus*) between Pristine (Cape Vidal) and Polluted (Durban basin) environment. Statistical differences at different p - values are indicated (two-tailed two sample Student's t-test).

4.4 Potential health risk assessment of consumption of marine fish species contaminated with heavy metal contamination in the Durban basin

4.4.1 Metal concentrations in relation to permissible limits

The metal concentrations obtained for fish muscle samples from four common edible fish and two baitfish species caught within Durban basin and grunter samples from Durban harbor in relation to maximum allowable limit (MAL) values and guidelines in South Africa and around the world are presented in Table 17. The levels of Cu and Mn in the muscles of the six studied fish species were lower than the maximum levels and guidelines values described in the literature. However, all fish species caught in the study site had higher

Table 17. The mean concentrations of heavy metals measured in different edible and bait species in different studies and maximum permissible limits for fish (mg/kg ww).

	Al	As	Cr	Cu	Mn	Ni	Pb	Zn
Fish species								
Rock cod	18.3±1.98	1.09±0.22	1.31±0.25	2.72±0.27	1.23±0.27	1.17±0.18	**2.79±0.35**	17.6±1.59
Soldier	21.0±1.92	1.09±0.18	1.48±0.20	2.17±0.22	1.58±0.21	0.99±0.14	2.82±0.28	25.7±1.75
Copper bream	27.6±2.51	1.61±0.20	1.97±0.23	3.54±0.25	2.29±0.24	1.55±0.16	3.17±0.32	28.9±1.79
Slinger	34.8±2.92	2.24± 0.19	2.65±0.22	3.56±0.24	3.25±0.23	1.96±0.15	4.13±0.31	30.3±2.00
Grunter	23.8±19.1	1.50±1.47	1.65±1.42	3.86±2.46	1.92±1.97	1.40±0.97	2.41±0.90	23.8±9.86
Maasbanker	24.5±3.91	1.04±0.03	1.76±0.30	5.60±0.64	1.23±0.10	1.64±0.22	4.72±0.61	52.4±3.05
Atlantic chub mackerel	7.73±0.90	1.41±0.19	1.76±0.22	5.49±0.43	0.95±0.07	1.01±0.11	3.12±0.37	34.0±2.36
Maximum permissible limits (MAL)								
FAO (FAO, 1983)	-	-	-	30	-	-	-	30
EC (EC, 2006)	-	-	-	-	-	-	0.3	-
Codex Alimentarius (WHO/FAO, 2015)	-	-	-	-	-	-	0.3	-
China (MHPRC, 2013)	-	0.1	2	-	-	-	0.5	-
Australia and New Zealand (FSANZ, 2013)	-	2	-	-	-	-	0.5	-
South Africa (DOH, 2004)	-	3	-	-	-	-	0.5	-
US (TRUMBO *et al.*, 2001)	-	-	-	10	11	1	-	40

[#] Values higher than maximum allowable limits (MAL) are shaded maroon, whereas values within the MAL are shaded green levels of Pb than the maximum allowable limits (0.5 mg/kg Pb) in South Africa (DOH, 2004), Australia/New Zealand (FSANZ, 2013) and China(MHPRC, 2013), and 0.5 mg/kg Pb limit set by European Commission (EC, 2006) and Codex Alimentarius Commission (WHO/FAO, 2015).

In terms of interspecific differences, rockcod, copper bream, and grunter had As, Cr, Cu, Mn and Zinc values within the MAL, with exception of Pb and Ni content. In contrast, soldier had mean metal concentration within the MAL, with exception of Pb levels. Overall, slinger had higher accumulation of patterns of the trace element within the muscle tissues, with the mean values for As, Cr, Ni, Pb and Zn being higher than the MAL levels. Both the baitfish species exhibited the mean concentration level of Ni, Pb and Zn higher than MAL; however, other metals content fell within the regulatory limits

4.4.2 Human health risk assessment (estimated daily intake (EDI), targeted hazard quotient (THQ) and cancer risk (CR))

In South Africa, average annual fish consumption per capita per person is estimated at 6-8kg (~21.92 g/day) (Grünberger, 2014). Therefore, daily intake of heavy metals was estimated based on the concentrations measured in fish muscle and daily fish consumption rate (21.92 g), and the metal intakes compared with the respective permissible tolerable daily intake for South African adult average body weight 60.7 kg ($PTDI_{60.7}$) (µg/day). The EDI values and the corresponding permissible tolerable daily intake for 60.7 kg adult person ($PTDI_{60.7}$) values of seven heavy metals through edible fish and baitfish consumption are presented in Table 18.

Results showed that EDI values for the examined fish species were well below the tolerable daily intake (TDI) limits for most metals, the only exception being Cr, indicating that there was no health risk associated with the intake studied heavy metals (Al, As, Cu, Mn, Ni, Pb and Zn) through the consumption of examined fish samples. In contrast, EDI values for Cr (in µg/day/person) in all fish species was higher than the permissible TDI (0.3 µg/day). The ranking order of EDI values for Cr for species studied was slinger (0.99) > copper bream > (0.70) > maasbanker (0.65) > Atlantic chub mackerel (0.63) > soldier

(0.54) > rockcod (0.49). Further, the corresponding maximum daily intake of Cr (in grams) for each fish species were lower (9.4-13.4 g/day) than the average daily fish intake, implying potential health risk associated with the Cr intake through the consumption of examined fish samples from Durban Basin.

Table 18. The estimated daily intake (EDI) of toxic metals (µg/day/person) through consumption of popular fish species by adult person (weighing 60.7 kg and having an average fish intake of 21.92 g/day) in the Durban Basin.

Metals	Estimated daily intake (EDI) (µg/day/person)						TDI[a]	$PTDI_{60.7}$[b]
	Copper bream	**Rockcod**	**Slinger**	**Soldier**	**Maasbanker**	**Mackerel**		
Al	9.97 (315)[c]	6.61 (474)	12.6 (249)	7.58 (413)	8.90 (352)	2.79 (1123)	143	8680.1
As	0.55 (85)	0.39 (120)	0.81 (58)	0.39 (119)	0.38 (125)	0.51 (93)	2.14	129.9
Cr	**0.70 (9.4)**	**0.49 (13.4)**	**0.99 (6.6)**	**0.54 (12.3)**	**0.65 (10)**	**0.63 (10)**	0.3	18.21
Cu	1.28 (8573)	0.98 (11158)	1.29 (8501)	0.78 (13986)	2.02 (5419)	1.98 (5526)	500	30350
Mn	0.83 (3711)	0.46 (6744)	1.23 (2492)	0.57 (5379)	0.44 (6906)	0.34 (8956)	140	8498
Ni	0.57 (191)	0.43 (253)	0.71 (155)	0.36 (307)	0.59 (185)	0.36 (301)	5	303.5
Pb	1.16 (68)	1.02 (77)	1.53 (51)	1.01 (77)	1.71 (46)	1.12 (70)	3.57	216.7
Zn	10.4 (2115)	10.8 (2037)	9.28 (2362)	6.36 (3449)	18.9 (1158)	12.3 (1788)	1000	60700

[a] TDI: tolerable daily intake (µg/kg body weight/day), calculated from tolerable weekly intake (TWI) cited in Türkmen et al. (2009) after FAO/WHO (2004); TWI for Cr (EFSA, 2014).
[b] $PTDI_{60.7}$: permissible tolerable daily intake for a 60.7 kg person (µg/day) = TDI x 60.7 kg.
[c] Values between brackets are the maximum daily intake (in g) of each fish species that should be consumed in order to attain the permissible tolerable daily intake of metal for 60.7 kg person (=$PTDI_{60.7}$ (µg/day)/metal concentration (µg/g) according to FAO/WHO (2004).

Table 19. Target hazard quotient (THQ), lifetime target cancer risk (TR) and hazard index (HI) values of toxic metals via consumption of popular fish species.

Parameter	Copper bream	Rockcod	Slinger	Soldier	Maasbanker	Chub mackerel
THQ[#]						
Al	0.070	0.046	0.089	0.053	0.062	0.020
As	0.258	0.182	0.378	0.184	0.177	0.237
Cr	**2.335**	**1.637**	**3.310**	**1.782**	**2.169**	**2.117**
Cu	0.003	0.002	0.003	0.002	0.004	0.004
Mn	0.006	0.003	0.009	0.004	0.003	0.003
Ni	0.115	0.087	0.142	0.072	0.118	0.073
Pb	0.324	0.286	0.430	0.284	0.478	0.315
Zn	0.010	0.012	0.009	0.006	0.019	0.012
HI[∂]	**3.121**	**2.255**	**4.370**	**2.386**	**3.029**	**2.781**
Carcinogenic health effects						
Target cancer risk (TR) [†]						
As	2.1×10^{-4}	1.5×10^{-4}	3.0×10^{-4}	1.5×10^{-4}	2.6×10^{-4}	3.6×10^{-4}
Ni	1.0×10^{-4}	7.8×10^{-5}	1.3×10^{-4}	6.5×10^{-4}	2.0×10^{-4}	1.2×10^{-4}
Pb	1.6×10^{-3}	1.2×10^{-4}	2.1×10^{-3}	1.4×10^{-4}	4.3×10^{-3}	2.8×10^{-3}
Daily and monthly consumption limits						
TR_{lim} **(kg/day)**						
As	0.251	0.371	0.181	0.371	0.389	0.287
Ni	0.230	0.305	0.182	0.361	0.218	0.354
Pb	0.021	0.024	0.016	0.024	0.014	0.022
TR_{mm} **(meals/month)**						
As	34	50	24	50	52	39
Ni	31	42	25	50	30	49
Pb	2.9	3.2	2.2	3.2	1.9	3.0

[#] THQ – is the non-carcinogenic risk and is dimensionless; (THQ > HI =1, indicate potential health risk of consuming the specific metal through fish (Varol and Sünbül, 2017).

[∂] HI (or TTHQ) – is the sum of the target hazard quotient; (HI >1 indicates potential health risk all the metal species through the fish consumption (Varol and Sünbül, 2017)).

[†] TR – is used to indicate the carcinogenic risk (lifetime TR > 10^{-4}, unacceptable; TR = 10^{-6} ~ 10^{-4} , an acceptable range; and TR < 10^{-6}, negligible (Ahmed *et al.*, 2016)).

Target hazard quotients (THQs) of the studied metals from consuming different fish species sampled from Durban basin is given in Table 19. Generally, a low THQ of below 1, indicates that the exposed population is unlikely to experience obvious adverse effects (Wang *et al.*, 2005). In this study, only Cr had THQ>1 in all the fish species, ranking in the order of: slinger (3.31) > copper bream (2.34) > maasbanker (2.17) > Atlantic chub mackerel (2.12) > soldier (1.78) > rockcod (1.64), indicating that Cr might pose a significant non-carcinogenic health hazard to human beings consuming these fish species in the Durban basin. Furthermore, all the fish species had HI > 1, implying that there is significant non-carcinogenic health risk for the adults in Durban basin due to the intake of either Cr or the seven metals contained in the different commonly consumed edible and baitfish species under study. Consistent with THQ results, slinger had comparatively higher HI value, whereas rockcod had the lowest HI recorded for the seven metals. To establish the potential carcinogenic risk of heavy metals due to fish intake, the target carcinogenic risks (TR) for the intake of As, Ni and Pb, three metals known to promote both non-carcinogenic and carcinogenic effects depending on the exposure level, was calculated. Lifetime cancer risk (TR) for As, Ni and Pb was estimated by using the cancer slope factor (CSF) of 1.5, 1.7 and 0.009 mg/kg/day, respectively (USEPA, 2016). As shown in Table 19, the TR values of As ranged from 1.5×10^{-4} in rockcod to 3.6×10^{-4} in Atlantic chub mackerel, whereas 1.0×10^{-4} in copper bream to 7.8×10^{-5} in rockcod for Ni. In contrast, TR values for Pb in copper bream, slinger, maasbanker and Atlantic chub mackerel were $>10^{-4}$, indicating potential cancer risk exposure due to Pb when consuming these fish species from Durban basin.

The results of the daily consumption limits (TR_{lim}) and the maximum allowable monthly consumption limit (TR_{mm}) for As, Ni and Pb relating to the number meals of fish that can safely be eaten per month with no adverse carcinogenic health effects are presented in Table 19. As and Ni had TR_{lim} ranging between 181-389 and 182-361 g/day, respectively, which are higher than average per adult consumption of fish in South Africa. Results also showed that an adult can safely consume 34, 50, 24, 50, 52 and 39 meals/month of copper bream, rockcod, slinger, soldier, maasbanker and Atlantic chub mackerel, respectively, for As. Similar to As results, between 25-50 meals/month of the fish species can safely be eaten without cancer health effects endpoints due to Ni exposure. In contrast, maximum allowable daily consumption limits (TR_{lim}) for the fish species for Pb were between 14-24 g/day, values that are within or lower than the daily consumption rate of fish by adult South African (21.9 g/day). Consistent with these results, the calculated TR_{mm} values were lower than the prescribed safe fish consumption rate of >16 meals/month by USEPA (2000). These results indicate health safety concerns of potential exposure to Pb for consumers of these fish species caught in the Durban basin.

CHAPTER 5:
DISCUSSION

The main objective of this study was to provide baseline levels of heavy metal content in marine fish species, representing a wide range of ecological groups and lifestyle within the Durban basin waters, and the potential public health risk that may be associated with their consumption. The fish species represent both the common pelagic/benthic and demersal communities consumed in large quantities in the area. In this section, interspecific and spatial variability on the presence/absence and the concentration of the 7 heavy metals (Al, As, Cr, Cu, Mn, Ni, Pb and Zn) in two baitfish and four common edible fish species, taking into account the observed heavy metal concentration values with current legal maximum limits is discussed. The potential public health implications on the consumption of fish contaminated with metal concentrations is also reported.

5.1 Heavy metal (HM) levels in the Durban basin

Globally, there is a direct link between human activities and surface water quality in different ecosystems, including marine environments. Specifically, factors such as economic development, industrial development and urbanization have led to significant anthropogenic pollutants input into the coastal areas (Muir *et al.*, 1999; Liu *et al.*, 2007; Stark, Kim & Oliver, 2014; Vetrimurugan *et al.*, 2019). The Durban basin is home to South Africa's largest and busiest port in terms of cargo values, in addition to being an economic hub that supports numerous manufacturing, petrochemical, sea trade and transport industries (Goble, van der Elst and Oellermann, 2014). The contribution of the rapid industrial economy coupled with urban and peri-urban development with its associated ancillary activities impacts on heavy metal (HM) pollution of the KZN coastal environment, this has been an area of increased research interest in the last decade (Moloney *et al.*, 2013; Mzimela, Wepener & Cyrus, 2014; Okoro *et al.*, 2016; Vetrimurugan *et al.*, 2016, 2017, 2018, 2019).

In estuarine and coastal environments, HM can partition into dissolved, particulate and sedimentary phases, through adsorption, flocculation, desorption and resuspension processes, leading to different biogeochemical behaviors and responses to environmental changes (Dekov *et al.*, 1998). For example, HM in aqueous and particulate phase can be desorbed from particulate matter into the seawater or deposited into the sediment (Yang *et al.*, 2012). Conversely, HM can redissolve back into the water column from the sediments by resuspension. Comparatively, marine sediments act as important repository of HM, specifically those in particulate phase, which may play a significant role in their transport and possible release in the aqueous phase. In this study, the HM concentrations were in elevated orders of magnitude above the concentration of quality guidelines given by Interim Sediment Quality Guidelines (ISQGs) in water, and we observed the differences showing spatial variability (Table 6). Globally, sediment samples showed accumulation patterns of HM above the background upper continental crust values; these values generally exhibiting spatial variability with samples from Durban South and harbor reporting higher values of Al, As, Mn, Cr, Cu and Ni than other sites. In contrast, Durban harbor had significantly higher average values for Cu, Pb and Zinc in the sediment samples compared with all other sites (Table 6). Consistent with current sediment analysis results, Vetrimurugan *et al*., (2019) also reported the enrichment of HM concentration levels in five different sites of Durban south coastline higher than the background reference values (avg. in $\mu g\ g^{-1}$) for Cr (223–352), Cu (27.67–42.10), Mo (3.11–4.70), Ni (93–118), Co (45.52–52.44), Zn (31.26–57.01) and Hg (1.13–2.36).

The presence of a strong spatial separation of HM levels indicates that there may be multiple metal sources or parameters influencing metal concentrations in this region. In contrast to other regions within the Durban basin, South Durban is densely populated and an economic center hosting a major port and have multifarious industries ranging from petroleum, chemical, paper, textile and automotive industries and may constitute the point sources of HM recorded in this study. Generally, highest HM levels in sea environments bordering industrialized regions (Yücel & Çam, 2019), where the contribution of HM pollution from storm water drains and streams which carry runoff from industrial, urban and residential sources are common. Similar trends have also been reported in East

London and Port Elizabeth harbor in Eastern Cape Province (Fatoki and Mathabatha, 2001) and Cape Town harbor (Okoro *et al.*, 2014, 2016) in South Africa, and elsewhere around the world (Dekov *et al.*, 1998; Angel *et al.*, 2010; Yang *et al.*, 2012; Guo *et al.*, 2017; Jupp *et al.*, 2017; Lao *et al.*, 2019; Yücel & Çam, 2019), having common economic activities such as shipping, petrochemical and automotive industries as located at Durban South. In the Durban harbour, ship repair activities, recurrent usage of antifouling paint rich in copper, oil dropping from boats coupled with coal handling activities in the docks, may also play a big role in the observed higher levels of HM such as Cu, Pb and Zn in the area. Furthermore, review of studies on As in African waters provides evidence of high concentrations in both surface water and groundwater mainly linked to mining operations, agricultural drains, local sediments, disposal, and municipal and industrial wastes (Ahoulé *et al.*, 2015). Collectively, these finding illustrate the urgent need to continuously monitor the levels of pollutants in various components of the marine environment.

5.2 Biomagnification of toxic HM in the Durban harbour

HM are generally known for their toxicity, intrinsic persistence, non-biodegradable nature, and accumulative behavior (Mann, Vijver & Peijnenburg, 2011; Gall, Boyd & Rajakaruna, 2015; Dar, Green & Khan, 2019). While chemical analyses on water and sediments samples may give a snapshot of the occurrence of pollutants in the environment, evaluation of the pollutant's bioaccumulation patterns, magnification along food chains and the associated biological responses in organisms is a good measure of the pollutant exposure over a period. The high HM levels (in both seawater and sediments) recorded in the Durban basin have a potential to strongly accumulate and biomagnify along water, sediment, and aquatic food chain. On entering the food chain, toxic HM may cause public health hazards related to consumption of HM enriched seafood's, e.g. fish (discussed in the later subsections). To test the potential bioaccumulation and trophic transfer of HM in a simple food chain, the metal concentrations were analysed in the seawater, sediments, cracker shrimp (*C. kraussi*) and grunter (*P. commersonni),* and their enrichment values in the trophic levels in the highly polluted Durban harbour were calculated (Table 8). Sand prawn or cracker shrimp (*C. kraussi*) is a prolific endobenthic crustaceans inhabiting the sediment layer of most estuarine habitats in South Africa, including Durban harbour (SAIAB, 2004; Maree *et al.*, 2016; Venter, 2019). They are generally detritivores, filtering silts and consuming bits of decaying biota in the sediments on the shallow sandbanks (SAIAB, 2004; Maree *et al.*, 2016). In contrast, spotted grunter (*P. commersonni)* is a benthic carnivore, which can feed on crustaceans, mollusks, shrimps or sand prawns. This fish species commonly found in the estuarine environments of Western and Eastern Cape seaboard of South Africa. However, it has been reported that the spatial distribution of macrobenthic prey is a dominant factor influencing this fish species diet and home-range parameters within an open estuary (Maree *et al.*, 2016). Due to higher relative abundance of both cracker shrimp and spotted grunter in the Durban Harbour, it was hypothesized that continuous exposure to the high HM-ladened sediments may lead to enrichment of toxic metals in cracker shrimp, that can potentially lead to their biomagnification along the trophic level involving spotted grunter.

Comparatively, there was overall significant (2-50-fold) enrichment of the heavy metals in the sediments from water, with exception of As that had lower concentration level in the sediment than seawater (Table 8). Interestingly, significant biomagnification of four metallic elements was evidenced at the sediment-cracker shrimp trophic level (average mg/kg dw): Cu (41.5±19.1), Mn (5.1±1.40), Pb (4.3±6.51) and Zn (2.35±0.73). In contrast, no enrichment values higher than 1.0 were found in the cracker shrimp-grunter trophic level relationship (Table 8). Congruent with findings of this study, numerous studies have reported high accumulation of heavy metals As, Cu, Fe, Zn and Pb dependent on the origin and sub-groups of shrimp species (Giri & Singh, 2013; Nascimento *et al.*, 2017; Bertrand *et al.*, 2018; Fakhri *et al.*, 2018; Griboff *et al.*, 2018; Suami *et al.*, 2019). Furthermore, dose–response relationships for bioaccumulation of Zn, Cu and Cr, related to total length and age (duration of exposure), in shrimp *Litopenaeus schmitti* from Sepetiba Bay, Rio de Janeiro, Brazil have also been previously reported (Nascimento *et al.*, 2017). Whereas Cu, Fe and Zn may have a major role in the respiratory and enzyme processes of shrimps, accumulation to toxic levels of As and Pb can lead to adverse effects on the organisms. HM accumulation patterns, however, have been reported to be more pronounced in juveniles compared with adult shrimps with a slow-down in metal absorption with age, a pattern proposed to mitigate the high initial concentrations typically observed for juveniles (Nascimento *et al.*, 2017). Due to their sensitivity and ability to accumulate HM, several biomonitoring programs have proposed the use of sentinel and native shrimp species, especially their juveniles, as suitable bioindicators of aquatic ecosystem pollution (Lebrun *et al.*, 2015; Ronci *et al.*, 2016; Bertrand *et al.*, 2018).

The observation that no significant biomagnification of HM was observed in spotted grunter could partly be attributed to inter-species differences in terms of metabolic rate, exposure route, metal mobility, bioavailability and species of the chelator present in water and sediment partitions of the coastal areas, including the time spent in the contaminated water (Maree *et al.*, 2016; Suami *et al.*, 2019). There are reports that spotted grunter mainly inhabits the estuarine environments along the Eastern and Western Cape of South Africa, and only undertake the spring/summer, northward spawning migration to KwaZulu Natal (Webb, 2002). Hence, compared with cracker shrimp that lives exclusively in the polluted harbour environments, the migratory nature of the spotted grunter may imply less exposure to HM. Furthermore, spotted grunter have also been reported to exhibit flexibility in diet, generally feeding on a wide range of macrobenthos present in a particular environment, even though crustaceans such cracker shrimp form the bulk of its prey (Pradervand *et al.*, 2003; Maree *et al.*, 2016). In cracker shrimps, HM tend to accumulate less in the muscles compared to other tissues such as hepatopancreas and exoskeleton (Shahsavani *et al.*, 2017). Furthermore, exposure and accumulation patterns of HM has been reported to be higher in juvenile crustaceans that lives exclusively deeply burrowed in sandbank sediments compared to adults that live closer to the seawater column (El-Moselhy *et al.*, 2014; Venter, 2019). It is plausible that the spotted grunter's habits of mainly feeding on the adult cracker shrimp's muscles which are generally low in HM content, while discarding high HM-laden tissues such as exoskeleton, coupled with an efficient metabolism, are contributing factors to low accumulation of HM within its tissues.

In the present study, the trophic groups inferred for their feeding habits within the Durban harbour poorly explained the HM variability in terms of bioaccumulation. It should be noted that only specific metals, especially the lipophilic organic form methyl mercury

(MeHg), cadmium (Cd) and selenium (Se), are known to persist and biomagnify in the environment (Gray, 2002; Mann, Vijver & Peijnenburg, 2011), with biomagnification of other metals being more difficult to demonstrate. However, several studies have recorded appreciably higher levels of Hg along the Durban coastline (Vetrimurugan *et al.*, 2017, 2018), a component not analysed in this study due to instrument limitations. Hence, future studies in the same area targeted to elucidate more precise determination of food sources, the progressive enrichment and transfer pathways of HM accumulation along trophic food web/chain, including Hg and MeHg analysis, are necessary.

5.3 HM accumulation in fish species in Durban basin

Marine fishes are one of the main sources of protein for human diet worldwide. However, fish species have been reported as the largest known bioaccumulator of HM, due to their location at the top of the food web/food chain in both freshwater (Thompson, Dunne & Woodward, 2012) and marine ecosystems (DeForest, Brix & Adams, 2007; Hernández-Almaraz *et al.*, 2014; Jitar *et al.*, 2015; Vilches *et al.*, 2019). There are several reports on the correlation between human health hazards and the consumption of contaminated fish and other aquatic foods (Dural, Göksu and Özak, 2007; Elnabris, Muzyed & El-Ashgar, 2013; Gu *et al.*, 2015; A.C. Bosch *et al.*, 2016; Yi *et al.*, 2017), with some studies proposing using fish species as potential pollution indicators and for monitoring toxic HM accumulation in the marine environment (Canli & Atli, 2003; El-Moselhy *et al.*, 2014; Jayaprakash *et al.*, 2015). In general, this study assessed metal levels in six fish species which are very important for two reasons: i) they are very popular fish caught off the Durban Coast for a typical local fish dish; and ii) HM accumulating patterns of these fish species have not been reported in literature before. Results from this study showed a significant difference in HM accumulation patterns largely dependent on fish species, fish organ type and sampling sites (location within the Durban basin), with some species recording levels of As, Cr, Ni, Pb and Zn in their muscles higher than international regulations set for human consumption (Table 17).

The water column metal levels in the Durban basin were relatively low in comparison to sediments (Table 6), and thus, it can be concluded that the contribution of water column uptake to the overall HM content in the fish species maybe minimal. As discussed in previous subsections, different anthropogenic pollution sources are associated with substantial variability in metal loads in the sediments in the different locations within the Durban basin, and thus, the spatial variability would be reflected in the metal levels of fauna that are associated with the specific area. For bait fishes, significant higher ($p<0.001$) levels of Al and Cr were observed in Durban Central, while average accumulation levels of As were higher in Durban South (Table 10). Furthermore, the inter-element relationships of HM in the baitfishes (Table 12) also suggested that they are external as the concentration patterns were higher due to localized anthropogenic activities. For example, Al showed strong positive correlations with Cu (r=0.78,), and Mn (r=0.95) at $p<0.001$, indicating their origin from similar pollution point sources, especially within the Durban Central area. Similar trend was also observed in cracker shrimp and grunter samples caught within Durban harbour. Since Durban harbour drains into Durban Central, the observed higher levels and the associated inter-element relationships in fish is highly dependent on the nature of the ports and human activities in the vicinity of the port area as has been reported in other seaports elsewhere (Verdouw, 2008; Mzimela, Wepener & Cyrus, 2014; Jupp *et al.*, 2017; Jahan & Strezov, 2019).

The Durban Central region is also home to the Central Works Outfall that discharges 135 mega liters per day of sanitary wastewater, coupled with a prominent vessel transportation industry in the region may account for the observed higher HM levels in fish species caught in the area. In this study, the mean metal concentrations in the four edible fish species could be summarized in descending order as follows: liver>gills>muscles, however the subtle differences could be ascribed to specific fish species and specific metals. However, HM accumulation in the gills and liver exhibited a spatial variability that can be attributed to different localized pollution (Figure 4.3). Among the fish organs, gills are the first target of water-borne metals due to their large surface area and direct contact with the aquatic environment. Gill surfaces consists of an epithelial membrane rich in negatively charged phospholipids and a mucous layer, that provides a potential site for gill-metal interaction for positively charged metals (Reid & McDonald, 1991; Crafford & Avenant-Oldewage, 2010). Thus, in heavily contaminated marine aquatic environments, gills will be the main route for the contaminants to enter the fish body (Abdolahpur *et al.*, 2013; Yancheva *et al.*, 2014; Aich *et al.*, 2015). The digestive system is the main route for HM contamination through feeding, where the absorbed metals mainly accumulates and/or are detoxified by the liver before excretion by kidneys (Yancheva *et al.*, 2014). Thus, there is general consensus that liver acts as an environmental indicator of water pollution, due to its ability to accumulate various kinds of pollutants at higher levels than the surrounding environment, and plays an important role in contaminant storage, detoxification, redistribution and transformation while acting as an active pathological site (Crafford & Avenant-Oldewage, 2010; Malik *et al.*, 2010; El-Moselhy *et al.*, 2014; Al-Ghanim *et al.*, 2015; Javed *et al.*, 2016; Vilches *et al.*, 2019). In contrast, muscle tissue does not accumulate metals and seems to have a very fast decontamination rate, and hence have lower HM contamination compared to other fish organs. Nevertheless, interspecific variations in muscle HM concentrations, that were metal-specific, were recorded in both bait and edible fish species caught within the same area, pointing to several factors in play.

Several studies have reported that factors such as diet (carnivores/omnivore, dietary/prey preferences, trophic level), fish size, time of exposure (age), fish physiology (storage or elimination) and fish species lifestyle (whether migratory, demersal, pelagic or benthic) may play an important role in the observed species HM variability, even in those inhabiting similar polluted environment (Canli & Atli, 2003; Mendoza-Carranza *et al.*, 2016; Okoro *et al.*, 2016; Orata & Birgen, 2016; Lozano-Bilbao *et al.*, 2020). In this study, baitfish Atlantic chub mackerel (*S. japonicas*) had significantly ($p<0.01$) higher levels of As (0.2-7.76 mg/kg), Cr (0.3-11.7 mg/kg), and Mn (0.3-9.96 mg/kg), when compared to the maasbanker (*T. trachurus*), who exhibited the higher concentration of Al (29.7 mg/kg) (Table 10). Among all metals, Pb and Ni were higher than maximum permissible limits of 0.3-0.5 and 1 mg/kg dw, respectively (FAO, 1983; DOH, 2004; EC, 2006; MHPRC, 2013; WHO/FAO, 2015). However, these values were comparable to similar fish species caught in coastal water of Turkey (Mutlu *et al.*, 2012), northwestern Africa (Roméo *et al.*, 1999; Lozano-Bilbao *et al.*, 2020), but lower than those caught in polluted coastal estuaries and harbors (Papetti & Rossi, 2009; Bae, Yoon and Lim, 2011; Aktan & Tekin-

Özan, 2012). In terms of lifestyle, maasbanker (*T. trachurus*) are pelagic-benthic species, mainly carnivorous feeding on a mixed diet of zooplankton, benthos (such as polychaeta, crustacea) and small fishes, with krill (Euphausiids) as the dominant prey (Georgieva *et al.*, 2019; Kadila *et al.*, 2020). In contrast, Atlantic chub mackerel (*S. japonicas*) species are exclusively pelagic and planktivorous during the initial stages of development and mainly exhibiting filter- and/or particulate feeding behavior (Cury *et al.*, 2000; Garrido *et al.*, 2015). Although pelagic fish have been reported to accumulate lower HM compared to the benthic fish (Gundogdu *et al.*, 2016), the filter feeding on suspended particulates and organic matter rich in metals such as Al, As Cu and Mn in the seawater column in addition to algae and small zooplanktons that have limited capacity to regulate metal levels (Bryan & Darracott, 1979), implies that Atlantic chub mackerel (*S. japonicas*) may have greater exposure to HM through its diet than maasbanker (*T. trachurus*). Such filter feeding behavior has also been implicated for accumulation of microplastics in the same species (Herrera *et al.*, 2019; Lopes *et al.*, 2020; Maaghloud *et al.*, 2020).

Among the edible fish, species effect on all the HM accumulation patterns was highly significant (p<0.01), irrespective of sampling location (Table 13). In marine environments, organisms may display a wide range of HM accumulation patterns, with trophic inputs depending on the type of prey consumed (Garrido *et al.*, 2015; Vilches *et al.*, 2019). Comparatively, catface rockcod (*E. andersoni*) and soldier (*C. nufar)* belong to a higher trophic level than copper bream (*P. grande*) and slinger (*C. puniceus*), with the species exhibiting different feeding behaviours. Interestingly, the lower trophic groups (slinger and copper bream) mainly feeding on benthos exhibited a higher HM accumulation pattern (Table 16). Specifically, slinger recorded significant ($p < 0.05$) higher accumulation of the As, Cr, Cu, Mn, Ni, Pb and Zn, while copper bream had comparable values for As, Cu and Zn. With exception of Mn, all the metal accumulation was higher in the liver compared to the fish muscles and gills (Figure 7), these results pointing to the importance of feeding habit and digestive route for heavy metal accumulation, which is not common in fish species. However, the status of slinger and copper bream as the lowest trophic level of the four species did not support the general consensus that HM and other pollutant levels increases in higher trophic species (Hernández-Almaraz *et al.*, 2014; Garrido *et al.*, 2015;

Vilches *et al.*, 2019). Catface rock cod and soldier are piscivorous demersal with smaller fish as their main prey. In contrast, the demersal slinger mainly feeds on bivalves, mollusks, crustaceans and small fish species whereas omnivorous and benthic copper bream feeds on algae and small invertebrates. In addition to difference in prey type and feeding it is plausible that the deviation observed in this study could be attributed to fish, physiology (some species may have a more efficient metabolism for storage and decontamination of HMs than others) or difference in exposure levels (that can be linked to fish size and age coupled with fish migration); factor not explored in this study.

Within species differences in fish sharing the same habitat indicates that they do not necessarily share the same levels of metal accumulation. Conversely, differences in location and the environment from which the fish are sampled could also cause variation in metal accumulation within and between fish species. It should be noted that the sampling sites in this study were limited to approximately a 50 km stretch along the Durban coast with no clear boundaries. While adult slinger, copper bream and catface rockcod are fairly residential, soldier are known to undertake extensive migrations with mean distance of over 29 km (Mann, 2013). Given the relatively small sampling area, easy dispersion of heavy metals by concentration gradients, wind/waves, with possible roaming of the fish within the sampling sites cannot be overruled. Overall, diet and lifestyle play an important role in interspecies variability of HM accumulation patterns of fish in the Durban basin.

5.4 Fish as pollution bio-monitor in Durban basin

Cape Vidal and Durban basin are habitats within the eastern seaboard of South Africa that differ significantly in terms of anthropogenic influence. Cape Vidal is a marine protected area believed to be rather pristine and unpolluted, whereas Durban basin on the other hand is heavily influenced by industrial and agricultural activity within its catchment area. It has been reported that certain fish species maybe better bioindicators of specific heavy metal contamination compared to others (Burger and Gochfeld, 2011). However, it should be noted that various intrinsic species factors make it difficult to compare metal concentration results, and thus a bio-indicator species to assess human health effects must: (1) be commonly consumed in the area; (2) be widely distributed geographically; and (3) have the potential to accumulate high metal concentrations, in addition to being large enough to provide adequate tissue mass for residue analysis (Cunningham *et al.*, 2019). In an effort to test fish as bio-indicators of heavy metal pollution from the two contrasting marine environments, this study pursued the comparison of trace element levels in two fish species meeting the above criteria - maasbanker **(***T. trachurus*), a common baitfish in the two habitats, and slinger (*C. puniceus*), a popular edible fish species with greater ability to bioaccumulate trace metals (see subsection 4.2.2).

Overall the metal pollution index (MPI) used to compare the total content of metals in different sampling points (Usero, Morillo & Gracia, 2005), were significantly higher in fish caught in Durban basin compared to Cape Vidal (Table 16), indicating greater cumulative accumulation of metals in the samples dependent on geographical location, with subtle differences observed in the different fish organs analyzed. Results also showed that a striking species-specific HM accumulation patterns differentiation associated with the contrasting environments of the anthropogenically disturbed Durban basin with that of the pristine Cape Vidal region. Calculation of the tissues of slinger from Durban south showed that the sum total of HM was highest in gills (11.6), followed by liver (9.52) and muscles (6.62). In contrast, slinger in Cape Vidal MPI values were 2-fold higher in liver and gill (6.86 vs 7.27) than in the muscles (3.40). Comparatively, MPIs for gut, frame and muscle samples of maasbanker from the Durban basin are also significantly higher, with elevated concentration of Al, Cr and Zn in the gut, Al, Cr, Cu, and Zn in the frame and Al, Cu, Ni, Pb and Zn in muscle tissue, this plays an important role in the difference in accumulation patterns.

The MPI values reported in this study were, however, lower than those reported for fresh water fish species in *Carassius auratus* (0.059), *Pelteobagrus fulvidraco* (0.073) and *Hypophthalmichthys nobilis* (0.046) from Nansi Lake, China (Li *et al.*, 2015). Similarly, Chi et al. (2007) have reported MPI values between 0.2-0.7 for *Cyprinus carpio*, *Carassius auratus*, *Hypophthalmichthys molitrix* and *Aristichthys nobilis* from Taihu Lake, China. However, marine fishes have reported higher MPI values than fresh water ecosystem, with the values being significantly higher in polluted marine and estuarine environments. (Ali & Khan, 2018). Higher MPI values for *C. puntatus* exposed to thermal power plant effluent have been reported for gills (53.6), kidneys (41.2), integument (34.2), liver (31.9) and muscles (13.5) (Javed *et al.*, 2016). These values are higher than those reported in this study, which is partly attributed to the dilution effect of the pollutants by seawater. Consistent with our findings, Rios-Fuster *et al*., (2019) also reported higher HM accumulation in *T.s mediterraneus*, a close relative to the maasbanker (*T. trachurus*), whereas time-dependent accumulation of Zn and Pb in *T. trachurus* in polluted environments have also been reported (Jitar *et al.*, 2013; Lozano-Bilbao *et al.*, 2020); this has potential as biomonitor for metal pollution. To our knowledge and literature surveys, this study is the first baseline report on higher HM accumulation in slinger (*C. puniceus*) compared to other species making it a promising candidate as bioindicator for pollution in the Durban coast. Furthermore, different patterns in both species collectively show that the fish muscle is not an active tissue in accumulating HM, whereas liver and gills are good monitors of water pollution with metals because their concentrations are proportional to those present in the environment.

This study has demonstrated the usefulness of native biota (both **maasbanker (***T. trachurus*) and slinger (*C. puniceus*)) to biomonitor moderate levels of between-location difference in heavy metal pollution in marine ecosystems. In conclusion, it should be noted that species-specific differences in metal levels, as is the case for the geographical differences discussed above, does not indicate an efficient monitor of small differences such as time trends, without a more detailed analysis of the monitoring data. Thus, future studies taking into account the comparisons between time trends in HM accumulation pattern in the water and fish species in the two geographical locations, to fully demonstrate the indicator capabilities of maasbanker (*T. trachurus*) and slinger (*Chrysoblephus puniceus*), are needed. Additionally, future biomonitoring studies evaluating native species responses and their ability to evidence environmental degradation are necessary.

5.5 Potential public health implications of fish consumption

Over the last two decades, there have been increased concerns on the potential adverse effects of pollutants laden with high content of heavy metals (HM), including both transitional metals and metalloids. The transitional metals includes Co, Fe, Cu, Zn, Ni, and Mn, that are generally essential in low concentrations for normal function in organisms, but may be toxic at high concentrations (Santamaria, 2008; de Romaña *et al.*, 2011; Nriagu, 2011; Jaishankar *et al.*, 2014; A.C. Bosch *et al.*, 2016). In contrast, metalloids such as As, Cd, Pb, Hg, Se, and Cr and their organometals such alkylated lead, tributyl tin and methylmercury as are not essential for normal function in organisms, and are extremely toxic even at very low concentrations (DeForest, Brix & Adams, 2007; Mann, Vijver & Peijnenburg, 2011; Bosch *et al.*, 2016; Ali & Khan, 2018). Ecologically, these non-biogenic HM are generally persistent in the environment due to their non-biodegradable and recalcitrant nature and can undergo trophic transfer and bioaccumulation along aquatic food webs forming a strong risk for both environment and human health. Results from this study have shown that fish can be good bioaccumulators, with the ability to biomagnify some HM in middle to higher trophic levels, which are eventually consumed by human populations. From a public health perspective, levels of HM in fish are therefore of great interest because fish is an important source of food for the general human population along the South Africa coastline.

In this study, HM levels in muscle tissues were compared with national and international permissible limits (Table 17). Overall, the levels of Cu and Mn in the muscles of the six fish species were lower than the maximum allowable levels (MAL) and guidelines values described in the literature. Of great public health concern, all fish species had higher Pb levels than the MAL (0.5 mg/kg Pb) in South Africa (DOH, 2004), Australia/New Zealand (FSANZ, 2013) and China (MHPRC, 2013), and 0.5 mg/kg Pb limit set by European Commission (EC, 2006) and Codex Alimentarius Commission (WHO/FAO, 2015). Among the HM, Pb is known to possess various adverse effects such as neuro- and nephron-toxicity, rapid behavioural malfunction, and decrease in the growth, metabolism, and survival rate, alteration of social behaviour in some mammals (Damiano, Papetti & Menesatti, 2011; Bosch *et al.*, 2016; Fakhri *et al.*, 2018). Consequently, elevated levels of Pb recorded in all the fish species in this study may not cause any alarm, however, the prolonged accumulation of this metal warrant some concern. Other metals such As, Cr, Ni, and Zn had in some fish species consistently exceeded MAL guidelines for levels in seafood and may pose a significant health risk. With exception of soldier, all other fish species had Ni levels above the MAL guidelines of 1 mg/kg dw (TRUMBO *et al.*, 2001). For Zn, only slinger, maasbanker and Atlantic chub mackerel had level above 30 mg/kg limits (FAO, 1983), but comparable or higher than 40mg/kg guidelines (TRUMBO *et al.*, 2001). In contrast, only slinger had As and Cr level higher than 0.1 and 2 mg/kg limits, respectively (MHPRC, 2013), 2 mg/kg As limits by Australia and New Zealand guidelines (FSANZ, 2013), but lower than 3 mg/kg limits set by South Africa Department of health (DOH, 2004).

Based on human-biomonitoring data, the risk assessment of different HM based on indices such as estimated daily intake (EDI) and tolerable daily intake (TDI) can be individually evaluated (Table 18). While EDI can be presumed as to be the daily consumption of a heavy metal residue, TDI refer to the permissible intake amount that can be ingested orally daily over a lifetime without an appreciable health risk, whose values have been determined for most HM and other pollutants (Varol & Sünbül, 2017; Nordberg & Fowler, 2019). In South Africa, average annual fish consumption per capita per person is estimated at 6-8kg (~21.92 g/day) (Grünberger, 2014). Therefore, daily intake of HM was estimated on the basis of the concentrations measured in fish muscle and daily fish consumption rate (21.92 g), and the metal intakes compared with the respective permissible tolerable daily intake for South African adult average body weight 60.7 kg ($PTDI_{60.7}$) (µg/day). Among the metals studied, EDI for Cr in all the fish species was higher than permissible TDI for an adult, implying potential health risk associated with the intake Cr through fish consumption. Further, this study evaluated the potential non-carcinogenic risk, target hazard quotient (THQ) and hazard index (HI). Generally, low THQ below 1 indicates that the exposed population is unlikely to experience obvious adverse effects (Wang *et al.*, 2005). Whereas HI > 1 imply potential health risk of all the metal species through the fish consumption. Only Cr had THQ > 1, whereas indicating that Cr might pose a significant non-carcinogenic health hazard to human beings consuming these fish species in the Durban basin. The findings that the hazard index (HI) values for each fish(obtained by summing up the THQ of all the metals detected and quantified in each fish) were greater than 1, further confirming that the potential health and food security concerns arising from metal bioaccumulation in the assessed fish species is, at the present stage, significant (Varol & Sünbül, 2017).

This study also determined the target carcinogenic risks (TR) for the intake of As, Ni and Pb, three metals known to promote both non-carcinogenic and carcinogenic effects depending on the exposure level. Result showed that an adult can safely consume 34, 50, 24, 50, 52 and 39 meals/month of copper bream, rockcod, slinger, soldier, maasbanker and Atlantic chub mackerel, respectively, without As overexposure. Similar to As results, between 25-50 meals/month of the fish species can safely be eaten without cancer health effects endpoints due to Ni exposure. In contrast, maximum allowable daily consumption limits (TR_{lim}) for the fish species for Pb were between 14-24 g/day, values that are within or lower than the daily consumption rate of fish by adult South African (21.9 g/day). Consistent with these results, the calculated TR_{mm} values were lower than the prescribed safe fish consumption rate of >16 meals/month by USEPA (2000). These results indicate health safety concerns of potential exposure to Pb consumers though intake of these fish species caught in the Durban basin.

CHAPTER 6:
CONCLUSION AND RECOMMENDATIONS

6.1 Conclusions

In summary, the study has revealed that anthropic HM levels in fish species in the Durban basin exhibited both spatial and interspecific variability, with some species recording As, Cr, Ni, Pb and Zn levels in their muscles higher than South African and international regulations for seafood and may pose a health risk. Moreover, exposure to high levels of Pb through intake of these fish species is a potential cancer risk that needs to be addressed urgently.

Further, the key findings of this study include:

i) HM levels varied between different species with diet/trophic level (carnivores/ omnivore, prey preferences) and lifestyle (demersal, pelagic or benthic) as the key factors hypothesized to contribute to this variability.

ii) The trophic transfer inferred for cracker shrimp and grunter feeding habits within the Durban harbor poorly explained the HM variability in terms of bioaccumulation. Nonetheless, the better resolution of heavy metal transfer between cracker shrimp and grunter can be achieved with better sampling procedures and duration.

iii) Species associated with sediments (cracker shrimps), filter feeding behavior (Atlantic chub mackerel) and lower trophic level fish feeding on microbenthos (slinger and copper bream) had comparatively higher HM accumulation (mainly Cu, Mn, Pb and Zn), that positively correlated to the sediment metal levels linked to the localized anthropogenic point pollution sources.

iv) Intraspecific regional differences in HM levels in both maasbanker and slinger from the pristine (Cape Vidal) and polluted (Durban basin) marine environments indicates their ability to bioaccumulate various kinds of pollutants at higher levels than the surrounding environment, and thus their potential use in pollution biomonitoring. Further, both species collectively exhibited higher accumulation of HM levels in the liver (Al, Cr Cu and Zn) and gills (Mn and As) that were proportional to their environment concentrations. This implies that level of heavy metals in liver and gills of these two species are potential bio-monitors of anthropic HM water pollution.

v) While the levels of Cu and Mn in the muscles of the six fish species were lower than the maximum allowable levels (MAL), As, Cr, Ni, Pb and Zn levels in some fish species consistently exceeded MAL guidelines for levels in seafood, and are thus likely of a major concern to human health. Perhaps the most significant finding of the study was the almost 2-fold higher levels of As, Cr and Zn in slinger than other fish species in the same location, which were also above the MAL. Based on these results, an advisory on limited consumption of slinger is warranted.

vi) Additionally, THQ>1 for Cr in all fish species indicating possible significant non-carcinogenic health risk. the reported maximum allowable daily consumption limits (TR_{lim}) for copper bream, slinger and maasbanker for Pb were within or lower than the daily consumption rate of fish (21.9 g/day fish), pointing to the potential cancer risk attributable to Pb exposure through fish consumption. Thus, a daily consumption limit of 21, 16, and 14 g/day for copper bream, slinger and maasbanker are recommended for health safety.

6.2 Recommendations

To best of our knowledge, this is the first study to report on the spatial and interspecific HM variability in fish species within the Durban coastline. However, it should be noted that South Africa is endowed with an exceptionally rich marine environment boasting of some 2200 fish species belonging to 270 families of fishes, representing 83% of all marine fish families known, and equivalent to about 15% of the total number of marine fish species worldwide (der Elst and Adkin, 2007). Along these lines, there might be no sensible grounds to sum up the findings of this current investigation to the general health state of the natural fisheries off the Durban coastline dependent on the diversity of the foraging behaviors of the fishes utilized in this study. Nevertheless, consistently higher anthropic HM levels reported in fish species exceeding the regulatory limits for seafood illustrates the urgent need for holistic spatial and temporal monitoring and comprehensive national and regional strategies critical to combat and manage HM pollution in the Durban basin.

To further improve the overall understanding of HM accumulation and better aid the management of Durban basin fish, human health, marine health and environment health, this study has identified some particular areas that require more research:-

i) One of the objectives of this study was to test whether trophic transfer of HM occurs in the Durban harbour by characterizing bioaccumulation and biomagnification in a simple food chain. The trophic groups in simple food chain involving cracker shrimp (*C. kraussi*) and grunter (*P. commersonni)* inferred for their feeding habits within the Durban harbour poorly explained the HM variability in terms of trophic enrichment. Thus, future work should look to elucidate more precise determination of food sources, trophic position in food webs, the progressive time-integrated enrichment and transfer pathways of HM based on stable isotope ratios of carbon (^{13}C: ^{12}C; $\delta^{13}C$) and nitrogen (^{15}N: ^{14}N; $\delta^{15}N$). These studies target metals such as MeHg, Cd and Se that are known to persist and biomagnify in the environment, taking into account intrinsic species factors such fish size, time of exposure (age), fish physiology (storage or elimination), and lifestyle (demersal, pelagic or benthic).

ii) Further, this study has highlighted that susceptible species were sediments-associated (cracker shrimps), benthic filter feeding (Atlantic chub mackerel) and lower trophic level fish feeding on microbenthos (slinger and copper bream); include those living in highly contaminated region. There is a need to better understand the influences of metal levels in the species studied.

iii) This study was based on a limited sampling area along 50 km long the Durban coastline where easy dispersion of heavy metals by concentration gradients, wind/waves, with possible roaming of the fish within the sampling sites cannot be overruled. Hence, studies considering the movements and dispersal patterns of fish species both within the Durban coastline and in other waters is warranted.

iv) To further, enable a better understanding of the pathways by which HM accumulation and the underlying mechanisms that influence metal uptake. Future studies focused on identifying location-specific environmental and biological parameters such as water depth, water and sediment temperature, organic matter levels in the water column and sediments, and identification of metal input sources which may favors the bioavailability of metals will likewise be significant.

REFERENCES

Abadi, M. *et al.* (2019) 'Distribution pattern and pollution status by analysis of selected heavy metal amounts in coastal sediments from the southern Caspian Sea', *Environmental Monitoring and Assessment*, 191(3). doi: 10.1007/s10661-019-7261-2.

Abbaspour, N. *et al.* (2014) 'Review on iron and its importance for human health', *Journal of research in medical sciences: the official journal of Isfahan University of Medical Sciences*, 19(2), p. 164.

Abdolahpur Monikh, F. *et al.* (2013) 'Heavy metals' concentration in sediment, shrimp and two fish species from the northwest Persian Gulf.', *Toxicology and industrial health*, 31(February), pp. 554–565. doi: 10.1177/0748233713475498.

Abernathy, C. O., Thomas, D. J. and Calderon, R. L. (2003) 'Health Effects and Risk Assessment of Arsenic', *The Journal of Nutrition*. Oxford University Press (OUP), 133(5), pp. 1536S-1538S. doi: 10.1093/jn/133.5.1536s.

Ahdy, H. H. H., Aly Abdallah, A. M. and Tayel, F. T. (2007) 'Assessment of heavy metals and nonessential content of some edible and soft tissues', *Egyptian Journal of Acuatic Research*, 33(1), pp. 85–97.

Ahmad, H. *et al.* (2015) 'Pollution problem in River Kabul: Accumulation estimates of heavy metals in native fish species', *BioMed Research International*, 2015. doi: 10.1155/2015/537368.

Ahmed, K. *et al.* (2016) 'Human health risks from heavy metals in fish of Buriganga river, Bangladesh', *SpringerPlus*. Springer International Publishing, 5(1), p. 1697. doi: 10.1186/s40064-016-3357-0.

Ahoulé, D. G. *et al.* (2015) 'Arsenic in African Waters: A Review', *Water, Air, and Soil Pollution*, 226(9). doi: 10.1007/s11270-015-2558-4.

Aich, A. *et al.* (2015) 'Ecotoxicological assessment of tannery effluent using guppy fish (Poecilia reticulata) as an experimental model: A biomarker study', *Journal of Toxicology and Environmental Health - Part A: Current Issues*. doi: 10.1080/15287394.2014.960045.

Aktan, N. and Tekin-Özan, S. (2012) 'Levels of some heavy metals in water and tissues of chub mackerel (Scomber Japonicus) compared with physico-chemical parameters, seasons and size of the fish', *Journal of Animal and Plant Sciences*, 22(3), pp. 605–613.

Al-Ghanim, K. A. *et al.* (2015) 'Differential uptake of heavy metals by gill, muscles and liver of four selected fish species from red sea', *Pakistan Journal of Zoology*, 47(4), pp. 1031–1036. Available at: http://www.scopus.com/inward/record.url?eid=2-s2.0-84937157191&partnerID=40&md5=ac6c4f23bbfdad078dfe8a92532fc856.

Ali, H. and Khan, E. (2018) 'Bioaccumulation of non-essential hazardous heavy metals and metalloids in freshwater fish. Risk to human health', *Environmental Chemistry*

Letters. Springer International Publishing, 16(3), pp. 903–917. doi: 10.1007/s10311-018-0734-7.

Alissa, E. M. and Ferns, G. A. (2011) ‘Heavy metal poisoning and cardiovascular disease’, *Journal of Toxicology*. doi: 10.1155/2011/870125.

Amirah, M. N. *et al.* (2013) ‘Human Health Risk Assessment of Metal Contamination through Consumption of Fish’, *Journal of Environment Pollution and Human Health*, 1(1), pp. 1–5. doi: 10.12691/jephh-1-1-1.

Anderson, R. A. (1997) ‘Chromium as an Essential Nutrient for Humans’, *Regulatory Toxicology and Pharmacology*. Academic Press Inc., 26(1 I). doi: 10.1006/rtph.1997.1136.

Angel, B. M. *et al.* (2010) ‘Spatial variability of cadmium, copper, manganese, nickel and zinc in the Port Curtis Estuary, Queensland, Australia’, *Marine and Freshwater Research*, 61(2), pp. 170–183.

Antoine, J. M. R., Fung, L. A. H. and Grant, C. N. (2017) ‘Assessment of the potential health risks associated with the aluminium, arsenic, cadmium and lead content in selected fruits and vegetables grown in Jamaica’, *Toxicology Reports*. Elsevier Inc., 4, pp. 181–187. doi: 10.1016/j.toxrep.2017.03.006.

Atkinson, L. (2008) ‘User profiles for the South African offshore environment’.

Attwood, C. *et al.* (2013a) ‘A DecADe After the emergency: the ProceeDings of the 4th Linefish symPosium’, in *WWF South Africa Rep Series–2013/Marine/001. Cape Town: WWF South Africa*.

Attwood, C. *et al.* (2013b) ‘A Decade After the Emergency’, in *The Proceedings of the 4 th Linefish Symposium*.

Attwood, C. G., Allen, J. and Claassen, P. J. (2002) ‘Nearshore surface current patterns in the Tsitsikamma National Park, South Africa’, *South African Journal of Marine Science*, 24(1), pp. 151–160. doi: 10.2989/025776102784528448.

Austin, B. (1999) ‘The effects of pollution on fish health’, *Journal of Applied Microbiology*, 85, pp. 234S-242S. doi: 10.1111/j.1365-2672.1998.tb05303.x.

Authman, M. M. *et al.* (2015) ‘Use of Fish as Bio-indicator of the Effects of Heavy Metals Pollution’, *Journal of Aquaculture Research & Development*, 6(4), pp. 1–3. doi: 10.4172/2155-9546.1000328.

Aylett, A. (2010) ‘Conflict, Collaboration and Climate Change: Participatory Democracy and Urban Environmental Struggles in Durban, South Africa’, *International Journal of Urban and Regional Research*, 34(3), pp. 478–495. doi: 10.1111/j.1468-2427.2010.00964.x.

Badmaev, V., Prakash, S. and Majeed, M. (1999) ‘Vanadium: A review of its potential role in the fight against diabetes’, *Journal of Alternative and Complementary Medicine*. Mary Ann Liebert Inc., pp. 273–291. doi: 10.1089/acm.1999.5.273.

Bae, J. H., Yoon, S. H. and Lim, S. Y. (2011) 'Heavy metal contents and chemical compositions of atlantic (Scomber scombrus), blue (Scomber australasicus), and chub (Scomber japonicus) mackerel muscles', *Food Science and Biotechnology*, 20(3), pp. 709–714. doi: 10.1007/s10068-011-0100-z.

Barbosa, F. *et al.* (2005) 'A critical review of biomarkers used for monitoring human exposure to lead: Advantages, limitations, and future needs', *Environmental Health Perspectives*. Public Health Services, US Dept of Health and Human Services, pp. 1669–1674. doi: 10.1289/ehp.7917.

Barrows, A. P. W., Cathey, S. E. and Petersen, C. W. (2018) 'Marine environment microfiber contamination: Global patterns and the diversity of microparticle origins', *Environmental Pollution*. Elsevier Ltd, 237, pp. 275–284. doi: 10.1016/j.envpol.2018.02.062.

Baruthio, F. (1992) 'Toxic effects of chromium and its compounds', *Biological Trace Element Research*. Humana Press, 32(1–3), pp. 145–153. doi: 10.1007/BF02784599.

Bastami, A. A. and Esmailian, M. (2012) 'Bioaccumulation of Heavy Metals in Sediment and Crab , Portunus pelagicus From Persian Gulf , Iran', *Middle-East Journal of Scientific Research*, 12(6), pp. 886–892. doi: 10.5829/idosi.mejsr.2012.12.6.661.

Belhabib, D., Sumaila, U. R. and Le Billon, P. (2019) 'The fisheries of Africa: Exploitation, policy, and maritime security trends', *Marine Policy*. Elsevier Ltd, 101(December), pp. 80–92. doi: 10.1016/j.marpol.2018.12.021.

Bennett, B. A. (1989) 'A comparison of the fish communities in nearby permanently open, seasonally open and normally closed estuaries in the South-Western cape, South Africa', *South African Journal of Marine Science*, 8(1), pp. 43–55. doi: 10.2989/02577618909504550.

Bertrand, L. *et al.* (2018) 'Native crustacean species as a bioindicator of freshwater ecosystem pollution: A multivariate and integrative study of multi-biomarker response in active river monitoring', *Chemosphere*. Elsevier Ltd, 206, pp. 265–277. doi: 10.1016/j.chemosphere.2018.05.002.

Bhupander, K. and P, M. D. (2011) 'Assessment of Human Health Risk for Arsenic, Copper, Nickel, Mercury and Zinc in Fish Collected from Tropical Wetlands in India'.

Borrell, A. *et al.* (2016) 'Trace element accumulation and trophic relationships in aquatic organisms of the Sundarbans mangrove ecosystem (Bangladesh)', *Science of the Total Environment*. Elsevier B.V., 545–546, pp. 414–423. doi: 10.1016/j.scitotenv.2015.12.046.

Bosch, A. C. (2015) 'Status of mercury and other heavy metals in South African marine fish species', *PhD Thesis, Stellenbosch University*, (December), p. 206.

Bosch, Adina C. *et al.* (2016a) 'Heavy metal accumulation and toxicity in smoothhound (Mustelus mustelus) shark from Langebaan Lagoon, South Africa', *Food Chemistry*. Elsevier Ltd, 190, pp. 871–878. doi: 10.1016/j.foodchem.2015.06.034.

Bosch, Adina C. *et al.* (2016b) 'Heavy metals in marine fish meat and consumer health:

A review', *Journal of the Science of Food and Agriculture*, 96(1), pp. 32–48. doi: 10.1002/jsfa.7360.

Bosch, A.C. *et al.* (2016) 'Heavy metals in marine fish meat and consumer health: A review', *Journal of the Science of Food and Agriculture*, pp. 32–48. doi: 10.1002/jsfa.7360.

Boyd, R. S. (2010) 'Heavy Metal Pollutants and Chemical Ecology : Exploring New Frontiers', pp. 46–58. doi: 10.1007/s10886-009-9730-5.

Brenneisen, P., Steinbrenner, H. and Sies, H. (2005) 'Selenium, oxidative stress, and health aspects', *Molecular Aspects of Medicine*, pp. 256–267. doi: 10.1016/j.mam.2005.07.004.

Brooks, S. *et al.* (2010) 'Integrating qualitative methodologies into risk assessment: Insights from South Durban', *South African Journal of Science*, 106(9/10). doi: 10.4102/sajs.v106i9/10.324.

Brouillette Price, E., Kabengi, N. and Goldstein, S. T. (2019) 'Effects of heavy-metal contaminants (Cd, Pb, Zn) on benthic foraminiferal assemblages grown from propagules, Sapelo Island, Georgia (USA)', *Marine Micropaleontology*. Elsevier, 147(January), pp. 1–11. doi: 10.1016/j.marmicro.2019.01.004.

Brouwer, S. L. *et al.* (2011) 'A survey of the South African shore-angling fishery', *South African Journal of Marine Science*, 18(1), pp. 165–177. doi: 10.2989/025776197784161126.

Bryan, G. W. and Darracott, A. (1979) 'Bioaccumulation of marine pollutants', *Philosophical Transactions of the Royal Society of London. B, Biological Sciences*. The Royal Society London, 286(1015), pp. 483–505.

Burger, J. and Gochfeld, M. (2011) 'Mercury and selenium levels in 19 species of saltwater fish from New Jersey as a function of species, size, and season', *Science of the Total Environment*. Elsevier, 409(8), pp. 1418–1429.

Buxton, C. D. and Clarke, J. R. (2015) ' The Biology of the bronze bream, Pachymetopon Grande (Teleostei: Sparidae) from the south-east Cape coast, South Africa ', *South African Journal of Zoology*, 27(1), pp. 21–32. doi: 10.1080/02541858.1992.11448256.

Cammilleri, G. *et al.* (2018) 'Mercury in fish products: what's the best for consumers between bluefin tuna and yellowfin tuna?', *Natural Product Research*. Taylor & Francis, 32(4), pp. 457–462. doi: 10.1080/14786419.2017.1309538.

Canli, M. and Atli, G. (2003) 'The relationships between heavy metal (Cd, Cr, Cu, Fe, Pb, Zn) levels and the size of six Mediterranean fish species', *Environmental Pollution*, 121(1), pp. 129–136. doi: 10.1016/S0269-7491(02)00194-X.

Cape May, N. J. and City, O. (2018) 'Chub Mackerel Amendment'.

Carić, H., Klobučar, G. and Štambuk, A. (2016) 'Ecotoxicological risk assessment of antifouling emissions in a cruise ship port', *Journal of Cleaner Production*, 121, pp. 159–

168. doi: 10.1016/j.jclepro.2014.08.072.

CCME (2002) *Canadian environmental quality guidelines*. Canadian Council of Ministers of the Environment.

Cerna, F. and Plaza, G. (2014) ‘Life history parameters of chub mackerel (Scomber japonicus) from two areas off Chile’, *Bulletin of Marine Science*. Rosenstiel School of Marine and Atmospheric Science, 90(3), pp. 833–848. doi: 10.5343/bms.2013.1077.

Chapman, P. M. (1991) *Environmental Quality Criteria: What type should we be developing?*, *Environmental Science and Technology*. doi: 10.1021/es00020a600.

Chasapis, C. T. *et al.* (2012) ‘Zinc and human health: an update.’, *Archives of toxicology*, 86(4), pp. 521–34. doi: 10.1007/s00204-011-0775-1.

Chou, H. Y. *et al.* (1999) ‘Effect of heavy metal stressors and salinity shock on the susceptibility of grouper (Epinephelus sp.) to infectious pancreatic necrosis virus’, *Virus Research*, 63(1–2), pp. 121–129. doi: 10.1016/S0168-1702(99)00065-9.

Chown, S. L. (2010) ‘Temporal biodiversity change in transformed landscapes: a southern African perspective.’, *Philosophical transactions of the Royal Society of London. Series B, Biological sciences*, 365(1558), pp. 3729–3742. doi: 10.1098/rstb.2010.0274.

Cid, B. P. *et al.* (2001) ‘Determination of trace metals in fish species of the Ria de Aveiro (Portugal) by electrothermal atomic absorption spectrometry’, *Food Chemistry*, 75(1), pp. 93–100. doi: 10.1016/S0308-8146(01)00184-4.

Clarke, J. R. and Buxton, C. D. (1989) ‘A survey of the recreational rock-angling fishery at port elizabeth, on the south-east coast of South Africa’, *South African Journal of Marine Science*, 8(1), pp. 183–194. doi: 10.2989/02577618909504560.

Cloete, C. . and Oliff, W. . (1975) *South African Marine Pollution Survey Report 1974 - 1975.*

Coetzee, L., Preez, H. H. and Vuren, J. H. J. Van (2006) ‘Metal concentrations in Clarias gariepinus and Labeo umbratus from the Olifants and Klein Olifants River , Mpumalanga , South Africa : Zinc , copper , manganese , lead , chromium , nickel , aluminium and iron’, *WaterSA*, 28(4), pp. 433–448.

Coetzee, P. S., Baird, D. and Tregoning, C. (1989) ‘Catch statistics and trends in the shore angling fishery of the east coast, South Africa, for the period 1959–1982’, *South African Journal of Marine Science*, 8(1), pp. 155–171. doi: 10.2989/02577618909504558.

Coppinger, C. R. *et al.* (2019) ‘Assessing the genetic diversity of catface grouper Epinephelus andersoni in the subtropical Western Indian Ocean’, *Fisheries Research*, 218, pp. 186–197. doi: 10.1016/j.fishres.2019.05.008.

Couet, D. *et al.* (2018) ‘Effects of copper and butyltin compounds on the growth, photosynthetic activity and toxin production of two HAB dinoflagellates: The planktonic Alexandrium catenella and the benthic Ostreopsis cf. ovata’, *Aquatic Toxicology*.

Elsevier B.V., 196, pp. 154–167. doi: 10.1016/j.aquatox.2018.01.005.

Cowley, P. D., Brouwer, S. L. and Tilney, R. L. (2011) ‘The role of the Tsitsikamma National Park in the management of four shore-angling fish along the south-eastern Cape coast of South Africa’, *South African Journal of Marine Science*, 24(1), pp. 27–35. doi: 10.2989/025776102784528664.

Crafford, D. and Avenant-Oldewage, A. (2010) ‘Bioaccumulation of non-essential trace metals in tissues and organs of Clarias gariepinus (sharptooth catfish) from the Vaal River system - strontium, aluminium, lead and nickel’, *Water SA*, 36(5), pp. 621–640. doi: 10.4314/wsa.v36i5.61996.

Crone, P. R. *et al.* (2019) *ASSESSMENT OF THE PACIFIC MACKEREL (Scomber japonicus) STOCK*.

CSIR (2010) *A CSIR perspective on water in South Africa - 2010*.

CSIR (2012) *Sea disposal of sewage: Environmental surveys in the Durban outfalls region. Report No 30: Surveys made in 2011. CSIR Report CSIR/NRE/CO/ER/2012/00xx/x.* Pretoria.

Cunningham, P. A. *et al.* (2019) ‘Assessment of metal contamination in Arabian/Persian Gulf fish: A review’, *Marine Pollution Bulletin*. Elsevier, 143(March), pp. 264–283. doi: 10.1016/j.marpolbul.2019.04.007.

Cury, P. *et al.* (2000) ‘Small pelagics in upwelling systems: patterns of interaction and structural changes in “wasp-waist” ecosystems’, *ICES Journal of Marine Science*. Oxford University Press, 57(3), pp. 603–618.

Dadar, M., Peyghan, R. and Memari, H. R. (2014) ‘Evaluation of the Bioaccumulation of Heavy Metals in White Shrimp (Litopenaeus vannamei) Along the Persian Gulf Coast’, *Bulletin of Environmental Contamination and Toxicology*, 93(3), pp. 339–343. doi: 10.1007/s00128-014-1334-2.

DAFF (2012) ‘Status of the South African marine fishery resources 2012’. Cape Town: DAFF.

DAFF (2014) ‘Status of the South African marine fishery resources 2014’, *Cape Town, Department of Agriculture, Forestry and Fisheries*.

DAFF (2017) ‘Recreational Fishing Brochure 2017-18’, *Department of Agriculture forestry and Fisheries*.

Daley, T. (2018) ‘Growth and Reproduction of Atlantic Chub Mackerel (Scomber Colias) in the Northwest Atlantic’, p. 78.

Damiano, S., Papetti, P. and Menesatti, P. (2011) ‘Accumulation of heavy metals to assess the health status of swordfish in a comparative analysis of Mediterranean and Atlantic areas’, *Marine Pollution Bulletin*. Elsevier Ltd, 62(8), pp. 1920–1925. doi: 10.1016/j.marpolbul.2011.04.028.

Damodharan, U. and Reddy, M. V. (2013) ‘Heavy metal bioaccumulation in edible fish species from an industrially polluted river and human health risk assessment', pp. 19–27. doi: 10.2478/aopf-2013-0003.

Dar, M. I., Green, I. D. and Khan, F. A. (2019) 'Trace metal contamination: transfer and fate in food chains of terrestrial invertebrates', *Food Webs*. Elsevier, p. e00116.

Das, K. K., Das, S. N. and Dhundasi, S. A. (2008) 'Nickel, its adverse health effects & oxidative stress', *Indian Journal of Medical Research*, pp. 412–425.

DEA (2018) *South African Water Quality Guidelines for Coastal Marine Waters - Natural Environment and Mariculture Use.* Cape Town, Republic of South Africa.

Debipersadh, S. *et al.* (2018) 'Investigating toxic metal levels in popular edible fishes from the South Durban basin : implications for food security', *Environmental Monitoring and Assessment*. Environmental Monitoring and Assessment, 190(476), pp. 1–12. doi: 10.1007/s10661-018-6862-5.

DeForest, D. K., Brix, K. V. and Adams, W. J. (2007) 'Assessing metal bioaccumulation in aquatic environments: The inverse relationship between bioaccumulation factors, trophic transfer factors and exposure concentration', *Aquatic Toxicology*, 84(2 SPEC. ISS.), pp. 236–246. doi: 10.1016/j.aquatox.2007.02.022.

Degger, N. *et al.* (2011) 'Application of artificial mussels (AMs) under South African marine conditions : A validation study', 63, pp. 108–118. doi: 10.1016/j.marpolbul.2011.04.040.

Dekov, V. M. *et al.* (1998) 'Chemical composition of sediments and suspended matter from the Cauvery and Brahmaputra rivers (India)', *Science of the Total Environment*. Elsevier, 212(2–3), pp. 89–105.

Dicken, M. L., Smale, M. J. and Booth, A. J. (2012) 'Long-term catch and effort trends in Eastern Cape Angling Week competitions', *African Journal of Marine Science*, 34(2), pp. 259–268. doi: 10.2989/1814232X.2012.709961.

Diop, S., Scheren, P. and Machiwa, J. F. (2016) *Estuaries: a lifeline of ecosystem services in the Western Indian Ocean*. Springer.

DOH (2004) *Regulation relating to maximum levels for metals in foodstuffs. Foodstuffs, Cosmetics and Disinfectants Act, 1972 (Act 54 of 1972), No. R. 500(April).* Pretoria.

Domingo, J. L. (1996) 'Vanadium: A review of the reproductive and developmental toxicity', *Reproductive Toxicology*. Elsevier Inc., pp. 175–182. doi: 10.1016/0890-6238(96)00019-6.

Donoghue, S. O. and Marshall, D. J. (2003) 'Marine pollution research in South Africa : a status report', *South African Journal of Marine Science*, 99(August), pp. 349–356.

Dórea, J. G. (2008) 'Persistent, bioaccumulative and toxic substances in fish: Human health considerations', *Science of the Total Environment*. Elsevier B.V., 400(1–3), pp. 93–114. doi: 10.1016/j.scitotenv.2008.06.017.

Duncan, M. *et al.* (2015) 'Genetic structure and consequences of stock exploitation of

Chrysoblephus puniceus, a commercially important sparid in the South West Indian Ocean', *Fisheries Research*, 164, pp. 64–72. doi: 10.1016/j.fishres.2014.10.019.

Dunlop, S. W., Mann, B. Q. and Van der Elst, R. P. (2013) 'A review of the Oceanographic Research Institute's Cooperative Fish Tagging Project: 27 years down the line', *African Journal of Marine Science*. Taylor & Francis, 35(2), pp. 209–221.

Dural, M., Göksu, M. Z. L. and Özak, A. A. (2007) 'Investigation of heavy metal levels in economically important fish species captured from the Tuzla lagoon', *Food Chemistry*, 102(1), pp. 415–421. doi: 10.1016/j.foodchem.2006.03.001.

DWAF (1996) *Water Quality Guidelines, Aquatic Ecosystem Use*, *Department of Water Affairs and Forestry*.

DWAF, W. R. C. (1995) 'Procedures to assess effluent discharge impacts', *WRC Report No. TT*, 64(94), pp. 973–980.

EC (2006) *Commission of the European Communities - Commission Regulation (EC) No 1881/2006 of 19 December 2006: setting maximum levels for certain contaminants in foodstuffs Official Journal of the European Union Legislation 364.* Brussels.

Edelman, I. S. and Leibman, J. (1959) 'Anatomy of body water and electrolytes', *The American Journal of Medicine*, pp. 256–277. doi: 10.1016/0002-9343(59)90346-8.

EFSA (2014) 'EFSA Panel on Dietetic Products, Nutrition and Allergies (NDA) - Scientific opinion on dietary reference values for chromium', *EFSA Journal*. Wiley Online Library, 12(10), p. 3845.

El-Moselhy, K. M. *et al.* (2014) 'Bioaccumulation of heavy metals in some tissues of fish in the Red Sea, Egypt', *Egyptian Journal of Basic and Applied Sciences*. Elsevier Ltd, 1(2), pp. 97–105. doi: 10.1016/j.ejbas.2014.06.001.

Elnabris, K. J., Muzyed, S. K. and El-Ashgar, N. M. (2013) 'Heavy metal concentrations in some commercially important fishes and their contribution to heavy metals exposure in palestinian people of Gaza Strip (Palestine)', *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 13(1), pp. 44–51. doi: 10.1016/j.jaubas.2012.06.001.

der Elst, R. Van and Adkin, F. (2007) 'Marine Linefish: Priority Species and Research Objectives in Southern Africa.', *Oceanographic Research Institute Special Publication No. 1*, 1.

Elst, R. Van Der, Biological, F. A.-S. A. A. for M. and 1991, undefined (no date) 'Marine Linefish: Priority Species and Research Objectives in Southern Africa. Oceanographic Research Institute Special Publication No. 1'.

Emami Khansari, F., Ghazi-Khansari, M. and Abdollahi, M. (2005) 'Heavy metals content of canned tuna fish', *Food Chemistry*, 93(2), pp. 293–296. doi: 10.1016/j.foodchem.2004.09.025.

EPA, A. B. D. (1989) *Risk assessment guidance for superfund. Volume I: human health evaluation manual (part a)*. EPA/540/1-89/002.

eThekwini Municipality (2014) *Economic Development and Growth in eThekwini*. Durban.

eThekwini Municipality (2016) *Final - Integrated Development Plan 2015 / 2016*. Durban.

Expansion, P. and Port, D. (2012) ‘Act now to save durban bay’.

Fakhri, Y. *et al.* (2018) ‘Systematic review and health risk assessment of arsenic and lead in the fished shrimps from the Persian gulf.’, *Food and chemical toxicology : an international journal published for the British Industrial Biological Research Association*. England, 113, pp. 278–286. doi: 10.1016/j.fct.2018.01.046.

Fan, F. *et al.* (2013) ‘Higher fish intake is associated with a lower risk of hip fractures in Chinese men and women: a matched case-control study.’, *PloS one*, 8(2), p. e56849. doi: 10.1371/journal.pone.0056849.

FAO/WHO (2004) ‘Summary of Evaluations Performed by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) 1956-2003 (First through Sixty-First Meetings)’. Food and Agriculture Organization of the United Nations (FAO) and the World ….

FAO (1983) *Food and Agriculture Organization - Compilation of legal limits for hazardous substances in fish and fishery products. FAO Fishery Circular No 464.* Rome, Italy.

FAO FishStat (2015) ‘Fisheries and aquaculture software. FishStatJ-software for fishery statistical time series. FAO Fisheries and Aquaculture Department, Rome’. Rome: Food and Agriculture Organization.

Farag, A. M. *et al.* (1998) ‘Concentrations of Metals Associated with MiningWaste in Sediments, Biofilm, Benthic Macroinvertebrates, and Fish from the Coeur d’Alene River Basin, Idaho’, *Archives of Environmental Contamination and Toxicology*, 34, pp. 119–127.

Fatoki, O. S. and Mathabatha, S. (2001) ‘An assessment of heavy metal pollution in the East London and Port Elizabeth harbours’, *Water Sa*. Water Research Commission (WRC), 27(2), pp. 233–240.

Fauziah, F. and Choesin, D. N. (2014) ‘Accumulation of Pb and Cu heavy metals in sea water, sediment, and leaf and root tissue of Enhalus sp. in the seagrass bed of Banten Bay’, *AIP Conference Proceedings*, 1589(2), pp. 329–333. doi: 10.1063/1.4868812.

Fellenberg, G. (2000) *The chemistry of pollution*. John Wiley & Sons.

Fennessy, S. (2000) ‘Comparative life histories and stock assessments of rockcods (Family Serranidae) from the east coast of South Africa’.

Fernandes, S. and Pillay, S. (2012) ‘A study of the net flux of nitrates from estuaries of the eThekwini Municipality of Durban, KwaZulu-Natal, South Africa’, *Environmental Earth Sciences*, 67(8), pp. 2193–2203. doi: 10.1007/s12665-012-1659-2.

Fernández-Severini, M. D. *et al.* (2019) ‘Metals in the particulate matter from surf zone waters of a Southwestern Atlantic sandy beach (Monte Hermoso, Argentina)', *Regional Studies in Marine Science*. Elsevier B.V., 29, p. 100646. doi: 10.1016/j.rsma.2019.100646.

Ferreira da Silva, E. *et al.* (2009) 'Heavy metal pollution downstream the abandoned Coval da Mó mine (Portugal) and associated effects on epilithic diatom communities.', *The Science of the total environment*. Elsevier B.V., 407(21), pp. 5620–36. doi: 10.1016/j.scitotenv.2009.06.047.

First, M. (2013) 'Biology of santer seabream', 29(3), pp. 33–34.

Fisher, B. *et al.* (2017) 'Integrating fisheries and agricultural programs for food security', *Agriculture and Food Security*. BioMed Central, 6(1), p. 1. doi: 10.1186/s40066-016-0078-0.

Fleming, L. *et al.* (2015) 'Environmental Science : Oxford Research Encyclopedias The Oceans and Human Health', (December), pp. 1–15. doi: 10.1093/acrefore/9780199389414.013.12.

Forti, E. *et al.* (2011) 'In vitro evaluation of the toxicity induced by nickel soluble and particulate forms in human airway epithelial cells', *Toxicology in Vitro*, 25(2), pp. 454–461. doi: 10.1016/j.tiv.2010.11.013.

Freund, B. (2001) 'Brown and Green in Durban: The Evolution of Environmental Policy in a Post-Apartheid City', *International Journal of Urban and Regional Research*, 25(4), pp. 717–739. doi: 10.1111/1468-2427.00341.

FSANZ (2013) *Food Standards Australia and New Zealand ####, Standard 141. Contaminants and natural toxicants.* Perth.

Gall, J. E., Boyd, R. S. and Rajakaruna, N. (2015) 'Transfer of heavy metals through terrestrial food webs: a review', *Environmental monitoring and assessment*. Springer, 187(4), p. 201.

Garrido, S. *et al.* (2015) 'Trophic ecology of pelagic fish species off the Iberian coast: diet overlap, cannibalism and intraguild predation', *Marine Ecology Progress Series*, 539, pp. 271–285.

Gárriz, Á. *et al.* (2019) 'Effects of heavy metals identified in Chascomús shallow lake on the endocrine-reproductive axis of pejerrey fish (Odontesthes bonariensis)', *General and Comparative Endocrinology*, 273, pp. 152–162. doi: 10.1016/j.ygcen.2018.06.013.

Geist, S. J. *et al.* (2014) 'Distribution, feeding behaviour, and condition of Cape horse mackerel early life stages, Trachurus capensis, under different environmental conditions in the northern Benguela upwelling ecosystem', *ICES Journal of Marine Science*, 71, pp. 2–15.

Genthe, B. R. W. J. L. S. K. O. P. J. A.-H. N. H. C. J. (2013) 'Health risk implications from simultaneous exposure to multiple environmental contaminants.', *Ecotoxicology and Environmental Safety; 2013*, pp. 1–9.

Georgieva, Y. G. *et al.* (2019) 'Seasonal diet and feeding strategy of horse mackerel trachurus mediterraneus (Steindachner, 1868) (Perciformes: Carangidae) in the South-Western Black Sea', *Acta Zoologica Bulgarica*, 71(2), pp. 201–210.

Giri, S. and Singh, A. K. (2013) 'Assessment of human health risk for heavy metals in fish and shrimp collected from Subarnarekha river, India.', *International journal of environmental health research*, (February 2014), pp. 37–41. doi: 10.1080/09603123.2013.857391.

Goble, B. J., van der Elst, R. P. and Oellermann, L. K. (2014) 'Ugu Lwethu–Our Coast. A Profile of Coastal KwaZulu-Natal'. KwaZulu-Natal: KwaZulu-Natal Department of Agriculture and Environmental ….

Godt, J. *et al.* (2006) 'The toxicity of cadmium and resulting hazards for human health', *Journal of Occupational Medicine and Toxicology*, 1(1). doi: 10.1186/1745-6673-1-22.

Gomgmt, B. and Tezt, Z. (1994) 'Heavy metal pollution in water, sediment and fish from from the Tigris river in Turkey', 29(1), pp. 111–116.

Grandjean, P. *et al.* (2010) 'Adverse effects of methylmercury: environmental health research implications.', *Environmental health perspectives*, 118(8), pp. 1137–45. doi: 10.1289/ehp.0901757.

Gray, J. S. (2002) 'Biomagnification in marine systems: the perspective of an ecologist', *Marine Pollution Bulletin*, 45(1), pp. 46–52. doi: https://doi.org/10.1016/S0025-326X(01)00323-X.

Griboff, J. *et al.* (2018) 'Bioaccumulation and trophic transfer of metals, As and Se through a freshwater food web affected by antrophic pollution in Córdoba, Argentina', *Ecotoxicology and Environmental Safety*. Academic Press, 148, pp. 275–284. doi: 10.1016/j.ecoenv.2017.10.028.

Griffiths, M. H. (2000) 'Long-term trends in catch and effort of commercial linefish off South Africa's Cape Province: snapshots of the 20th century', *African Journal of Marine Science*. NISC, 22.

Grünberger, K. (2014) 'Estimating food consumption patterns by reconciling food balance sheets and household budget surveys', *Rome: Food and Agriculture Organization of the United Nations*.

Gu, Y.-G. *et al.* (2015) 'Heavy metal concentrations in wild fishes captured from the South China Sea and associated health risks.', *Marine pollution bulletin*. Elsevier Ltd, 96(1–2), pp. 508–512. doi: 10.1016/j.marpolbul.2015.04.022.

Guastella, L. a-M. (1994) 'A quantitative assessment of recreational angling in Durban Harbour, South Africa', *South African Journal of Marine Science*, pp. 187–203. doi: 10.2989/025776194784287120.

Guastella, L. and Knudsen, S. (2007) 'South Durban basin multi-point plan: case study report', *Output A*, 2.

Gundogdu, A. *et al.* (2016) 'Heavy Metal Accummulation in muscles and total bodies of mullus barbatus, trachurus trachurus and engraulis encrasicolus captured from the coast of sinop, black sea', *Pakistan Journal of Zoology*, 48(1), pp. 25–34.

Guo, H. *et al.* (2017) 'Distribution and controls of heavy metals and organic matter in the surface sediments of the Southern Yellow Sea, China', *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, 24(29), pp. 23069–23079. doi: 10.1007/s11356-017-9940-2.

Guo, Y. and Yang, S. (2016) 'Heavy metal enrichments in the Changjiang (Yangtze River) catchment and on the inner shelf of the East China Sea over the last 150years', *Science of the Total Environment*. Elsevier B.V., 543, pp. 105–115. doi: 10.1016/j.scitotenv.2015.11.012.

Guo, Z. *et al.* (2016) 'Developmental patterns of copper bioaccumulation in a marine fish model Oryzias melastigma', *Aquatic Toxicology*. Elsevier B.V., 170, pp. 216–222. doi: 10.1016/j.aquatox.2015.11.026.

Gusso-Choueri, P. K. *et al.* (2015) 'Assessing genotoxic effects in fish from a marine protected area influenced by former mining activities and other stressors', *Marine Pollution Bulletin*. Elsevier Ltd, 104(1–2), pp. 229–239. doi: 10.1016/j.marpolbul.2016.01.025.

Hadzi, G. Y., Essumang, D. K. and Adjei, J. K. (2015) 'Distribution and Risk Assessment of Heavy Metals in Surface Water from Pristine Environments and Major Mining Areas in Ghana', *Journal of Health and Pollution*. Blacksmith Institute, 5(9), pp. 86–99. doi: 10.5696/2156-9614-5-9.86.

Haggard, K. (2015) 'South African fishing is sustainable', *Mail & Guardian*, November.

Hall, S. J. (2001) 'Is offshore oil exploration good for benthic conservation?', *Trends in Ecology and Evolution*. Elsevier Ltd, p. 58. doi: 10.1016/S0169-5347(00)02015-2.

Hamilton, L. C. and Safford, T. G. (2015) 'Environmental Views from the Coast: Public Concern about Local to Global Marine Issues', *Society & Natural Resources*, 28(1), pp. 57–74. doi: 10.1080/08941920.2014.933926.

Hartley, B. L. *et al.* (2018) 'Exploring public views on marine litter in Europe: Perceived causes, consequences and pathways to change', *Marine Pollution Bulletin*. Elsevier Ltd, pp. 945–955. doi: 10.1016/j.marpolbul.2018.05.061.

Hassan, D. (2017) *Protecting the Marine Environment from Land-Based Sources of Pollution*, *Protecting the Marine Environment from Land-Based Sources of Pollution*. Routledge. doi: 10.4324/9781315245829.

'"Hazardous to health?" Sugar mills and river pollution in Natal, 1869 – 1901 Duncan Du Bois *' (2018), 1910(May), pp. 24–44.

He, F. J. and MacGregor, G. A. (2008) 'Beneficial effects of potassium on human health', in *Physiologia Plantarum*, pp. 725–735. doi: 10.1111/j.1399-3054.2007.01033.x.

Hecht, T. (1990) 'On the life history of Cape horse mackerel Trachurus trachurus capensis off the south-east coast of South Africa', *South African Journal of Marine Science*. Taylor & Francis, 9(1), pp. 317–326.

Hedge, L. H., Knott, N. A. and Johnston, E. L. (2009) ‘Dredging related metal bioaccumulation in oysters’, *Marine Pollution Bulletin*, 58(6), pp. 832–840. doi: 10.1016/j.marpolbul.2009.01.020.

Heemstra, P. and Heemstra, E. (2004) *Coastal fishes of southern Africa*.

Heidari, M. (2019) ‘Role of Natural Flocculation in Eliminating Toxic Metals’, *Archives of Environmental Contamination and Toxicology*. Springer US, 76(3), pp. 366–374. doi: 10.1007/s00244-019-00597-x.

Hernández-Almaraz, P. *et al.* (2014) ‘Metal mobility and bioaccumulation differences at lower trophic levels in marine ecosystems dominated by Sargassum species’, *Journal of the Marine Biological Association of the United Kingdom*, pp. 435–442. doi: 10.1017/S0025315413001653.

Herrera, A. *et al.* (2019) ‘Microplastic ingestion by Atlantic chub mackerel (Scomber colias) in the Canary Islands coast’, *Marine Pollution Bulletin*, 139(December 2018), pp. 127–135. doi: 10.1016/j.marpolbul.2018.12.022.

Hesami, R., Salimi, A. and Ghaderian, S. M. (2018) ‘Lead, zinc, and cadmium uptake, accumulation, and phytoremediation by plants growing around Tang-e Douzan lead–zinc mine, Iran’, *Environmental Science and Pollution Research*. Springer Verlag, 25(9), pp. 8701–8714. doi: 10.1007/s11356-017-1156-y.

HLPE (2014) *Sustainable fisheries and aquaculture for food security and nutrition. A report by the High Level Panel of Experts on Food Security and Nutrition of the Committe on world Food Security*, *FAO*. Rome.

Hollis, L. *et al.* (2000) ‘Effects of long term sublethal Cd exposure in rainbow trout during soft water exposure: Implications for biotic ligand modelling’, *Aquatic Toxicology*, 51(1), pp. 93–105. doi: 10.1016/S0166-445X(00)00099-0.

Holtz, P. (1971) ‘The construction of the single buoy mooring at Reunion near Durban’, *Civil Engineering - Siviele Ingenieurswese*, 13(2), pp. 47–49.

Hough, R. L. *et al.* (2004) ‘Assessing potential risk of heavy metal exposure from consumption of home-produced vegetables by urban populations’, *Environmental Health Perspectives*, 112(2), pp. 215–221. doi: 10.1289/ehp.5589.

Interciencia Venezuela Pérez-Moreno, A. *et al.* (2016) ‘KEYWORDS / Heavy Metal / Mexican Pacific Coast / Seawater’, 41(6), pp. 419–423.

Iqbal, A. *et al.* (2017) ‘Heavy Metal Uptake and Toxicity in Tissues of Commercially Important Freshwater Fish (Labeo rohita and Wallago attu) from the Indus River, Pakistan’, *Polish Journal of Environmental Studies*, 26(2), pp. 627–633. doi: 10.15244/pjoes/66850.

Isaacs, M. and Witbooi, E. (2019) ‘Fisheries crime, human rights and small-scale fisheries in South Africa: A case of bigger fish to fry’, *Marine Policy*, 105, pp. 158–168. doi: https://doi.org/10.1016/j.marpol.2018.12.023.

Ismail, A. *et al.* (2015) ‘Spatial assessment and source identification of heavy metals pollution in surface water using several chemometric techniques', *Marine Pollution Bulletin*, 106, pp. 292–300. doi: 10.1016/j.marpolbul.2015.10.019.

IUCN (2019) *The IUCN Red List of Threatened Species. Version 2019-3.* IUCN.

Jacobs, S. *et al.* (2015) 'Marine environmental contamination: public awareness, concern and perceived effectiveness in five European countries', *Environmental Research*. Academic Press, 143, pp. 4–10. doi: 10.1016/J.ENVRES.2015.08.009.

Jahan, S. and Strezov, V. (2019) 'Assessment of trace elements pollution in the sea ports of New South Wales (NSW), Australia using oysters as bioindicators', *Scientific Reports*. Springer US, 9(1), pp. 1–10. doi: 10.1038/s41598-018-38196-w.

Jaishankar, M. *et al.* (2014) 'Toxicity, mechanism and health effects of some heavy metals', *Interdisciplinary Toxicology*, 7(2), pp. 60–72. doi: 10.2478/intox-2014-0009.

Järup, L. (2003) 'Hazards of heavy metal contamination', *British Medical Bulletin*, 68, pp. 167–182. doi: 10.1093/bmb/ldg032.

Javed, M. *et al.* (2016) 'Bioaccumulation, oxidative stress and genotoxicity in fish (Channa punctatus) exposed to a thermal power plant effluent', *Ecotoxicology and Environmental Safety*. Elsevier, 127, pp. 163–169. doi: 10.1016/j.ecoenv.2016.01.007.

Jayaprakash, M. *et al.* (2015) 'Bioaccumulation of metals in fish species from water and sediments in macrotidal Ennore creek, Chennai, SE coast of India: A metropolitan city effect', *Ecotoxicology and Environmental Safety*. Elsevier, 120, pp. 243–255. doi: 10.1016/j.ecoenv.2015.05.042.

Jennings, S. *et al.* (2016) 'Aquatic food security: insights into challenges and solutions from an analysis of interactions between fisheries, aquaculture, food safety, human health, fish and human welfare, economy and environment', *Fish and Fisheries*, 17(4), pp. 893–938. doi: 10.1111/faf.12152.

Jitar, O. *et al.* (2013) 'Study of heavy metal pollution and bioaccumulation in the Black Sea living environment', *Environmental Engineering and Management Journal*, 12(2), pp. 271–276. doi: 10.30638/eemj.2013.032.

Jitar, O. *et al.* (2015) 'Bioaccumulation of heavy metals in marine organisms from the Romanian sector of the Black Sea', *New Biotechnology*. Elsevier B.V., 32(3), pp. 369–378. doi: 10.1016/j.nbt.2014.11.004.

Jones, K. R. *et al.* (2018) 'The Location and Protection Status of Earth's Diminishing Marine Wilderness', *Current Biology*. Elsevier Ltd., 28(15), pp. 2506-2512.e3. doi: 10.1016/j.cub.2018.06.010.

Jones, R. J. and Kerswell, A. P. (2003) 'Phototoxicity of PSII herbicides to coral', *MARINE ECOLOGY PROGRESS SERIES*, 261, pp. 149–159. Available at: file:///C:/Users/Jess/Downloads/(2003) Jones and Kerswell - Marine Ecology Progress Series.pdf.

Joubert, C. S. W. and Hanekom, P. B. (2015) 'A Study of Feeding in Some Inshore Reef Fish of the Natal Coast, South Africa', *South African Journal of Zoology*, 15(4), pp. 262–

274. doi: 10.1080/02541858.1980.11447721.

Jupp, B. P. *et al.* (2017) ‘Assessment of heavy metal and petroleum hydrocarbon contamination in the Sultanate of Oman with emphasis on harbours, marinas, terminals and ports’, *Marine Pollution Bulletin*. Elsevier, 121(1–2), pp. 260–273. doi: 10.1016/j.marpolbul.2017.05.015.

Kadila, H. K. *et al.* (2020) ‘Insights into feeding interactions of shallow water cape hake (Merluccius capensis) and cape horse mackerel (Trachurus capensis) from the Northern Benguela (Namibia)’, *Regional Studies in Marine Science*. Elsevier B.V., 34, p. 101071. doi: 10.1016/j.rsma.2020.101071.

Kaplan, N. M. (2000) ‘The dietary guideline for sodium: Should we shake it up? No’, *American Journal of Clinical Nutrition*, pp. 1020–1026. doi: 10.1093/ajcn/71.5.1020.

Kearns, J. and Turner, A. (2016) ‘An evaluation of the toxicity and bioaccumulation of bismuth in the coastal environment using three species of macroalga’, *Environmental Pollution*. Elsevier, 208, pp. 435–441. doi: 10.1016/j.envpol.2015.10.011.

Keč, V. Č. and Zorica, B. (2013) ‘Length–weight relationship, age, growth and mortality of Atlantic chub mackerel Scomber colias in the Adriatic Sea’, *Journal of the Marine Biological Association of the United Kingdom*. Cambridge University Press, 93(2), pp. 341–349.

Kepel, T. L., Salim, H. L. and Heriati, A. (2019) ‘Preliminary study of lead and mercury concentrations in seven commercial seafood at Lombok Island , Indonesia’, 12(2), pp. 696–705.

Kibria, G. *et al.* (2016) ‘Monitoring of metal pollution in waterways across Bangladesh and ecological and public health implications of pollution’, *Chemosphere*. Elsevier Ltd, 165, pp. 1–9. doi: 10.1016/j.chemosphere.2016.08.121.

Kim, N. H. *et al.* (2015) ‘Environmental heavy metal exposure and chronic kidney disease in the general population’, *Journal of Korean Medical Science*. Korean Academy of Medical Science, 30(3), pp. 272–277. doi: 10.3346/jkms.2015.30.3.272.

Kim, S. W. *et al.* (2019) ‘Heavy metal accumulation in and food safety of shark meat from Jeju island, Republic of Korea’, *PLoS ONE*. Public Library of Science, 14(3). doi: 10.1371/journal.pone.0212410.

Kohzadi, S. *et al.* (2019) ‘Concentration, Source, and Potential Human Health Risk of Heavy Metals in the Commonly Consumed Medicinal Plants’, *Biological Trace Element Research*. Biological Trace Element Research, 187(1), pp. 41–50. doi: 10.1007/s12011-018-1357-3.

Kovekovdova, L. T. and Simokon’, M. V. (2002) ‘Heavy metals in the tissues of commercially important fish of Amurskii Bay, Sea of Japan’, *Russian Journal of Marine Biology*, 28(2), pp. 113–119. doi: 10.1023/A:1015344528080.

Kovesdy, C. P. *et al.* (2017) ‘Potassium homeostasis in health and disease: A scientific workshop cosponsored by the National Kidney Foundation and the American Society of Hypertension’, in *Journal of the American Society of Hypertension*. Elsevier Ireland Ltd, pp. 783–800. doi: 10.1016/j.jash.2017.09.011.

Kroeze, C. *et al.* (2016) ‘Global modelling of surface water quality: a multi-pollutant approach’, *Current Opinion in Environmental Sustainability*. Elsevier B.V., pp. 35–45. doi: 10.1016/j.cosust.2016.11.014.

Kroon, F. J. *et al.* (2016) ‘Towards protecting the Great Barrier Reef from land-based pollution’, *Global Change Biology*. Blackwell Publishing Ltd, 22(6), pp. 1985–2002. doi: 10.1111/gcb.13262.

Lamberth, S. J. and Turpie, J. K. (2003) ‘The role of estuaries in south african fisheries: Economic importance and management implications’, *African Journal of Marine Science*, 25(1), pp. 131–157. doi: 10.2989/18142320309504005.

Lao, Q. *et al.* (2019) ‘Spatial distribution of and historical changes in heavy metals in the surface seawater and sediments of the Beibu Gulf, China’, *Marine Pollution Bulletin*, 146, pp. 427–434. doi: https://doi.org/10.1016/j.marpolbul.2019.06.080.

Lau, S. *et al.* (1998) ‘Accumulation of heavy metals in freshwater molluscs’, *Science of the Total Environment*, 214(1–3), pp. 113–121. doi: 10.1016/S0048-9697(98)00058-8.

Lebrun, J. D. *et al.* (2015) ‘Seasonal variability and inter-species comparison of metal bioaccumulation in caged gammarids under urban diffuse contamination gradient: implications for biomonitoring investigations’, *Science of the Total Environment*. Elsevier, 511, pp. 501–508.

Lentini, P. *et al.* (2017) ‘Lead and Heavy Metals and the Kidney’, in *Critical Care Nephrology: Third Edition*. Elsevier Inc., pp. 1324-1330.e1. doi: 10.1016/B978-0-323-44942-7.00222-3.

Leppänen, J. J., Weckström, J. and Korhola, A. (2017) ‘Paleolimnological Fingerprinting of the Impact of Acid Mine Drainage After 50 Years of Chronic Pollution in a Southern Finnish Lake’, *Water, Air, and Soil Pollution*. Springer International Publishing, 228(6). doi: 10.1007/s11270-017-3417-2.

Li, P. *et al.* (2015) ‘Heavy metal bioaccumulation and health hazard assessment for three fish species from Nansi Lake, China’, *Bulletin of Environmental Contamination and Toxicology*, 94(4), pp. 431–436. doi: 10.1007/s00128-015-1475-y.

Lichucha, I. D. L. T. (2001) ‘Management of the Linefish Resource in Southern Mozambique : a Case Study for Marreco (Chrysoblephus Puniceus)’, p. 99.

Lin, Y. *et al.* (2018) ‘Ecological risk assessment to marine organisms induced by heavy metals in China’s coastal waters’, *Marine Pollution Bulletin*. Elsevier Ltd, 126, pp. 349–356. doi: 10.1016/j.marpolbul.2017.11.019.

Lines, J. A. and Spence, J. (2014) *Humane harvesting and slaughter of farmed fish*, *Rev. sci. tech. Off. int. Epiz*.

Liu, J. *et al.* (2007) ‘Complexity of coupled human and natural systems’, *science*. American Association for the Advancement of Science, 317(5844), pp. 1513–1516.

Lopes, C. *et al.* (2020) 'Microplastic ingestion and diet composition of planktivorous fish', *Limnology and Oceanography Letters*. John Wiley & Sons, Ltd, 5(1), pp. 103–112. doi: 10.1002/lol2.10144.

Lord, D. A., Anderson, F. P. and Basson, J. K. (1984) *Pipeline discharges of effluents to sea*. National Scientific Programmes Unit: CSIR.

Love, M. S. and Schroeder, D. M. (2005) *Distribution of bocaccio (Sebastes paucispinis) and cowcod (Sebastes levis) around oil platforms and natural outcrops off California with implications for larval production*.

Lozano-Bilbao, E. *et al.* (2020) 'Ontogenic and seasonal variations of metal content in a small pelagic fish (Trachurus picturatus) in northwestern African waters', *Marine Pollution Bulletin*, 156, p. 111251. doi: https://doi.org/10.1016/j.marpolbul.2020.111251.

Maaghloud, H. *et al.* (2020) 'Ingestion of microplastics by pelagic fish from the Moroccan Central Atlantic coast', *Environmental Pollution*. Elsevier Ltd, 261, p. 114194. doi: 10.1016/j.envpol.2020.114194.

Maggs, J. Q., Mann, B. Q. and Cowley, P. D. (2013) 'Contribution of a large no-take zone to the management of vulnerable reef fishes in the South-West Indian Ocean', *Fisheries Research*, 144, pp. 38–47. doi: 10.1016/j.fishres.2012.10.003.

Malik, N. *et al.* (2010) 'Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal', *Environmental Monitoring and Assessment*, 160(1–4), pp. 267–276. doi: 10.1007/s10661-008-0693-8.

Mangel, M., Quinn, T. and Deriso, R. (2000) 'Quantitative Fish Dynamics', *Ecology*, 81. doi: 10.2307/177155.

Mann, B. (2000) *Southern African marine linefish status reports*.

Mann, B. Q. *et al.* (2003) 'Evaluation of participation in and management of the transkei shore linefishery', *African Journal of Marine Science*, 25(1), pp. 79–97. doi: 10.2989/18142320309504002.

Mann, B. Q. (2013) *Southern African Marine Linefish Species Profiles*, *Biodiversity for Life.Special Publication No.9*. doi: http://dx.doi.org/10.1016/j.marpol.2013.05.006.

Mann, B. Q. *et al.* (2016) 'Monitoring the recovery of a previously exploited surf-zone fish community in the St Lucia Marine Reserve, South Africa, using a no-take sanctuary area as a benchmark', *African Journal of Marine Science*. National Inquiry Services Centre Ltd, 38(3), pp. 423–441. doi: 10.2989/1814232X.2016.1224779.

Mann, B. Q., Cowley, P. D. and Fennessy, S. T. (2015) 'Movement patterns of surf-zone fish species in a subtropical marine protected area on the east coast of South Africa', *African Journal of Marine Science*. National Inquiry Services Centre Ltd, 37(1), pp. 99–114. doi: 10.2989/1814232X.2015.1023220.

Mann, Bq. (2013) *Southern African marine linefish species profiles*, *Special publication*.

Mann, R. M., Vijver, M. G. and Peijnenburg, W. (2011) 'Metals and metalloids i n terrestrial systems: Bioaccumulation, biomagnification and subsequent advers e effects’, *Ecologica l impacts of toxic chemicals. Bentham Science Publishers*, pp. 43–62.

Mansour, A. M. *et al.* (2013) ‘Assessment and comparison of heavy-metal concentrations in marine sediments in view of tourism activities in Hurghada area, northern Red Sea, Egypt’, *The Egyptian Journal of Aquatic Research*. National Institute of Oceanography and Fisheries, 39(2), pp. 91–103. doi: 10.1016/j.ejar.2013.07.004.

Maree, B. A. *et al.* (2016) ‘Influence of prey abundance and abiotic factors on the long-term home-range and movement dynamics of spotted grunter Pomadasys commersonnii in an intermittently open estuary’, *African Journal of Marine Science*, 38(2), pp. 171–180. doi: 10.2989/1814232X.2016.1176956.

Martins, M. M. *et al.* (2013) ‘Changes in the abundance and spatial distribution of the Atlantic chub mackerel (*Scomber colias*) in the pelagic ecosystem and fisheries off Portugal’, *Scientia Marina*, 77(4), pp. 551–563. doi: 10.3989/scimar.03861.07b.

Masood, N. *et al.* (2016) ‘Anthropogenic waste indicators (AWIs), particularly PAHs and LABs, in Malaysian sediments: Application of aquatic environment for identifying anthropogenic pollution’, *Marine Pollution Bulletin*. Elsevier Ltd, 102(1), pp. 160–175. doi: 10.1016/j.marpolbul.2015.11.032.

Mcclanahan, T. R., Maina, J. M. and Muthiga, N. a. (2011) ‘Associations between climate stress and coral reef diversity in the western Indian Ocean’, *Global Change Biology*, 17(6), pp. 2023–2032. doi: 10.1111/j.1365-2486.2011.02395.x.

McClurg, T. P. *et al.* (2006) *Sea disposal of sewage: environmental surveys in the Durban outfalls region–surveys made in 2006*. CSIR Report No. CSIR/NRE/PW.

McGeer, J. C. *et al.* (2000) ‘Effects of chronic sublethal exposure to waterborne Cu, Cd or Zn in rainbow trout. 1: Iono-regulatory disturbance and metabolic costs’, *Aquatic Toxicology*, 50(3), pp. 231–243. doi: 10.1016/S0166-445X(99)00105-8.

McGlashan, J. E. and Macleod, D. C. (1986) ‘The effect of sewage sludge disposal to sea through pipelines previously discharging only settled effluent’, *Water Science and Technology*, 18(11), pp. 93–104.

McIlwain, J. *et al.* (2006) ‘Spawning and reproductive patterns of six exploited finfish species from the Arabian Sea, Sultanate of Oman’, *Journal of Applied Ichthyology*, 22(2), pp. 167–176. doi: 10.1111/j.1439-0426.2006.00723.x.

Mendoza-Carranza, M. *et al.* (2016) ‘Distribution and bioconcentration of heavy metals in a tropical aquatic food web: A case study of a tropical estuarine lagoon in SE Mexico’, *Environmental Pollution*. Elsevier Ltd, 210, pp. 155–165. doi: 10.1016/j.envpol.2015.12.014.

Mentz, G. *et al.* (2018) ‘Acute respiratory symptoms associated with short term fluctuations in ambient pollutants among schoolchildren in Durban, South Africa’, *Environmental Pollution*, 233(2), pp. 529–539. doi: 10.1016/j.envpol.2017.10.108.

MHPRC (2013) *Ministry of Health of the People’s Republic of China - National Food*

Safety Standard. Maximum Levels of Contaminants in Foods (GB2762-2012). Beijing.

Moloney, C. L. *et al.* (2013) 'Reviewing evidence of marine ecosystem change off South Africa', *African Journal of Marine Science*, 35(3), pp. 427–448. doi: 10.2989/1814232X.2013.836135.

Molony, B. (2003) 'Minamata: Pollution and the Struggle for Democracy in Postwar Japan (review)', *Bulletin of the History of Medicine*, 77(2), pp. 460–461. doi: 10.1353/bhm.2003.0076.

Mondi (2015) *Mondi Merebank Mill Operation: Socio-economic assessment toolbox (SEAT) Report 2015*. Durban.

Moodley, K. *et al.* (2014) 'Full Length Research Paper Heavy Metal Contamination of the Palmiet River : KwaZulu Natal South Africa', 2(11), pp. 397–409.

Moodley, K. and Pillay, S. (2015) 'Spatiotemporal characterization of water chemistry and pollution sources of the Umhlatuzana , Umbilo and Amanzimnyama River catchments of Durban , KwaZulu-Natal , South Africa', *Environmental Earth Sciences*. Springer Berlin Heidelberg, pp. 1273–1289. doi: 10.1007/s12665-015-4118-z.

Mozaffarian, D. *et al.* (2014) 'Global sodium consumption and death from cardiovascular causes', *New England Journal of Medicine*. Massachussetts Medical Society, 371(7), pp. 624–634. doi: 10.1056/NEJMoa1304127.

Mudgal, V. *et al.* (2010) 'Effect of toxic metals on human health', *The Open Nutraceuticals Journal*, 3(1).

Muir, D. *et al.* (1999) 'Spatial and temporal trends and effects of contaminants in the Canadian Arctic marine ecosystem: A review', *Science of the Total Environment*, 230(1–3), pp. 83–144. doi: 10.1016/S0048-9697(99)00037-6.

Mutlu, C. *et al.* (2012) 'Comparison of the heavy metal concentrations in atlantic horse mackerel, trachurus trachurus, from coastal waters of turkey', *Fresenius Environmental Bulletin*, 21(2), pp. 304–307.

Mzimela, H. M., Wepener, V. and Cyrus, D. P. (2014) 'Spatial and temporal variations in selected heavy metals in water and sediment from the Mhlathuze Estuary, Richards Bay', *African Journal of Environmental Science and Technology*. Academic Journals, 8(11), pp. 670–683.

Mziray, P. and Kimirei, A. (2016) 'Bioaccumulation of heavy metals in marine fishes (Siganus sutor, Lethrinus harak, and Rastrelliger kanagurta) from Dar es Salaam Tanzania', *Regional Studies in Marine Science*. Elsevier Ltd, 7, pp. 72–80. doi: 10.1016/j.rsma.2016.05.014.

Al Naggar, Y. *et al.* (2018) 'Environmental Pollution by Heavy Metals in the Aquatic Ecosystems of Egypt The potential toxicity of heavy metal nanoparticles on honey bees (Hymenoptera: Apis mellifera L.) View project Non-chemical strategies for managing plant parasitic nematodes View ', *Open Acc J of Toxicol*, 3(1). doi: 10.19080/OAJT.2018.03.555603.

Nascimento, J. R. *et al.* (2017) 'Bioaccumulation of heavy metals by shrimp (Litopenaeus schmitti): A dose–response approach for coastal resources management', *Marine Pollution Bulletin*. Elsevier Ltd, 114(2), pp. 1007–1013. doi: 10.1016/j.marpolbul.2016.11.013.

Nazir, R. *et al.* (2015) 'Accumulation of Heavy Metals (Ni , Cu , Cd , Cr , Pb , Zn , Fe) in the Soil , Water and Plants and Analysis of Physico-Chemical Parameters of Soil and Water Collected from Tanda Dam kohat', *Journal of Pharmaceutical Sciences and Research*, 7(3), pp. 89–97.

Nordberg, G. F. and Fowler, B. A. (2019) 'Chapter Two - Exposure, Internal Dose, and Toxicokinetics (TK)', in Nordberg, G. F. and Fowler, B. A. B. T.-R. A. for H. M. E. (eds). Academic Press, pp. 31–73. doi: https://doi.org/10.1016/B978-0-12-804227-4.00002-9.

Nriagu, J. (2011) 'Zinc Toxicity in Humans', in *Encyclopedia of Environmental Health*. Elsevier, pp. 801–807. doi: 10.1016/b978-0-444-52272-6.00675-9.

O'Connor, M. C. *et al.* (2009) 'Practice versus policy-led coastal defence management', *Marine Policy*, 33(6), pp. 923–929. doi: 10.1016/j.marpol.2009.03.007.

Okoro, H. K. *et al.* (2014) 'Fractionation, mobility and multivariate statistical evaluation of metals in marine sediments of Cape Town harbour, South Africa', *Chemical Speciation and Bioavailability*, 26(3), pp. 126–138. doi: 10.3184/095422914X14038001068544.

Okoro, H. K. *et al.* (2016) 'Distribution and Seasonal Variations of Selected Heavy Metals in Seawater from Cape Town Harbour of Western Cape Province , Republic of South Africa', 11, pp. 82–97.

Olaniran, A. O., Naicker, K. and Pillay, B. (2014) 'Assessment of physico-chemical qualities and heavy metal concentrations of Umgeni and Umdloti Rivers in Durban, South Africa', *Environmental Monitoring and Assessment*, 186(4), pp. 2629–2639. doi: 10.1007/s10661-013-3566-8.

Oosthoek, S. (2015) *Deep-sea fish show signs of exposure to pollution: Study suggests industrial chemicals may be causing tumors*, *ScienceNewsforStudents*.

Orata, F. and Birgen, F. (2016) 'Fish Tissue Bio-concentration and Interspecies Uptake of Heavy Metals from Waste Water Lagoons', *Journal of Pollution Effects & Control*, 04(02). doi: 10.4172/2375-4397.1000157.

Oruko, R. O. *et al.* (2020) 'Contemporary and future direction of chromium tanning and management in sub Saharan Africa tanneries', *Process Safety and Environmental Protection*, pp. 369–386. doi: 10.1016/j.psep.2019.11.013.

Ozyurt, C. E. *et al.* (2016) 'Assessment of Some of the Feeding Aspects and Reproduction of S. undosquamis Distributed in the İskenderun Bay', *Turkish Journal of Fisheries and Aquatic Sciences*, 109, pp. 1–12. doi: 10.4194/1303-2712-v17.

Paches, M. *et al.* (2019) 'Assessment of the impact of heavy metals in sediments along the Spanish Mediterranean coastline: pollution indices', *Environmental Science and Pollution Research*. Environmental Science and Pollution Research, 26(11), pp. 10887–

10901. doi: 10.1007/s11356-019-04485-8.

Padayachee, N. (2010) ‘Environmental Challenges Facing the Sugar Manufacturing Industry’, pp. 365–372.

Palmer, B. Van der Elst, R. Parak, O. (2011) *Understanding our Coast: A synopsis of KZN’s coastal zone.*

Papetti, P. and Rossi, G. (2009) ‘Heavy metals in the fishery products of low Lazio and the use of metallothionein as a biomarker of contamination’, *Environmental Monitoring and Assessment*, 159(1), p. 589. doi: 10.1007/s10661-008-0725-4.

Paz, S. *et al.* (2019) ‘Toxic metals (Al, Cd, Pb and Hg) in the most consumed edible seaweeds in Europe’, *Chemosphere*, 218, pp. 879–884. doi: 10.1016/j.chemosphere.2018.11.165.

Pedley, S. and Pond, K. (2003) *Emerging issues in water and infectious disease*.

Pek, J., Wong, O. and Wong, A. C. M. (2018) ‘How to Address Non-normality: A Taxonomy of Approaches, Reviewed, and Illustrated ’, *Frontiers in Psychology* , p. 2104.

Penney, A. J. *et al.* (1999) ‘Long-term trends in catch and effort in the KwaZulu-Natal nearshore linefisheries’, *African Journal of Marine Science*. NISC, 21.

Pérez-Granados, A. M. and Vaquero, M. P. (2002) ‘Silicon, Aluminium, Arsenic and Lithium: Essentiality and Human Health Implications’, *Journal of Nutrition Health and Aging*, 6(2), pp. 154–62.

Pradervand, S. Glassom, P. Fennessy, D. (2004) *KWAZULU-NATAL STATE OF THE ENVIRONMENT 2004 MARINE AND COASTAL*.

Pradervand, P. *et al.* (2003) ‘Assessment of the linefishery in two urban estuarine systems in KwaZulu-Natal, South Africa’, *African Journal of Marine Science*. Taylor & Francis, 25(1), pp. 111–130.

Pradervand, P. and Van Der Elst, R. (2008) ‘Assessment of the charter-boat fishery in KwaZulu-Natal South Africa’, *African Journal of Marine Science*, 30(1), pp. 101–112. doi: 10.2989/AJMS.2008.30.1.10.460.

Pu, F., Chen, N. and Xue, S. (2016) ‘Calcium intake, calcium homeostasis and health’, *Food Science and Human Wellness*. Elsevier BV, 5(1), pp. 8–16. doi: 10.1016/j.fshw.2016.01.001.

Qiu, Y.-W. (2015) ‘Bioaccumulation of heavy metals both in wild and mariculture food chains in Daya Bay, South China’, *Estuarine, Coastal and Shelf Science*. Elsevier Ltd, 163, pp. 7–14. doi: 10.1016/j.ecss.2015.05.036.

Qu, Q. *et al.* (2016) ‘Marine ecological environment management based on ecological compensation mechanisms’, *Sustainability (Switzerland)*. MDPI AG, 8(12). doi: 10.3390/su8121267.

Rahmani, J. *et al.* (2018) ‘A systematic review and meta-analysis of metal concentrations in canned tuna fish in Iran and human health risk assessment', *Food and chemical toxicology*. Elsevier, 118, pp. 753–765.

Rajeshkumar, S. and Li, X. (2018) 'Bioaccumulation of heavy metals in fish species from the Meiliang Bay, Taihu Lake, China', *Toxicology Reports*, 5, pp. 288–295. doi: 10.1016/j.toxrep.2018.01.007.

Raoult, V. *et al.* (2018) 'Localized zinc distribution in shark vertebrae suggests differential deposition during ontogeny and across vertebral structures', *PLOS ONE*. Edited by H. M. Patterson, 13(1), p. e0190927. doi: 10.1371/journal.pone.0190927.

Rayman, M. P. (2019) 'The argument for increasing selenium intake', *Proceedings of the Nutrition Society*, 61, pp. 203–215. doi: 10.1079/PNS2002153.

Reid, S. D. and McDonald, D. G. (1991) 'Metal binding activity of the gills of rainbow trout (Oncorhynchus mykiss)', *Canadian Journal of Fisheries and Aquatic Sciences*. NRC Research Press, 48(6), pp. 1061–1068.

Reopanichkul, P. *et al.* (2009) 'Sewage impacts coral reefs at multiple levels of ecological organization', *Marine Pollution Bulletin*, 58(9), pp. 1356–1362. doi: 10.1016/j.marpolbul.2009.04.024.

Republic of South Africa (1973) *Sea Fisheries Act No. 58 of 1973*. South Africa: Gazette Notice.

Republic of South Africa (1988) *Sea Fisheries Act No. 12 of 1988*. South Africa: Gazette Notice No. 527.

Republic of South Africa (1998) *Marine Living Resources Act No. 18 of 1998*. South Africa: Gavernment Gazette Vol 395 No395.

Rice, J. C. and Garcia, S. M. (2011) 'Fisheries, food security, climate change, and biodiversity: Characteristics of the sector and perspectives on emerging issues', *ICES Journal of Marine Science*, 68(6), pp. 1343–1353. doi: 10.1093/icesjms/fsr041.

Rios-Fuster, B. *et al.* (2019) 'Anthropogenic particles ingestion in fish species from two areas of the western Mediterranean Sea', *Marine Pollution Bulletin*. Elsevier, 144(February), pp. 325–333. doi: 10.1016/j.marpolbul.2019.04.064.

Roberts, D. (2008) 'Thinking globally, acting locally - Institutionalizing climate change at the local government level in Durban, South Africa', *Environment and Urbanization*, 20(2), pp. 521–537. doi: 10.1177/0956247808096126.

de Romaña, D. L. *et al.* (2011) 'Risks and benefits of copper in light of new insights of copper homeostasis.', *Journal of trace elements in medicine and biology : organ of the Society for Minerals and Trace Elements (GMS)*, 25(1), pp. 3–13. doi: 10.1016/j.jtemb.2010.11.004.

Roméo, M. *et al.* (1999) 'Heavy metal distribution in different fish species from the Mauritania coast', *Science of the Total Environment*, 232(3), pp. 169–175. doi: 10.1016/S0048-9697(99)00099-6.

Ronci, L. *et al.* (2016) ‘Comparison between active and passive biomonitoring strategies for the assessment of genotoxicity and metal bioaccumulation in Echinogammarus veneris (Crustacea: Amphipoda)’, *Italian Journal of Zoology*. Taylor & Francis, 83(2), pp. 162–172.

RSPCA (2012) *Welfare standards for farmed Atlantic salmon*. West Sussex, UK.

Ryckebosch, E. *et al.* (2014) ‘Nutritional evaluation of microalgae oils rich in omega-3 long chain polyunsaturated fatty acids as an alternative for fish oil.’, *Food chemistry*, 160, pp. 393–400. doi: 10.1016/j.foodchem.2014.03.087.

SAIAB (2004) ‘South African Institute for Aquatic Biodiversity: COASTAL FISHERY RESOURCES an easy guide’.

Salam, M. A. *et al.* (2019) ‘Contamination profile of heavy metals in marine fish and shellfish’, *Global Journal ofEnvironmental Science and Management*, 5(2), pp. 225–236. doi: 10.22034/gjesm.2019.02.08.

Santamaria, A. B. (2008) ‘Manganese exposure, essentiality & toxicity.’, *The Indian journal of medical research*, 128(4), pp. 484–500.

Sarkar, T. *et al.* (2016) ‘Assessment of heavy metals contamination and human health risk in shrimp collected from different farms and rivers at Khulna-Satkhira region, Bangladesh’, *Toxicology Reports*, 3, pp. 346–350. doi: https://doi.org/10.1016/j.toxrep.2016.03.003.

SASSI (2018) ‘SASSI Pocket Card September-2018’, *e Southern African Sustainable Seafood Initiative List*.

Sawyer, J. E. (2003) *Integrated Crop Management News Agriculture and Natural Resources Soil calcium:magnesium ratios*.

Schleyer, M. H., Kruger, A. and Celliers, L. (2008) ‘Long-term community changes on a high-latitude coral reef in the Greater St Lucia Wetland Park, South Africa’, *Marine Pollution Bulletin*, 56(3), pp. 493–502. doi: 10.1016/j.marpolbul.2007.11.011.

Sea, B. *et al.* (2015) ‘Heavy Metal Levels in Four Commercial Fishes Caught in Sinop Coasts of’, 405, pp. 399–405. doi: 10.4194/1303-2712-v15.

Sea, I. *et al.* (2006) ‘Heavy metals in marine sediments of Taranto Gulf’, 99, pp. 227–235. doi: 10.1016/j.marchem.2005.09.009.

Seabream, S. and Russell, A. (2015) ‘Cheimerius nufar’, 8235.

El Shafay, S. M., Ali, S. S. and El-Sheekh, M. M. (2016) ‘Antimicrobial activity of some seaweeds species from Red sea, against multidrug resistant bacteria’, *Egyptian Journal of Aquatic Research*. National Institute of Oceanography and Fisheries, 42(1), pp. 65–74. doi: 10.1016/j.ejar.2015.11.006.

Shahsavani, A. *et al.* (2017) ‘increase the risk for consumers (Movahed et al., 2013; Pourang & Dennis, 2005).increase the risk for consumers (Movahed et al., 2013; Pourang & Dennis, 2005).’, *Toxin Reviews*, 36(4), pp. 322–330. doi:

10.1080/15569543.2017.1312451.

Simon, C. *et al.* (2019) 'Bait Collecting by Subsistence and Recreational Fishers in Knysna Estuary May Impact Management and Conservation', *African Zoology*. African Zoology Circulation Office, 54(2), pp. 91–103. doi: 10.1080/15627020.2019.1608862.

Smith, M. and Heemstra, P. (2003) 'Smith's Sea Fishes. Cape Town'.

Song, B. *et al.* (2009) 'Assessing the health risk of heavy metals in vegetables to the general population in Beijing, China', *Journal of Environmental Sciences*. The Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, 21(12), pp. 1702–1709. doi: 10.1016/S1001-0742(08)62476-6.

South Africa (2002) *Environmental Indicators for National State of the Environment Reporting*. Pretoria.

South Africa (2003) *NATIONAL ENVIRONMENTAL MANAGEMENT: PROTECTED AREAS ACT, 2003 (ACT NO. 57 OF 2003)*. South Africa.

South Africa (2012) *2nd South Africa Environment Outlook. A report on the state of the environment. Executive Summary*. Pretoria.

Sridhara Chary, N., Kamala, C. T. and Samuel Suman Raj, D. (2008) 'Assessing risk of heavy metals from consuming food grown on sewage irrigated soils and food chain transfer', *Ecotoxicology and Environmental Safety*, 69(3), pp. 513–524. doi: 10.1016/j.ecoenv.2007.04.013.

STAP (2012) *GEF guidance on emerging chemicals management issues in developing countries and countries with economies in transition.* Washington, DC, Global Environment Facility.

Stark, J. S., Kim, S. L. and Oliver, J. S. (2014) 'Anthropogenic disturbance and biodiversity of marine benthic communities in Antarctica: a regional comparison', *PloS one*. Public Library of Science, 9(6).

Suami, R. B. *et al.* (2018) 'Concentration of heavy metals in edible fishes from Atlantic Coast of Muanda, Democratic Republic of the Congo', *Journal of Food Composition and Analysis*. Academic Press Inc., 73, pp. 1–9. doi: 10.1016/j.jfca.2018.07.006.

Suami, R. B. *et al.* (2019) 'Assessment of metal concentrations in oysters and shrimp from Atlantic Coast of the Democratic Republic of the Congo', *Heliyon*, 5(12), p. e03049. doi: https://doi.org/10.1016/j.heliyon.2019.e03049.

Taylor, P. *et al.* (2010) 'South African Journal of Marine Science Assessing the impact of liquid wastes discharge in the sea . A case study off Amanzimtoti , near Durban , Natal , South Africa', (July 2015). doi: 10.2989/02577619109504646.

Tchounwou, P. B. *et al.* (2013) *Molecular, clinical and environmental toxicology: v.2: Clinical toxicology*, *Choice Reviews Online*. doi: 10.5860/choice.47-5683.

Thawley, S., Morris, S. and Vosloo, A. (2004) 'Zn and Cd accumulation in Potamonautes warreni from sites in the North – West Province of South Africa', 1275, pp. 180–188. doi: 10.1016/j.ics.2004.09.036.

Thompson, R. M., Dunne, J. A. and Woodward, G. U. Y. (2012) ‘Freshwater food webs: towards a more fundamental understanding of biodiversity and community dynamics’, *Freshwater Biology*. Wiley Online Library, 57(7), pp. 1329–1341.

Topcuoğlu, S., Kirbaşoğlu, Ç. and Güngör, N. (2001) ‘Heavy metals in organisms and sediments from Turkish coast of the Black Sea, 1997-1998’, *Environment International*, 27(7), pp. 521–526. doi: 10.1016/S0160-4120(01)00099-X.

TRUMBO, P. *et al.* (2001) ‘Dietary Reference Intakes for Vitamin A, Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon, Vanadium, and Zinc’, *Journal of the American Dietetic Association*. Washington, D.C.: National Academies Press, 101(3), pp. 294–301. doi: 10.17226/10026.

Türkmen, M. *et al.* (2009) ‘Determination of metals in fish species from Aegean and Mediterranean seas’, *Food chemistry*. Elsevier, 113(1), pp. 233–237.

Tüzen, M. (2003) ‘Determination of heavy metals in fish samples of the middle Black Sea (Turkey) by graphite furnace atomic absorption spectrometry’, *Food Chemistry*, 80(1), pp. 119–123. doi: 10.1016/S0308-8146(02)00264-9.

U.S. EPA (1991) *Methods forthedetermination of metals inenvironmental samples. EPA/600 4-91-101*. Washington, DC.

U.S.EPA (1993) *Methods for the determination of inorganic substances in environmental-EPA/600/R-93/100*. Cincinnati, OH, USA.

U.S.EPA (2011) *United States Environmental Protection Agency - Regional Screening Level (RSL) Summary Table: November 2011*. Philadelphia, Pennsylvania, USA.

U.S.EPA (2012) *EPA Region III Risk-Based Concentration (RBC) Table 2008*. Philadelphia, Pennsylvania, USA.

UNEP-WCMC (2019) *Protected Planet*, *Explore the World’s MARINE PROTECTED AREAS*.

US-EPA (2000) *Guidance for assessing chemical contaminant data for use in fish advisories. Volume 1: Risk assessment and fish consumption limits, 3rd edition*, *United States Environmental Protection Agency, Washington, DC*. doi: EPA 823-B-00-008.

US.EPA (2009) *Draft 2009 Update - Aquatic Life Ambient Water Quality Criteria for Ammonia*.

USAID (2016) *Fishing for Food Security The Importance of Wild Fisheries for Food Security and Nutrition*.

USEPA (2000) *Guidance for assessing chemical contaminant data for use in fish advisories, volume 1: Fish sampling and analysis, 3rd ed. EPA-823-B-00-007.* Washington, DC.

USEPA (2011) *Chromium in Drinking Water*, *Environmental Protection Agency: USA*.

USEPA (2016) *Integrated Risk Information System*, *Bisphenol A*. Washington.

Usero, J., Gonzalez-Regalado, E. and Gracia, I. (1997) ‘Trace metals in the bivalve molluscs Ruditapes decussatus and Ruditapes philippinarum from the Atlantic Coast of Southern Spain’, *Environment International*. Elsevier, 23(3), pp. 291–298.

Usero, J., Morillo, J. and Gracia, I. (2005) ‘Heavy metal concentrations in molluscs from the Atlantic coast of southern Spain’, *Chemosphere*. Elsevier, 59(8), pp. 1175–1181.

Vandermeersch, G. *et al.* (2015) ‘Environmental contaminants of emerging concern in seafood – European database on contaminant levels’, *Environmental Research*. Academic Press, 143, pp. 29–45. doi: 10.1016/J.ENVRES.2015.06.011.

Varol, M. and Sünbül, M. R. (2017) ‘Comparison of heavy metal levels of farmed and escaped farmed rainbow trout and health risk assessment associated with their consumption’, *Environmental Science and Pollution Research*. Springer, 24(29), pp. 23114–23124.

Velusamy, A. *et al.* (2014) ‘Bioaccumulation of heavy metals in commercially important marine fishes from Mumbai Harbor, India’, *Marine Pollution Bulletin*. Elsevier Ltd, 81(1), pp. 218–224. doi: 10.1016/j.marpolbul.2014.01.049.

Venter, O. (2019) ‘Effects of burrowing sandprawns (Callichirus kraussi) on urban estuarine water quality’.

Verdouw, J. (2008) ‘Heavy metal contamination in muscle tissue of four key recreational fish species from the Derwent estuary’, *University of Tasmania*.

Vermeulen, L. A. and Wepener, V. (1999) ‘Spatial and Temporal Variations of Metals in Richards Bay Harbour (RBH), South Africa’, 39, pp. 304–307.

Vetrimurugan, E. *et al.* (2016) ‘Bioavailable metals in tourist beaches of Richards Bay, Kwazulu-Natal, South Africa’, *Marine Pollution Bulletin*. Elsevier Ltd, 105(1), pp. 430–436. doi: 10.1016/j.marpolbul.2016.01.045.

Vetrimurugan, E. *et al.* (2017) ‘Metal concentration in the tourist beaches of South Durban: An industrial hub of South Africa’, *Marine Pollution Bulletin*. Elsevier Ltd, 117(1–2), pp. 538–546. doi: 10.1016/j.marpolbul.2017.02.036.

Vetrimurugan, E. *et al.* (2018) *A View on South Africa’s KwaZulu-Natal Coast: Stressors and Coastal Management*, *Coastal Management*. Elsevier Inc. doi: 10.1016/b978-0-12-810473-6.00009-1.

Vetrimurugan, E. *et al.* (2019) ‘Comprehensive study on metal contents and their ecological risks in beach sediments of KwaZulu-Natal province, South Africa’, *Marine Pollution Bulletin*. Elsevier, 149(July), p. 110555. doi: 10.1016/j.marpolbul.2019.110555.

Vikas, M. and Dwarakish, G. S. (2015) ‘Coastal Pollution: A Review’, *Aquatic Procedia*. Elsevier BV, 4, pp. 381–388. doi: 10.1016/j.aqpro.2015.02.051.

Vilches, F. O. *et al.* (2019) ‘Metals concentration and bioaccumulation in the marine-coastal trophic web from Buenos Aires province southern coast, Argentina’, *Chemistry* *and Ecology*. Taylor & Francis, 35(6), pp. 501–523. doi: 10.1080/02757540.2019.1604693.

Vogt, T. *et al.* (2019) 'Biological toxicity estimates show involvement of a wider range of toxic compounds in sediments from Durban, South Africa than indicated from instrumental analyses', *Marine Pollution Bulletin*, pp. 49–57. doi: 10.1016/j.marpolbul.2018.11.019.

Volpe, S. L. (2013) 'Magnesium in Disease Prevention and Overall Health', *Advances in Nutrition*. Oxford University Press (OUP), 4(3), pp. 378S-383S. doi: 10.3945/an.112.003483.

Walpole, S. *et al.* (2012) 'The weight of nations: an estimation of adult human biomass', *BMC Public Health*. ???, 12(1), p. 439. doi: 10.1186/1471-2458-12-439.

Wang, X. *et al.* (2005) 'Health risks of heavy metals to the general public in Tianjin, China via consumption of vegetables and fish', *Science of the total environment*. Elsevier, 350(1–3), pp. 28–37.

Webb, G. A. (2002) 'Biology and demography of spotted grunter *Pomadasys commersonnii*', (August), p. 148.

Wepener, V. (2008) 'Application of active biomonitoring within an integrated water resources management framework in South Africa', *South African Journal of Science*, 104(9–10), pp. 367–373.

Wepener, V. and Degger, N. (2012) 'Status of marine pollution research in South Africa (1960 – present)', *Marine Pollution Bulletin*. Elsevier Ltd, 64(7), pp. 1508–1512. doi: 10.1016/j.marpolbul.2012.05.037.

Wepener, V. and Vermeulen, L. A. (2005) 'A note on the concentrations and bioavailability of selected metals in sediments of Richards Bay Harbour, South Africa', *Water SA*. Water Research Commission (WRC), 31(4), pp. 589–596.

Whitfield, A. (2000) 'Available scientific information on individual South African estuarine systems. Consortium for Estuarine Research and Management'.

WHO/FAO (2015) 'Codex Alimentarius Commission General standard for contaminants and toxins in food and feed (Codex Stan 193-1995)'. Rome, Italy: World Health Organization/Food and Agriculture Organization).

WHO (1993) *Guidelines for drinking-water quality*. 3rd edn. Geneva: World Health Organization.

WHO (2003) *The world health report 2003: shaping the future*. Geneva.

Xia, W. *et al.* (2019) 'Spatial and interspecies differences in concentrations of eight trace elements in wild freshwater fishes at different trophic levels from middle and eastern China', *Science of The Total Environment*. Elsevier, 672, pp. 883–892. doi: 10.1016/J.SCITOTENV.2019.03.134.

Yancheva, V. *et al.* (2014) 'Metal bioaccumulation in common carp and rudd from the

Topolnitsa reservoir, Bulgaria’, *Arhiv za Higijenu Rada i Toksikologiju*, 65(1), pp. 57–66. doi: 10.2478/10004-1254-65-2014-2451.

Yang, C. *et al.* (2012) ‘Using an integrated model to track the fate and transport of suspended solids and heavy metals in the tidal wetlands’, *International Journal of Sediment Research*. Elsevier, 27(2), pp. 201–212.

Yang, T. *et al.* (2019) ‘Comparative study of polycyclic aromatic hydrocarbons (PAHs) and heavy metals (HMs) in corals, surrounding sediments and surface water at the Dazhou Island, China’, *Chemosphere*. Elsevier Ltd, pp. 157–168. doi: 10.1016/j.chemosphere.2018.11.063.

Yasuda, T., Yukami, R. and Ohshimo, S. (2014) ‘Fishing ground hotspots reveal long-term variation in chub mackerel Scomber japonicus habitat in the East China Sea’, *Marine Ecology Progress Series*. Inter-Research, 501, pp. 239–250. doi: 10.3354/meps10679.

Yi, Y. *et al.* (2017) ‘Health risk assessment of heavy metals in fish and accumulation patterns in food web in the upper Yangtze River, China’, *Ecotoxicology and Environmental Safety*. Elsevier Inc., 145(October), pp. 295–302. doi: 10.1016/j.ecoenv.2017.07.022.

Yi, Y. J. and Zhang, S. H. (2012) ‘The relationships between fish heavy metal concentrations and fish size in the upper and middle reach of Yangtze River’, *Procedia Environmental Sciences*, 13(2011), pp. 1699–1707. doi: 10.1016/j.proenv.2012.01.163.

Yücel, Y. and Çam, A. R. (2019) ‘Assessment of industrial pollution effects in coastal seawater (Northeastern Mediterranean Sea) with chemometric approach’, *International Journal of Environmental Analytical Chemistry*. Taylor & Francis, 00(00), pp. 1–18. doi: 10.1080/03067319.2019.1660877.

Zampoukas, N. *et al.* (2012) *Monitoring for the Marine Strategy Framework Directive: Requirements and Options*. doi: 10.2788/77640.

Zheng, L., Diamond, J. M. and Denton, D. L. (2013) ‘Evaluation of whole effluent toxicity data characteristics and use of Welch’s T-test in the test of significant toxicity analysis’, *Environmental Toxicology and Chemistry*. John Wiley & Sons, Ltd, 32(2), pp. 468–474. doi: 10.1002/etc.2075.

Zhu, B. *et al.* (no date) ‘Effect of combined exposure to lead and decabromodiphenyl ether on neurodevelopment of zebrafish larvae’, *Elsevier*.

Zhu, L. *et al.* (2017) ‘Deposition behavior, risk assessment and source identification of heavy metals in reservoir sediments of Northeast China’, *Ecotoxicology and Environmental Safety*. Academic Press, 142, pp. 454–463. doi: 10.1016/j.ecoenv.2017.04.039.

Ziemacki, G. *et al.* (1989) ‘Heavy metals: sources and environmental presence.’, *Annali dell’Istituto superiore di sanita*. Italy, 25(3), pp. 531–535.

Zlotkin, S. H., Atkinson, S. and Lockitch, G. (1995) ‘Trace elements in nutrition for premature infants. - PubMed - NCBI’, *Clinics in perinatology*, 22(1), pp. 223–240.

El Zrelli, R. *et al.* (2018) 'Seawater quality assessment and identification of pollution sources along the central coastal area of Gabes Gulf (SE Tunisia): Evidence of industrial impact and implications for marine environment protection', *Marine Pollution Bulletin*. Elsevier Ltd, 127, pp. 445–452. doi: 10.1016/j.marpolbul.2017.12.012.

Zrnčić, S. *et al.* (2013) 'Biomonitoring of heavy metals in fish from the Danube River', *Environmental Monitoring and Assessment*, 185(2), pp. 1189–1198. doi: 10.1007/s10661-012-2625-x.